UNIVERSIDAD DE OVIEDO
Departamento de Energía

PROGRAMA DE DOCTORADO EN
INGENIERÍA ENERGÉTICA

PRODUCCIÓN DE GAS DE SÍNTESIS A PARTIR DE PIRÓLISIS DE RESIDUOS INDUCIDA POR MICROONDAS PARA SU UTILIZACIÓN EN LA OBTENCIÓN DE BIOPLÁSTICOS

Universidad de Oviedo

TESIS DOCTORAL

Daniel Beneroso Vallejo

2016

Universidad de Oviedo

Programa de Doctorado en Ingeniería Energética

PRODUCCIÓN DE GAS DE SÍNTESIS A PARTIR DE PIRÓLISIS DE RESIDUOS INDUCIDA POR MICROONDAS PARA SU UTILIZACIÓN EN LA OBTENCIÓN DE BIOPLÁSTICOS

TESIS DOCTORAL

DANIEL BENEROSO VALLEJO

2016

Universidad de Oviedo

Programa de Doctorado en Ingeniería Energética

PRODUCCIÓN DE GAS DE SÍNTESIS A PARTIR DE PIRÓLISIS DE RESIDUOS INDUCIDA POR MICROONDAS PARA SU UTILIZACIÓN EN LA OBTENCIÓN DE BIOPLÁSTICOS

MICROWAVE-INDUCED PYROLYSIS OF ORGANIC WASTES FOR SYNGAS-DERIVED BIOPLASTICS PRODUCTION

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Tesis Doctoral presentada por el Ingeniero Químico Daniel Beneroso Vallejo para optar al grado de Doctor por la Universidad de Oviedo.

Febrero 2016

Η ανδρεία είναι η μεσότητα σε σχέση με τη δειλία και το αλόγιστο θάρρος

El valor es el punto intermedio entre la cobardía y la impetuosidad irreflexiva.

Aristóteles

El éxito no es definitivo, el fracaso no es fatídico. Lo que cuenta es el valor para continuar

Winston Churchill

A la memoria de
mi abuela Frasquita

ÍNDICE

Lista de Figuras y Tablas

Figuras

Tablas

Lista de Símbolos y Abreviaturas

CODH	*Monóxido de carbono deshidrogenasa*
CP	*Pirólisis convencional*
$\mathbf{D_s}$	*Distancia de penetración de las microondas*
E	*Magnitud del campo eléctrico aplicado*
f	*Frecuencia de la radiación microondas*
GC-MS	*Cromatografía de gases acoplada a espectrometría de masas*
MIP	*Pirólisis inducida por microondas*
MSW	*Fracción orgánica de residuo sólido urbano húmeda*
MSWd	*Fracción orgánica de residuo sólido urbano seca*
P	*Potencia absorbida por unidad de volumen*
PLA	*Fracción de plásticos de residuo sólido urbano*
RSU	*Residuos sólidos urbanos*
SSd	*Fracción de lodo de depuradora seca*
STR	*Fracción de residuos agrícolas*
PAH	*Hidrocarburos aromáticos policíclicos*
PHB	*Poli(3-hidroxibutirato)*
PHBV	*Poli(3-hidroxibutirato-co-3-hidroxivalerato)*
Syngas	*Gas de síntesis*
$\tan \delta$	*Factor de disipación*
ε'	*Constante dieléctrica relativa*
ε''	*Factor de pérdida dieléctrica relativo*
ε_0	*Permitividad del vacío*
λ_0	*Longitud de onda incidente*

Lista de Ecuaciones

Lista de Reacciones

Reacción 1	$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO$
Reacción 2	$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO$
Reacción 3	$C_nH_m + n\ CO_2 \leftrightarrow 2n\ CO + (n/2)\ H_2$
Reacción 4	$C_nH_m + n\ H_2O \leftrightarrow n\ CO + (n + m/2)\ H_2$
Reacción 5	$C + H_2O \leftrightarrow H_2 + CO$
Reacción 6	$C + 2\ H_2O \leftrightarrow 2\ H_2 + CO_2$

Agradecimientos

Durante los últimos días del mes de Noviembre de 2012 tuve la enorme suerte de contactar con mis, ahora, directores de Tesis, el doctor J. Ángel Menéndez Díaz y la doctora Ana Arenillas de la Puente. Desde el principio supe que en ellos estaba la oportunidad de iniciar mi carrera científica. Es por ello que mi mayor agradecimiento por la realización de esta Tesis Doctoral es para ellos, por el constante apoyo que me han brindado durante estos años, por el asesoramiento para transformar interesantes ideas en resultados y por la confianza depositada en mí. Gracias por motivar, ayudar y generar un ambiente muy positivo dentro del grupo de investigación MCAT cada día. ***Gracias Ángel. Gracias Ana.***

A la Fundación para el Fomento en Asturias de la Investigación Científica Aplicada y la Tecnología (FICYT) por la concesión de una beca predoctoral Severo Ochoa para desarrollar este trabajo y al Instituto Nacional del Carbón (INCAR-CSIC) por permitirme utilizar sus instalaciones en el desarrollo de esta Tesis Doctoral. Así mismo, *agradezco a la Dra. Belén Folgueras de la Escuela de Ingeniería de Minas, Energía y Materiales de Oviedo aceptar ser tutora de esta Tesis.*

Al proyecto europeo SYNPOL (Biopolymers from Syngas Fermentation) perteneciente al 7º Programa Marco de la Unión Europea y a todos los integrantes del mismo.

También quiero expresar mi gratitud al Doctor José M. Bermúdez Menéndez, por haberme asesorado en todas las tareas en el laboratorio, por sus ideas y, en general, por toda la ayuda brindada durante el desarrollo de esta Tesis Doctoral, además de por ser un gran compañero y amigo.

Al grupo de investigación de Biotecnología Medioambiental del Centro de Investigaciones Biológicas (CIB-CSIC) de Madrid, liderado por la doctora Auxiliadora Prieto, por permitirme realizar una pequeña estancia en sus laboratorios y, en especial, a la doctora Olga Revelles por enseñarme un poquito del apasionante mundo de la biotecnología.

A las compañeras de mi grupo de investigación MCAT: Sara, Esther, Natalia e Isa, por los momentos compartidos tanto en el despacho como fuera de él. Gracias por haber sido un gran pilar de apoyo durante estos años. Así mismo, quiero agradecer a Fer, a Nuria y *a Laura que me han hecho sentir como si estuviera en casa a pesar de los cientos de kilómetros que separan Oviedo de Benalmádena. Ellos han sido mi familia en esta maravillosa tierra del norte de España. Tampoco me quiero olvidar de Tan y de Adrià.*

A mis antiguos compañeros del INCAR, que se vieron obligados a abandonar "la tierrina": Clau, Marga, Rebe y, especialmente, Marina. Gracias Marina por haber sido toda una referencia en mi vida a nivel profesional, pero sobre todo, a nivel personal. He aprendido mucho junto a ti. Sé que me llevo una amiga para toda la vida. Gracias.

A Bea, porque gracias a ti he vivido una gran experiencia durante mi estancia en la Universidad de Cranfield en Reino Unido. Gracias por los consejos y por los momentos compartidos en la última etapa de mi Tesis. Estoy seguro de que nos reencontraremos muy pronto.

A las personas que he conocido durante estos años, pero especialmente a Ana, a Isa y a Fran por tantos momentos de risas compartidos y por hacer que me viniese arriba en los momentos más duros. Y, por supuesto, a mi gaditano favorito, Ramón.

A mis abuelas y, en especial, a mi abuela Frasquita que tanto amor nos dio a toda la familia y a la que el destino quiso apartarme de su *lado hace muy pocos meses sin poder despedirme de Ella. En mi vida podré olvidarte, Abuela.*

A mis padres y a mi hermana. A pesar de la distancia, ellos siempre han estado ahí, han hecho posible que haya llegado hasta aquí, enseñándome que había que trabajar duro para conseguir mis objetivos. Gracias, porque este trabajo es también vuestro.

DANIEL BENEROSO VALLEJO

Instituto Nacional del Carbón (INCAR-CSIC)

Oviedo, Febrero 2016

Resumen

En la Unión Europea se generan anualmente hasta 3000 millones de toneladas de residuos. Entre ellos, los residuos sólidos de origen orgánico tienen un gran potencial para satisfacer parcialmente la producción de productos químicos, reduciéndose el impacto medioambiental e incrementándose la sostenibilidad de los procesos respecto a los basados en recursos fósiles. Sin embargo, este tipo de residuos son complejos debido a su alta heterogeneidad, por lo que se requieren nuevos procesos de conversión que permitan reducir su complejidad en compuestos sencillos antes de convertirlos en productos de alto valor como, por ejemplo, plásticos biodegradables. Una de las posibilidades consiste en combinar la gasificación de los residuos para producir moléculas sencillas (principalmente H_2 y CO, más conocido como *syngas*) con la fermentación de dicho gas para producir bioplásticos.

El trabajo realizado durante esta Tesis se ha centrado en la optimización del proceso de producción de gas de síntesis (syngas), a partir de diferentes residuos orgánicos, mediante una novedosa tecnología de pirólisis inducida por microondas como alternativa a un proceso convencional de gasificación. La finalidad del syngas producido es ser utilizado como sustrato en un proceso de biocatálisis (fermentación) para la síntesis de bioplásticos; en particular, del biopolímero PHB. Esta memoria se ha estructurado en las tres secciones que se indican a continuación.

La primera sección de esta memoria comprende el trabajo experimental consistente en la evaluación de la idoneidad de diferentes residuos sólidos orgánicos para producir syngas mediante la tecnología de pirólisis inducida por microondas. Para ello, se han utilizado residuos sólidos urbanos (tanto la fracción orgánica como la fracción de

plásticos), residuos agrícolas, lodo de depuradora y microalgas, habiéndose llevado a cabo una comparativa con la tecnología de pirólisis convencional a diferentes temperaturas. Además, se han estudiado las características de la fracción de aceites obtenida así como las alternativas más apropiadas para la gestión de la fracción sólida resultante del proceso de pirólisis y su composición. La segunda sección de esta Tesis está centrada en la influencia que diferentes parámetros, como son la concentración de material captador de microondas, la humedad de los residuos, el gas portador o las propiedades dieléctricas de los residuos, tienen en la pirólisis inducida por microondas. Por último, la tercera sección aborda el estudio de aplicación de syngas preparado a partir de residuos en el crecimiento de la bacteria *Rhodospirillum rubrum* y en la producción del biopolímero PHB.

La versatilidad del proceso de pirólisis inducida por microondas es especialmente atractiva, ya que se pueden ajustar las condiciones para producir el syngas más apropiado en función de los requerimientos de las bacterias que llevan a cabo el proceso de fermentación.

Abstract

Up to 3000 million tons of waste are generated in the European Union every year. Of these, organic solid wastes have the potential to partially satisfy the production of chemicals, whilst the environmental impact can be minimized and the sustainability of the processes increased compared to the production processes based on fossil resources. However, these wastes are complex due to their high heterogeneity and new conversion processes are necessary before they can be converted into high value products; e.g., biodegradable plastics. One possibility is to combine the gasification of wastes to produce simple molecules (mainly H_2 and CO, known as *syngas*), which could then be easily metabolized by bacteria to produce bioplastics.

The work conducted for this Thesis has been focused on optimizing the production process of synthesis gas (syngas) from different organic residues by means of a novel technology, microwave-induced pyrolysis as an alternative to the conventional gasification process. The objective is to produce syngas for use as a substrate in a biocatalytic process (fermentation) for the synthesis of bioplastics; mainly, the biopolymer 'PHB'. This dissertation is divided into the three sections outlined below.

The first section comprises the experimental tests performed to evaluate the suitability of various solid organic wastes for producing syngas by means of microwave-induced pyrolysis. These wastes include municipal solid waste (both the organic fraction as well as the plastic fraction), agricultural waste, sewage sludge and algae. First, a comparison with the production of syngas from conventional pyrolysis at different temperatures was carried out. In addition, the most appropriate alternative for valorizing the solid fraction resulting from pyrolysis and its composition as well as the characteristics of the oil

fraction were studied. The second section of this Thesis is focused on the influence of key parameters on microwave-induced pyrolysis, such as the concentration of microwave absorbent materials, the moisture content of the residues, the carrier gas used and the dielectric properties of the wastes. Finally, the third section deals with the application of the syngas prepared from wastes to the growth of the bacterium *Rhodospirillum rubrum* and PHB production.

Microwave-induced pyrolysis has been demonstrated to be a highly versatile process as the operating conditions can be easily tailored to produce the most appropriate syngas depending on the requirements of different syngas-fermenting bacteria.

Prólogo

La presente Tesis Doctoral describe la posibilidad de integrar un proceso de pirólisis inducido por microondas, para la generación de un gas de síntesis (*syngas*) adecuado, en la producción de bioplásticos a partir de dicho *syngas*. Las publicaciones científicas generadas a partir de este trabajo ya publicadas (7), aceptadas (1) o en preparación para enviar (1) a diferentes revistas científicas, constituyen el núcleo de esta tesis, que ha sido organizada tal y como se ilustra en la Figura I.

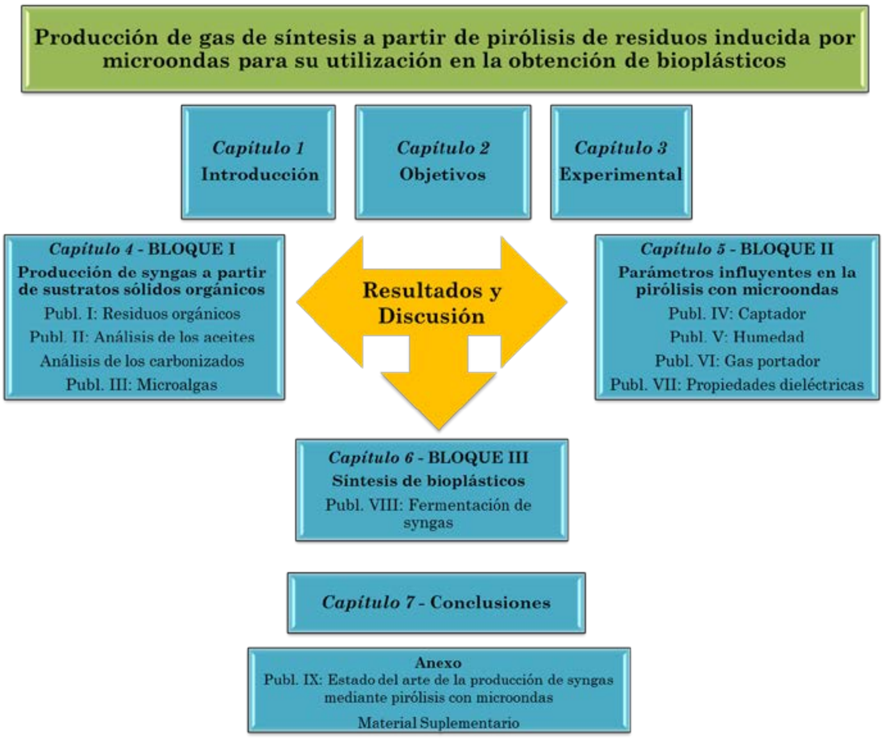


Figura I Estructura de la Tesis Doctoral

En la sección de **Introducción** (Capítulo 1)**,** se presenta la posibilidad de integrar distintos procesos de diferentes tipos de biorefinería. Particularmente, se analiza la posibilidad de utilizar procesos de biorefinerías termoquímicas (pirólisis y gasificación) junto a procesos de biorefinerías lignocelulósicas (fermentación microbiológica). Concretamente, se evalúa la posibilidad de obtener syngas a partir de residuos sólidos orgánicos complejos muy diferentes entre sí, para ser posteriormente utilizado como sustrato para la producción de productos químicos como el etanol o materiales de alto valor como los biopolímeros. Posteriormente, se presenta el proceso de pirólisis y la posible utilización de la radiación microondas para llevarlo a cabo, junto a las potenciales ventajas que este método de calentamiento ofrece.

Después de esta sección, se especifican los diferentes **Objetivos** de esta Tesis Doctoral (Capítulo 2), así como una descripción somera de los materiales y equipos utilizados durante la parte **Experimental** (Capítulo 3).

La sección de **Resultados y Discusión** se divide en tres bloques principales que contienen los resultados más relevantes y las principales conclusiones de los artículos que se incluyen en cada bloque. El Bloque I (Capítulo 4, ***Publicaciones I, II y III***) contiene un análisis sobre la idoneidad de diferentes residuos orgánicos para la producción de syngas mediante tecnologías de pirólisis convencionales y novedosas (asistidas con microondas), así como la influencia de la temperatura en dicho proceso. Además, se propone el uso de la fracción sólida resultante del proceso como aditivo a suelos de cultivo. El Bloque II (Capítulo 5, ***Publicaciones IV, V, VI y VII***) presenta la influencia de diversos factores sobre la pirólisis con microondas, como son la presencia de materiales captadores de microondas en el reactor, la humedad del residuo y la utilización de un gas portador. Así mismo, se estudia el comportamiento dieléctrico de los residuos para un posible diseño de un prototipo donde llevar a cabo la pirólisis. Por último, en el Bloque III (Capítulo 6, ***Publicación VIII***) se presenta por primera vez un estudio acerca de producción de bioplásticos (PHB) a partir de syngas procedente de la pirólisis de residuos sólidos urbanos.

Las principales conclusiones que se derivan de la presente Tesis Doctoral se resumen en el Capítulo 7, **Conclusiones**.

Para finalizar, en el **Anexo** se adjunta, como ***Publicación IX***, un capítulo de libro perteneciente a la serie *Production of Biofuels and Chemicals with Microwave* de la editorial *Springer*, donde se puede encontrar una extensa recopilación de estudios acerca del uso de las microondas como fuente de calentamiento para llevar a cabo la pirólisis de residuos orgánicos y su aplicación a la producción de bioplásticos. Además, en el Anexo se incluye el **Material Suplementario** correspondiente a las Publicaciones I, II, III y VII.

En la Tabla I se presenta una descripción detallada de las publicaciones incluidas en este trabajo.

Tabla I Revistas y libros científicos que recogen las publicaciones incluidas en la presente Memoria (© *Thomson Reuters Journal Citation Reports 2015*)

Capítulo	Publicación	Índice de Impacto
4. Resultados y Discusión: Bloque I (Producción de syngas a partir de sustratos sólidos orgánicos)	Publ. I: Journal of Analytical and Applied Pyrolysis 111 (2015) 55-63	3.564
	Publ. II: Journal of Analytical and Applied Pyrolysis 114 (2015) 256-264	3.564
	Publ. III: Bioresource Technology 144 (2013) 240-246	4.494
5. Resultados y Discusión: Bloque II (Parámetros influyentes en la pirólisis con microondas)	Publ. IV: Journal of Analytical and Applied Pyrolysis 105 (2014) 234-240	3.564
	Publ. V: Fuel 132 (2014) 20-26	3.520
	Publ. VI: Journal of Analytical and Applied Pyrolysis 113 (2015) 153-157	3.564
	Publ. VII: Fuel (Aceptado); doi: 10.1016/j.fuel.2016.01.016	3.520
6. Resultados y Discusión: Bloque III (Síntesis de bioplásticos)	Publ. VIII: En preparación	-
Anexo	Publ. IX: Biofuels and Biorefineries 3 (2015) 99-127	-

De forma complementaria a las publicaciones indicadas anteriormente, han sido aceptados para su comunicación en congresos los siguientes trabajos:

- *Influencia del captador carbonoso en la pirólisis con microondas de residuos sólidos urbanos*. D. Beneroso, J.M. Bermúdez, E.G. Calvo, A. Arenillas, J.A. Menéndez. XII Reunión del Grupo Español del Carbón. Madrid – 20 al 23 de Octubre del 2013. Comunicación en Póster.

- *Syngas from waste valorization for bioplastics production*. D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez. 20th International Symposium on Analytical and Applied Pyrolysis. Birmingham – 19 al 23 de Mayo al 2014. Comunicación en Póster.

- *Influence of carrier gas on the microwave-induced pyrolysis*. J.M. Bermúdez, D. Beneroso, A. Arenillas, J.A. Menéndez. 20th International Symposium on Analytical and Applied Pyrolysis. Birmingham – 19 al 23 de Mayo al 2014. Comunicación en Póster.

- *Drying, pyrolysis and gasification (all in one microwave induced process) of municipal solid wastes for syngas production*. D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez. International Conference on Clean Energy. Estambul – 8 al 12 de Junio del 2014. Comunicación Oral.

- *Microwaving municipal solid wastes for a better outcome*. D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, F. de la Peña, J.L. García, M.A. Prieto. II International Congress of Chemical Engineering of ANQUE. Madrid – 1 al 4 de Julio del 2014. Comunicación en Póster.

- *New insights into microwave-based biorefinery approaches*. D. Beneroso, A. Arenillas, M.A. Montes-Morán, J.A. Menéndez. 15th International Conference on Microwave and High Frequency Heating. Cracovia – 14 al 17 de Septiembre del 2015. Comunicación Oral.

- *Escalado de procesos de conversión de materiales carbonosos asistidos con microondas*. D. Beneroso, A. Arenillas, J.A. Menéndez. XIII Reunión del Grupo Español del Carbón. Alicante – 18 al 21 de Octubre del 2015. Comunicación en Póster.

Además, se presentó la siguiente ponencia invitada en el Curso "*Biomass & Waste Conversion Technologies: Syngas production and biotechnological application*", organizado por el Proyecto Europeo SYNPOL:

- *Syngas production for biotechnological fermentations*. D. Beneroso. Curso "Biomass & Waste Conversion Technologies: Syngas production and biotechnological application". Oviedo – 31 de Octubre del 2014.

Por otra parte, se han publicado otros artículos científicos durante el desarrollo de esta Tesis Doctoral dentro de la temática de procesos de conversión asistidos por microondas:

- *Energy consumption estimation in the scaling-up of microwave heating processes*. J.M. Bermúdez, D. Beneroso, N. Rey-Raap, A. Arenillas, J.A. Menéndez. *Chemical Engineering and Processing: Process Intensification* 95 (2015) 1-8.

- *Bioplastics via microwave pyrolysis of wastes*. D. Beneroso, J.A. Menéndez. *Ampere Newsletter* 79 (2013) 1-5.

Capítulo 1

Introducción

1.1 Nuevo concepto de biorefinería: hacia la producción de bioplásticos

El uso de recursos de origen fósil como combustibles para el transporte o como precursores en la fabricación de productos químicos está profundamente arraigado en la sociedad actual, pero es evidente que al ritmo actual la utilización de los mismos no es sostenible. Esto es debido tanto a que las reservas son finitas como, además, al impacto medioambiental negativo que provocan. Por ejemplo, en 2012 se produjeron a nivel mundial 288 millones de toneladas de materiales poliméricos, de los cuales más del 99% procedían de fuentes fósiles, lo cual supuso que más de 25 millones de toneladas de plásticos terminasen en vertederos o directamente en el propio medioambiente (EUROPEAN BIOPLASTICS, 2014).

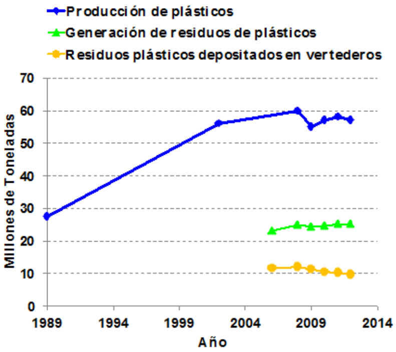


Figura 1.1 Evolución de la producción y vertidos de plásticos en la Unión Europea

En la Figura 1.1, se observa la evolución en la producción de plásticos y los residuos asociados en la Unión Europea durante los últimos años, habiéndose aumentado de manera leve la generación de residuos. Sin embargo, la disposición en vertederos ha ido disminuyendo a favor del reciclado y del uso como combustible en proyectos de valorización energética, pasando de representar en 2006 el 50% a un 38% en el año 2012.

El hecho de que estos residuos plásticos acaben vertidos en el medioambiente, supone un gran problema, ya que este tipo de plásticos presentan una alta resistencia a la degradación. Es por ello que surge la necesidad de desarrollar alternativas que permitan convertir recursos renovables en plásticos sostenibles a bajo coste como, por ejemplo, nuevos biopolímeros. De esta forma, se podría reducir considerablemente el impacto medioambiental que provocan los recursos fósiles, así como generar materiales biodegradables. Evidentemente, el desarrollo e implantación de esta alternativa necesita de un tiempo considerable; sin embargo, una posible estrategia es comenzar adoptando medidas a corto plazo que permitan reducir el impacto de los combustibles fósiles. En este sentido, la valorización de residuos de origen antropogénico mediante tecnologías de conversión termoquímicas y bioquímicas hacia productos de alto valor que sustituyan a los recursos fósiles parece ser el camino a seguir. Es por ello que en los últimos años existe un creciente interés en actividades I+D centradas en dicho campo (GAVRILESCU, 2010).

La generación de residuos de origen antropogénico es una cuestión que afecta a toda la sociedad. De media, cada una de las 500 millones de personas que viven en la UE genera alrededor de media tonelada de residuos urbanos anualmente. A éstos, hay que añadir los residuos generados por otras actividades como la construcción (900 millones de toneladas), la industria (360 millones de toneladas) y las fuentes de producción de energía y suministro de aguas (95 millones de toneladas), entre otras. Entre todas estas actividades, la UE produce hasta 3000 millones de toneladas de residuos al año (EUROPEAN COMMISSION, 2010). Los residuos generados de este tipo de actividades se pueden clasificar en función de su composición o de su origen. Respecto de la composición, es común clasificarlos como orgánicos (subproductos de la biomasa y residuos biomásicos) e inorgánicos (plásticos, vidrios, metales, etc.). En cuanto a su origen, los residuos pueden ser municipales o industriales, lo cual influye en que sean homogéneos o que presenten una composición más heterogénea (UNITED NATIONS ENVIRONMENT PROGRAMME, 2009).

Cuanto más compleja sea la naturaleza de los residuos, la eliminación y/o reciclado de los mismos se hace más dificultosa, lo que requiere la integración de diferentes tecnologías para conseguir procesos eficientes. En el caso particular de los residuos biomásicos, dicha integración de procesos se conoce bajo el nombre de biorefinería. Este término se basa en un concepto análogo al de una refinería petroquímica convencional y ha sido ampliamente utilizado para describir los procesos que generan productos de alto valor a partir de materia orgánica. La biomasa y los residuos biomásicos tienen un gran potencial para satisfacer parcialmente la producción de productos químicos, a la vez de minimizar el impacto medioambiental e incrementar la sostenibilidad de los procesos. Sin embargo, la posibilidad de reciclar de forma eficiente este tipo de residuos en una biorefinería depende, sobre todo, de la complejidad de los mismos. En la Tabla 1.1 se muestra un resumen de las diferentes configuraciones de biorefinería existentes junto con las tecnologías empleadas. Como se observa, la biorefinería termoquímica es la única capaz de procesar todo tipo de residuos orgánicos, lo que es un punto a favor de esta alternativa, y su principal objetivo es producir combustibles de segunda generación. Este tipo de biorefinería se suele dividir en dos partes: la primera dedicada a la producción de gas de síntesis o syngas (H_2+CO) mediante vías termoquímicas, y la segunda dedicada a utilizar dicho syngas para la síntesis de biocombustibles, productos químicos o en procesos de generación de calor y electricidad.

Los procesos termoquímicos producen una amplia gama de productos, a través de la descomposición térmica de la biomasa y el reformado de los productos generados de la misma. Los procesos termoquímicos se llevan a cabo bajo diferentes concentraciones de agentes oxidantes, variando desde la combustión, en la que se usa aire, hasta la pirólisis que se realiza en ausencia de oxígeno, pasando por la gasificación, en la cual tiene lugar una oxidación parcial de la biomasa.

Tabla 1.1 Diferentes tipos de biorefinería (CÁRDENAS VARGAS, 2012)

Tipo	Biomasa utilizada	Tecnologías utilizadas
Biorefinería verde	Biomasa húmeda: pastos y cultivos verdes	Pretratamiento, prensado, fraccionado, separación y digestión
Biorefinería de cultivo completo	Cultivos completos: paja de trigo, centeno y maíz	Molido y conversión bioquímica
Biorefinería lignocelulósica	Madera, residuos agrícolas, cultivos energéticos y residuos municipales	Pretratamiento, hidrólisis química y enzimática, fermentación y separación
Biorefinería marina	Biomasa acuática: microalgas y macroalgas	Extracción y separación
Biorefinería termoquímica	Todo tipo de biomasa	Conversión termoquímica: torrefacción, pirólisis y gasificación. Separación y síntesis catalítica

Aunque estos procesos presentan altos costes de capital y costes operacionales debido a las altas temperaturas utilizadas, presentan una gran ventaja sobre los procesos bioquímicos, ya que pueden convertir todos los componentes orgánicos presentes en la biomasa, aprovechando plenamente su potencial para la producción de combustibles y productos químicos (SUN, 2002, BRIDGWATER, 2006, LUQUE, 2008). Por lo tanto, parece estar claro que lo que se necesita para aprovechar dicho potencial es un proceso a baja temperatura que pueda maximizar la conversión a productos útiles. Cada uno de los principales procesos termoquímicos (gasificación, pirólisis y torrefacción) genera una distribución de productos diferente. La Figura 1.2 muestra una visión general de las aplicaciones de dichos productos.

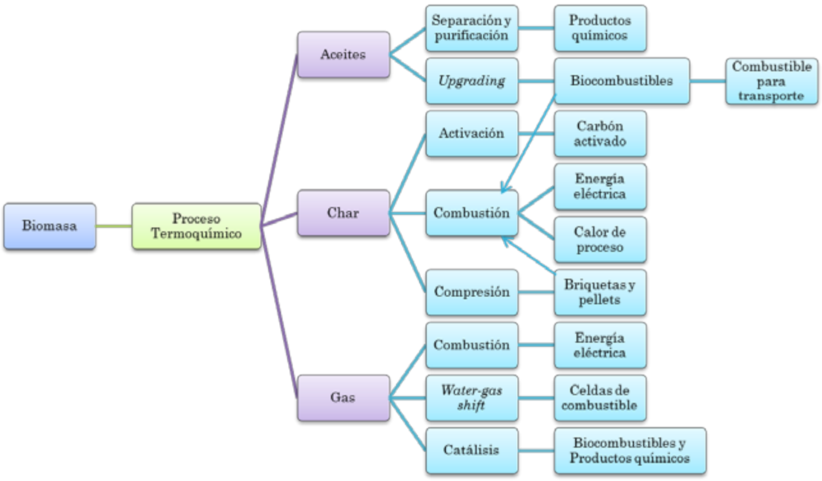


Figura 1.2 Distribución de productos a partir de diferentes procesos termoquímicos de la biomasa

Aunque las biorefinerías son una alternativa a las refinerías petroquímicas convencionales, en cuanto a la producción de diferentes productos químicos, en algunos casos se requieren nuevos procesos para el tratamiento de residuos más complejos, como los residuos sólidos urbanos (RSU). Una de las posibilidades consiste en integrar entre sí diferentes configuraciones de biorefinería, como es el caso de la biorefinería de "dos plataformas" combinando la gasificación de residuos (biorefinería termoquímica) seguida de una etapa de fermentación biológica de los gases producidos (HENSTRA, 2007, MUNASINGHE, 2010, WILKINS, 2011), como se observa en la Figura 1.3.

La gasificación de materia orgánica produce una fracción gaseosa rica en H_2, CO y, en menor medida, CO_2 e hidrocarburos ligeros. En general, se considera syngas a la mezcla de H_2 y CO, aunque para determinadas aplicaciones, como es el caso de la fermentación del gas de síntesis, el CO_2 también se puede considerar como componente del syngas.

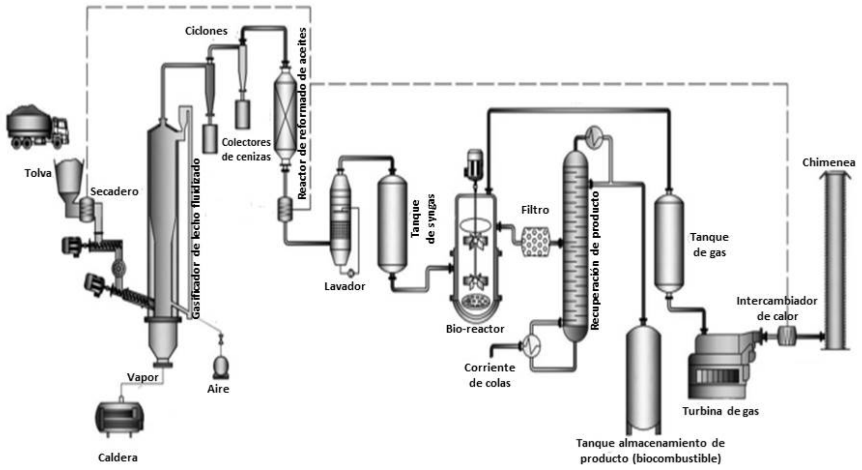


Figura 1.3 Gasificación de biomasa integrada en un proceso de fermentación de syngas para producir biocombustibles (MOHAMMADI, 2011)

Este syngas puede utilizarse como producto base para la síntesis de productos químicos de alto valor a través del conocido proceso Fischer–Tropsch. En la actualidad, el syngas es un importante intermediario en la industria química, siendo su principal mercado la industria del amoníaco, la producción de metanol (VAN DER DRIFT, 2006) o la producción de hidrógeno para ser posteriormente utilizado en refinerías.

Sin embargo, la conversión de los componentes del syngas puede tener un excesivo coste, además de ser muy susceptible al envenenamiento de los catalizadores empleados, limitando de esta manera la producción (TIRADO-ACEVEDO, 2010). Una de las posibles soluciones consiste en el uso de microorganismos capaces de convertir el CO en compuestos de cadena carbonada de interés, como el etanol o el butanol. Es por ello, que el uso combinado de un proceso termoquímico para generar syngas con un proceso de fermentación biológica se haya convertido en una alternativa (MOHAMMADI, 2011). Para ello, es necesario diseñar unas bacterias con herramientas propias del campo de la ingeniería genética que permitan transformar eficientemente el syngas en los bioproductos deseados (KÖPKE, 2010). Además, también se está trabajando en el diseño y la optimización de los reactores para mejorar la productividad de los microorganismos capaces de fermentar el syngas, de forma que el proceso pueda ser más competitivo a nivel de costes (WILKINS, 2011). De hecho, la fermentación de syngas ya está siendo explotada por varias compañías en EEUU (Coskata, INEOS Bio, LanzaTech, Syngas Biofuels Energy o BRI Energy) para la producción de etanol.

Hasta ahora, la aplicación de tecnologías de fermentación utilizando productos procedentes de la gasificación de biomasa o de residuos biomásicos, se ha enfocado principalmente hacia la producción de biocombustibles. Sin embargo, existen pocos estudios en la bibliografía que integren la tecnología de gasificación con la fermentación para la producción de biopolímeros (DO, 2007, CHOI, 2010). Para producir biopolímeros, los especialistas en ingeniería genética también deben diseñar de forma óptima unas *super-bacterias* que conviertan de manera eficiente el gas de síntesis tanto en precursores de biopolímeros (por ejemplo, el ácido succínico, el butanodiol o el ácido hidroxibutírico), como en biopolímeros directamente, como los polihidroxialcanoatos.

Los biopolímeros, no solo son aquellos polímeros procedentes de fuentes biológicas, sino que también pueden considerarse como biopolímeros aquellos que son biodegradables incluso si proceden de fuentes fósiles. Desde un punto de vista sostenible, los biopolímeros más interesantes son aquellos que cumplen las dos condiciones anteriores. Uno de los ejemplos más conocidos son los polihidroxialcanoatos, como el PHB poli(3-hidroxibutirato) o el PHBV poli(3-hidroxibutirato-co-3-hidroxivalerato). Estos biopolímeros se pueden utilizar en procesos de moldeo por inyección, extrusión o recubrimiento de papeles, y en otras numerosas aplicaciones como material de envases, cubertería o productos de oficina. Además, también han demostrado su potencial en el campo de la biomedicina, como en la reparación de tejidos o en sistemas de administración de fármacos. Este amplio abanico de utilidades se debe a que los polihidroxialcanoatos son poliésteres con una estructura muy versátil, de forma que sus propiedades termo-mecánicas se pueden ajustar a las de los plásticos convencionales (SUDESH, 2000, LOO, 2007).

De acuerdo a un informe de la organización *European Bioplastics* (EUROPEAN BIOPLASTICS, 2014), la producción mundial de biopolímeros en 2009 fue de 0,25 millones de toneladas, habiéndose incrementado en el año 2012 hasta 1,40 millones de toneladas. Además, para el año 2017 se estima una producción de 6,19 millones de toneladas (THE FREEDONIA GROUP, 2009), dentro de la cual, los polihidroxialcanoatos y el ácido poliláctico procedente de fuentes renovables, parece que encabezarán la producción de biopolímeros.

Los polihidroxialcanoatos se pueden obtener a partir de determinados cultivos vegetales, ya que algunos tejidos de plantas son capaces de generarlos mediante la fotosíntesis (SURIYAMONGKOL, 2007), o mediante procesos de fermentación, aunque el primer método todavía presenta importantes desafíos que resolver. El proceso de fermentación se lleva a cabo en un reactor en el que se encuentra un medio acuoso mineralizado, en el cual se inocula el microorganismo y una fuente carbonosa que permita el crecimiento del mismo y, por ende, la producción de polihidroxialcanoatos. Hasta el momento, se han utilizado sustratos carbonosos como la fructosa, la glucosa, el metanol o el butirato, que pueden llegar a suponer hasta el 50% del coste total de producción de los polihidroxialcanoatos. Por esta razón, para asegurar la viabilidad comercial de este proceso, es esencial el uso de recursos renovables más baratos, como pueden ser los RSU, previa gasificación de los mismos.

El uso de bacterias como biocatalizadores para la fermentación del syngas presenta importantes ventajas frente al uso de catalizadores metálicos convencionales utilizados en procesos de conversión de syngas, tal como se muestra en la Tabla 1.2.

A pesar de que el CO es tóxico para la mayoría de la materia viva, existen numerosos microorganismos que pueden metabolizarlo como fuente de carbono y/o energía para su crecimiento. Por ello, el syngas puede ser utilizado por determinados microorganismos como sustrato para su crecimiento y producción de determinados metabolitos (HENSTRA, 2007, MUNASINGHE, 2010, WILKINS, 2011).

Tabla 1.2 Valoración de los procesos biocatalíticos frente a catalíticos convencionales (BROWN, 2007)

Ventajas	Inconvenientes
Residuos orgánicos para producir syngas: disponibles abundantemente, no requieren costes de producción adicionales y no son un sustrato que comprometan la cadena alimentaria La fermentación de syngas se lleva a cabo a bajas temperaturas y presiones, lo que reduce los costes de operación En general, los biocatalizadores presentan cierta tolerancia hacia compuestos sulfurosos, ≥2% H_2S o COS Al ser el syngas gaseoso, el tiempo de residencia es independiente de la alimentación de sustrato, lo que permite controlar la inhibición que pueda provocar y la formación de determinados subproductos Los procesos de fermentación son poco sensibles a la relación H_2/CO, debido a la alta especificidad de las reacciones enzimáticas	La transferencia de materia de los componentes del syngas hacia el medio de fermentación es limitada, debida a las bajas solubilidades del CO y H_2, aunque existen alternativas en el diseño para su mejora (BREDWELL, 1999) La producción volumétrica es relativamente baja Algunos componentes orgánicos que pueda contener el flujo de syngas pueden inhibir el proceso biocatalítico

Estos microorganismos se pueden clasificar en:

- *Autótrofos*, que usan compuestos con un solo átomo de carbono (C1) como única fuente de carbono, e hidrógeno o luz como fuente de energía.
- *Unicarbonótrofos*, que usan compuestos C1 como fuente tanto de carbono como de energía.

Estas bacterias son capaces de oxidar el CO, proceso que está acoplado a otros procesos bioquímicos, como la desulfuración, hidrogenogénesis, acetogénesis y metanogénesis (OELGESCHLÄGER, 2008). De esta forma, existen, entre otros, diferentes mecanismos que involucran la oxidación del CO:

- Bacterias que pueden llevar a cabo el ciclo metabólico de *Calvin*. Estas bacterias pueden utilizar la luz para producir hidrógeno y CO_2 a partir de CO mediante la reacción *water-gas shift* biocatalizada por la enzima CODH (FERRY, 1995). Un ejemplo de estas bacterias es la *Rhodospirillum rubrum*, capaz de crecer bajo una amplia variedad de condiciones anaerobias, siendo una bacteria particularmente apropiada para crecer en syngas (DO, 2007). *R. rubrum* puede metabolizar CO en condiciones anaerobias como única fuente de carbono y energía, tanto en presencia como en ausencia de luz. De esta forma, la materia celular asimila parte del CO_2 producido, mientras que la cantidad no asimilada se desprende al ambiente junto con el H_2 producido. Aunque el H_2 es un subproducto del metabolismo, se puede separar fácilmente de la fase acuosa debido a su baja solubilidad y se considera como un producto de alto valor, hecho que ha supuesto que *R. Rubrum* sea un microorganismo muy atractivo para la conversión de syngas en productos de valor añadido. La Figura 1.4 muestra cómo esta bacteria puede utilizar CO contenido en el syngas para producir biopolímeros (PHB).

- Bacterias que pueden metabolizar los componentes del syngas para producir compuestos químicos de interés como el ácido acético o el etanol mediante la ruta metabólica acetyl-CoA o *Wood–Ljungdahl*, como se observa en la Figura 1.5. Esta ruta puede utilizar CO y H_2 como fuentes de energía (mediante la generación de electrones vía enzimática CODH o hidrogenasa, respectivamente) y CO y CO_2 como fuentes de carbono. Algunos ejemplos de estas bacterias son *Clostridium aceticum, Acetobacterium woodii, Clostridium ljungdahlii, Clostridium thermoaceticum, Clostridium autoethanogenum, Clostridium ragsdalei* o *Butyribacterium methylotrophicum* (OELGESCHLÄGER, 2008).

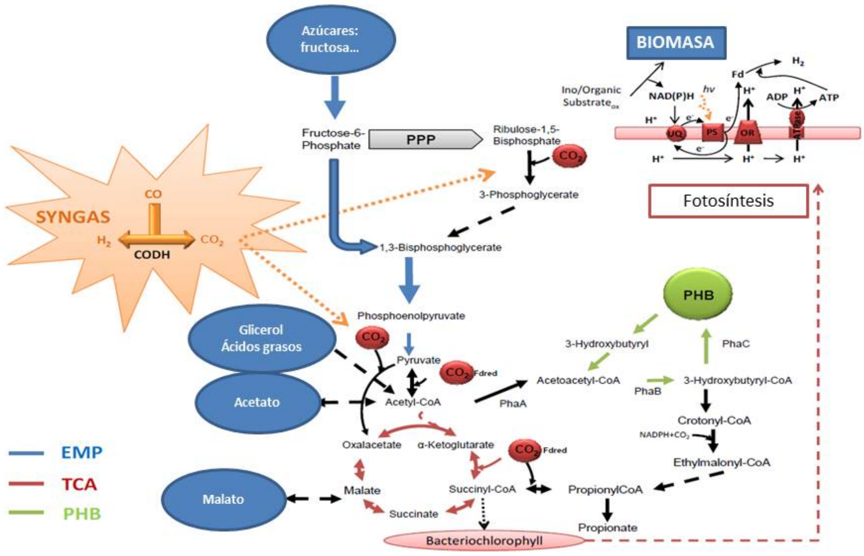


Figura 1.4 Esquema simplificado de las rutas metabólicas de *R. rubrum* para la producción de PHB a partir de diferentes sustratos incluyendo syngas. EMP: ruta de *Entner-Doudoroff*; TCA: ciclo de Krebs; PHB: ruta del polihidroxibutirato (SYNPOL, 2014)

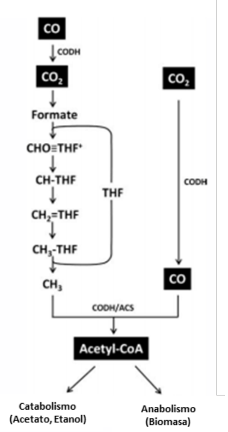


Figura 1.5. Esquema simplificado de la ruta metabólica *Wood-Ljungdahl*. CODH: CO deshidrogenasa; ACS: Acil-CoA sintetasa; THF: tetrahidrofolato.

En el contexto de la producción de biopolímeros (polihidroxialcanoatos), las rutas metabólicas son complejas y diversas y, de hecho, hoy en día continúan bajo investigación (LARA L. MADISON, 1999).

1.2 Integración de las microondas en la biorefinería termoquímica

Como se ha citado anteriormente, la tecnología más apropiada para producir syngas a partir de biomasa es la gasificación; es decir, mediante una oxidación parcial a altas temperaturas con un agente oxidante (vapor de agua, aire u oxígeno). Sin embargo, la tecnología de pirólisis también puede ser contemplada como una ruta de conversión apropiada, ya que también permite una alta recuperación de la energía contenida en los residuos y produce menos especies contaminantes que otras tecnologías como la incineración. Además, los procesos de pirólisis producen una distribución de productos en forma de fracción sólida (char), fracción líquida y fracción gaseosa, con numerosas aplicaciones, y que puede ser controlada mediante la modificación de la velocidad de calentamiento, la temperatura y el tiempo de residencia (DOMÍNGUEZ, 2007b). De esta forma, y dada la naturaleza endotérmica de la pirólisis, las altas temperaturas y velocidades de calentamiento favorecen las reacciones de descomposición. A baja temperatura y velocidad de calentamiento y alto tiempo de residencia, se favorece la producción de char; sin embargo, alta temperatura y velocidad de calentamiento durante un alto tiempo de residencia favorecen la producción de gases, mientras que para optimizar la producción de aceites son necesarias temperaturas moderadas y tiempos de residencia bajos.

En la Figura 1.6, se representa de forma esquemática la distribución de productos resultantes de la pirólisis de residuos. En primer lugar, tiene lugar una primera etapa, denominada pirólisis primaria. En esta etapa (300 – 700 ºC) tiene lugar la descomposición termoquímica del residuo y se produce un sólido (char), aceites, gases ligeros y agua, cuya distribución depende principalmente de la temperatura de pirólisis. A medida que aumenta la temperatura, se evapora la humedad del residuo, seguido de la desvolatilización y degradación térmica del residuo seco. Por encima de los 700 ºC, tiene lugar la etapa secundaria, denominada pirólisis secundaria. En esta etapa tienen lugar la gasificación del residuo sólido y las reacciones secundarias de reformado y craqueo de los aceites, incluyendo la descarboxilación, la descarbonilación, la deshidrogenación, la ciclación, la aromatización y la polimerización de los aceites. Como resultado, los aceites (especialmente los más pesados) se adsorben en la superficie del residuo sólido y pueden ser craqueados por alguna fase metálica que pueda contener el sólido, produciéndose de esta forma más H_2O, CO_2, CO, alcanos, alquenos y aromáticos.

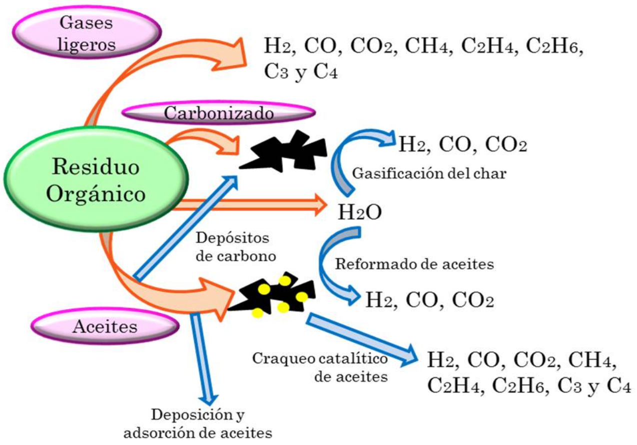


Figura 1.6 Proceso de pirólisis de un residuo orgánico

A pesar de que los métodos más estudiados para la producción de syngas a partir de biomasa están basados, principalmente, en procesos de gasificación, el uso de nuevas condiciones de operación en procesos de pirólisis puede contribuir a obtener un mayor rendimiento en syngas y, por tanto a reducir los costes ya que no sería necesario suministrar agentes oxidantes como el vapor de agua. En este sentido, el uso de las microondas como método de calentamiento en procesos de pirólisis hace que la distribución de temperaturas del material sea totalmente diferente, siendo posible obtener velocidades de calentamiento rápidas y apareciendo en el residuo unos puntos calientes denominados *microplasmas* (MENÉNDEZ, 2011). Todos estos factores parecen incrementar el rendimiento en fracción gaseosa y el contenido en syngas.

La radiación microondas pertenece a la zona del espectro electromagnético comprendida entre 0,3 y 300 GHz. Al igual que los microondas domésticos, aquellos que se han utilizado en el estudio de la química asistida con microondas operan a 2,45 GHz, aunque parece ser que el uso de una frecuencia de 915 MHz es también apropiada, sobre todo para procesos que tengan lugar a mayor escala, ya que la distancia de penetración de las ondas es mayor. Desde principios de la década de 1980, el interés en el campo de los procesos inducidos por microondas ha ido creciendo, debido principalmente a las grandes ventajas que esta tecnología ofrece frente al calentamiento convencional, como son las siguientes:

- Eficiencia energética. Puesto que no es necesario calentar el aire ni las paredes de un horno para producir el calentamiento, sino que la energía actúa directamente sobre el material, se consigue disminuir el consumo energético. Esto implica que en el microondas, el material se encuentra a mayor temperatura que la atmósfera que lo rodea, dándose la situación contraria a la del calentamiento convencional.

- Rapidez de tratamiento. El calentamiento con microondas es un calentamiento volumétrico que no depende de la transferencia de calor por convección o conducción. Así, se evitan los tiempos de calentamiento y enfriamiento del equipo, lo cual reduce el tiempo y coste del proceso.

- Calentamiento uniforme. Al considerar el material que se calienta de manera aislada, no podría decirse que existe un gradiente de temperatura en su interior, puesto que la energía microondas se aplica directamente a todo el volumen considerado. Sin embargo, con materiales carbonosos pueden llegar a aparecer microplasmas que originan puntos calientes, y por tanto, “microgradientes” de temperatura, puesto que estos microplasmas se encuentran a temperaturas mucho mayores que la temperatura media del material. Dependiendo del tipo de aplicación, la formación de microplasmas puede resultar un inconveniente o una gran ventaja (MENÉNDEZ, 2006, DOMÍNGUEZ, 2007a, DOMÍNGUEZ, 2007b).

- Control electrónico instantáneo. La energía microondas tiene la ventaja de que se puede aplicar y retirar de manera instantánea. Además, se puede regular fácilmente la intensidad del tratamiento variando la potencia emitida.

- Equipos compactos. Los equipos para tratamiento en microondas suelen ser de menor tamaño que los equipos convencionales. Esto, unido a la rapidez del calentamiento, permite disminuir el espacio para el procesamiento, lo que implica menores costes.

- Calentamiento selectivo. Las diferencias en el comportamiento de distintos materiales frente a las microondas, pueden ser una gran ventaja en el ámbito industrial. De esta forma, existen materiales trasparentes que no interfieren con las microondas (vidrio, cerámica o cuarzo), materiales absorbentes de microondas, conocidos como dieléctricos (agua, aceite o materiales carbonosos) o materiales que las reflejan, como los metálicos.

Por todas estas ventajas, el calentamiento con microondas se ha aplicado a un amplio abanico de procesos diferentes como la valorización de biomasa y residuos orgánicos (LUDLOW-PALAFOX, 2001, MENÉNDEZ, 2002, MIURA, 2004, ROBINSON, 2007, HUSSAIN, 2012), síntesis de materiales (BOGDAL, 2003, TOMPSETT, 2006), procesos metalúrgicos (HAQUE, 1999), catálisis (ZHANG, 2006), síntesis orgánica (LIDSTRÖM, 2001), procesos de extracción (CRAVOTTO, 2008), etc.

Es importante tener en cuenta que las microondas no son una forma de calor, sino una forma de energía que se manifiesta en forma de calor a través de su interacción con los materiales. El calentamiento con microondas se lleva a cabo, principalmente, a través de dos mecanismos que poseen la misma escala de tiempo que la oscilación del campo eléctrico, dando lugar a un desfase entre la polarización y el campo: la polarización por orientación dipolar y la polarización de carga espacial (conocida como efecto *Maxwell-Wagner*). Como resultado, tiene lugar una absorción de energía y un calentamiento por efecto *Joule* (ZLOTORZYNSKI, 1995). El mecanismo de polarización por orientación dipolar, mostrado en la Figura 1.7, tiene lugar cuando las moléculas que presentan un momento dipolar se exponen a la acción de un campo eléctrico, tratándose éstas de alinear con el campo. Cuando el campo eléctrico se relaja (amplitud con valor cero), los dipolos se orientan al azar (Figura 1.7 (a)) para ser empujados a alinearse de nuevo cuando la intensidad del campo eléctrico aumenta hasta llegar a un máximo (Figura 1.7 (b)). Cuando este proceso ocurre millones de veces por segundo, se produce una conversión de energía del campo eléctrico en energía potencial almacenada en el material, y luego, en energía térmica por fricción molecular (MUJUMDAR, 2006).

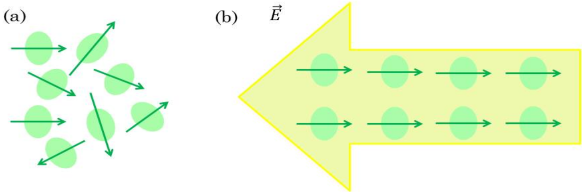


Figura 1.7 (a) Disposición al azar de los dipolos sin estar sometidos a un campo eléctrico externo y (b) Alineación de los dipolos cuando se les somete a un campo eléctrico externo

En cuanto al mecanismo de *Maxwell-Wagner*, éste aparece en materiales que poseen electrones libres cuyos desplazamientos están restringidos por obstáculos, tales como bordes de partícula. Cuando se aplica un campo eléctrico externo, los electrones se acumulan sobre el obstáculo y el resultado es una separación de cargas que polariza el material. Algunos materiales carbonosos, como los carbones activados o el carbonizado procedente de una pirólisis, presentan electrones π deslocalizados con amplia movilidad, que permiten el calentamiento del material a través de este mecanismo (Figura 1.8).

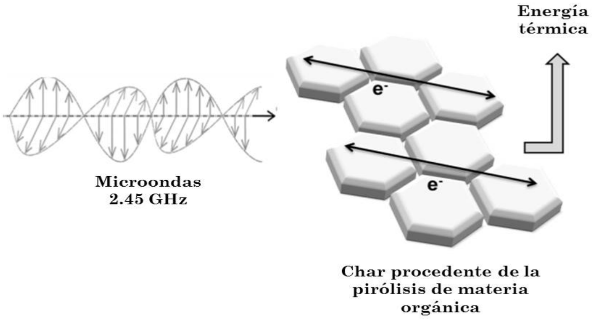


Figura 1.8 Desfase entre el campo eléctrico y la polarización de los electrones π deslocalizados en materiales carbonosos

La capacidad que presentan los materiales dieléctricos para ser calentados bajo la acción de microondas viene determinada por el factor de disipación, tg δ, que a su vez está compuesto de dos parámetros: la constante dieléctrica (ε') y el factor de pérdida dieléctrica (ε''):

$$\text{tg}\,\delta = \frac{\varepsilon''}{\varepsilon'} \qquad \text{(Ec. 1)}$$

La constante dieléctrica representa la capacidad del material para ser polarizado, y el factor de pérdida dieléctrica representa la disipación de energía del campo eléctrico en forma de calor en el interior del material, que depende de la conductividad del mismo. En general, los materiales que poseen un alto factor de disipación son los que permiten una mayor conversión de las microondas en energía térmica, con lo que se calientan más rápidamente. Para diseñar un proceso asistido con microondas, es esencial contar con una buena estimación de estas propiedades para determinar la velocidad a la cual el calor será absorbido por el material y la distribución del campo eléctrico. Estas constantes varían con la composición, la temperatura, la frecuencia de la radiación microondas y la densidad del material (SALSMAN, 1990).

Por otra parte, conocer las propiedades dieléctricas anteriores permite determinar la distancia de penetración de las microondas dentro de un material (D_S). Este parámetro es importante ya que determinará si el calentamiento es uniforme en todo el volumen del material, y suele referirse a la distancia de penetración a la cual la potencia incidente se ha reducido en un factor e^{-1} respecto de la superficie:

$$D_s = \frac{\lambda_0\sqrt{\varepsilon'}}{2\pi\varepsilon''} \qquad \text{(Ec. 2)}$$

donde λ_0 es la longitud de onda incidente, ε' es la constante dieléctrica del material relativa a la del vacío y ε" es el factor de pérdida dieléctrica del material relativa a la del vacío (CLARK, 2000). Por tanto, cuanto mayor sea el factor de disipación, menor será la distancia de penetración pero mayor la conversión en energía térmica. Así, la susceptibilidad de un material a ser calentado mediante radiación microondas, además de por su conductividad térmica, está mucho más influenciado por la distancia de penetración de las microondas en el interior del material. Así mismo, a partir de las propiedades dieléctricas se puede determinar la potencia absorbida por unidad de volumen (P), que viene dada por la siguiente ecuación:

$$P = 2\pi f \varepsilon_0 \varepsilon'' E^2 \qquad \text{(Ec. 3)}$$

donde f es la frecuencia de la radiación microondas y E es la magnitud del campo eléctrico generado en el volumen del material.

En el caso de materiales formados por macromoléculas, como es el caso de los residuos biomásicos o los residuos plásticos, la polarización solo ocurre en pequeñas partes de las moléculas debido a la rigidez de las estructuras cristalinas, por lo que solo las regiones amorfas son capaces de alinearse con el campo eléctrico aplicado. Estas macromoléculas presentan generalmente una amplia distribución de tiempos de relajación (que es el tiempo empleado por el dipolo en revertir su posición después de ser polarizado), dando lugar a un factor de pérdida dieléctrica muy bajo en un amplio intervalo de frecuencias. Es por ello que en la mayoría de los estudios, para conseguir una temperatura lo suficientemente alta como para que tenga lugar la pirólisis se añaden captadores de microondas a la materia a pirolizar, tales como materiales carbonosos como char, carbón activado o grafito. Una vez que la pirólisis comienza, tiene lugar la desvolatilización de la materia produciendo char que actuará como captador de microondas.

El uso de microondas en el tratamiento de biomasa data de principios de la década de 1970. Los sustratos empleados son, por tanto, numerosos e incluyen biomasa vegetal como la madera o residuos agrícolas, plásticos y residuos urbanos. Además, las investigaciones llevadas a cabo indican que diferentes factores como el tamaño de partícula, la potencia de la radiación microondas, el tiempo de radiación o la naturaleza del material están directamente ligados a la eficiencia del proceso asistido con microondas. En lo que concierne a los procesos termoquímicos, se ha estudiado el uso del calentamiento con microondas en procesos de gasificación, pirólisis, torrefacción o licuefacción. Por ejemplo, para la producción de una fracción gaseosa rica en syngas se han utilizado lodos de depuradora, habiéndose obtenido concentraciones de H_2 + CO del 62 vol.% en comparación con un 25 vol.% mediante tecnologías de calentamiento convencional (MENÉNDEZ, 2004). Otro residuo que presenta serios problemas para el medioambiente es el aceite residual de los automóviles. Mediante una pirólisis inducida por microondas fue posible obtener un rendimiento en gas del 41%, conteniendo hasta un 35 vol.% de H_2 + CO, junto a una gran cantidad de hidrocarburos ligeros de especial interés como combustible (LAM, 2012). Por otra parte, el uso de residuos lignocelulósicos como sustrato para la pirólisis con microondas es muy interesante para producir una fracción gaseosa rica en hidrógeno, como, por ejemplo, la paja (ZHAO, 2010). Y es que la principal ventaja de la pirólisis inducida por microondas frente a la pirólisis convencional parece no solo ser la mejor calidad del gas producido (en cuanto a concentración en syngas se refiere), sino también la mejora del rendimiento en fracción gaseosa, la reducción en procesos de pretratamiento y el ahorro energético (LUQUE, 2012). Por todas estas razones, la pirólisis inducida por microondas ofrece una oportunidad excelente para la valorización de residuos y evitar procesos de tratamiento posteriores.

En general, los principales factores que afectan a la pirólisis inducida con microondas en las características del gas producido son la naturaleza del sustrato y su contenido en humedad, la potencia de las microondas (y, por tanto, la temperatura de pirólisis), la presencia de materiales captadores de microondas y su concentración, y el diseño del reactor. Debido a la influencia de tantos parámetros y a las interrelaciones entre ellos, un pequeño cambio en alguno de estos parámetros podría producir un syngas diferente, lo cual hace a la pirólisis inducida por microondas un proceso muy versátil.

En la mayoría de las publicaciones científicas, las cavidades utilizadas son, simplemente, microondas domésticos modificados con controladores de temperatura. Sin embargo, para llevar a cabo su implementación industrial, y particularmente para tratar materiales heterogéneos como residuos urbanos, hay que llevar a cabo un diseño específico de la cavidad para controlar y maximizar la velocidad de calentamiento, el tiempo de residencia y, sobre todo, mejorar el grado de uniformidad en el calentamiento del material. Sin embargo, el escalado de procesos asistidos con microondas no es una tarea fácil, debido a diversos factores como la dificultad de generar una buena dispersión de las microondas cuando se incrementa el volumen del reactor (DOUCET, 2014).

La comercialización de esta tecnología se basa no sólo en las áreas de uso y las propiedades de los materiales producidos, sino también en la economía del proceso. En este sentido, la viabilidad económica es un *mix* por el que deben evaluarse los costes de capital, el coste de la energía, las leyes medioambientales y los costes de operación frente al mercado de los productos finales, las características especiales de los productos y la mejora de la producción a través del uso de las microondas (y, como consecuencia, la reducción de espacio de la planta y de los costes de mano de obra que supondría). En los procesos industriales asistidos con microondas que se han implantado con éxito, como es el caso de procesos de secado o en la vulcanización del caucho, los dos últimos factores son, probablemente, las principales razones por las que seleccionar un proceso inducido por microondas respecto a los procesos convencionales. Un buen ejemplo de ellos es el caso de la síntesis asistida con microondas de xerogeles de resorcinol - formaldehído, mediante la cual el tiempo de síntesis disminuye de 4 días (mediante procesos de calentamiento convencionales) a 5 h (CALVO, 2011); mejorándose enormemente no sólo la productividad, sino también el consumo energético.

En cuanto a los costes de capital de una planta de procesado con microondas, se suele establecer que para plantas con una potencia instalada mayor de 20 kW, el coste se sitúa en la horquilla 3000 – 6000$ por kW. En el caso de plantas con menor potencia o para plantas que necesiten de un diseño muy específico, estos costes pueden exceder los 7500$ por kW (KORAL, 2013). En cualquier caso, el coste del generador de microondas, conocido como magnetrón, representa menos del 50% del coste total del sistema, lo que permitiría trabajar con equipos modulares en lugar de sistemas de grandes dimensiones y, probablemente, menos eficientes. Sin embargo, es importante tener en cuenta que debido a las diferencias técnicas existentes entre equipos de calentamiento convencionales y microondas, los equipos de procesos asistidos con microondas suelen ser más caros, aunque esto puede ser ampliamente compensado por las ventajas que proporcionan las microondas en el producto obtenido. Respecto a los costes de operación de una planta de procesado con microondas, éstos incluirían el coste de la energía, que depende de la localización de la planta, la eficiencia de conversión de energía eléctrica en microondas por parte del magnetrón, que suele estar entre el 50 y el 75% dependiendo de la frecuencia usada, o el coste de mantenimiento y reparación.

En cuanto al caso específico de la pirólisis inducida por microondas, se han llevado a cabo algunos intentos de escalado, como los reactores diseñados por el *Centre for Biorefining* de la Universidad de Minnesota, la compañía *Scandinavian Biofuel* (SCANDINAVIANBIOFUELS, 2014) o el *King Mongkut's Institute of Technology Ladkrabang* (PAYAKKAWAN, 2012), mostrando resultados prometedores para esta tecnología. Sin embargo, el objetivo de estas plantas ha estado enfocado en la obtención de la fracción líquida o la fracción sólida, por lo que desde el punto de vista de la producción de syngas, no se encuentra disponible ninguna información. En este sentido, se pueden encontrar trabajos a una escala de 100 – 300 g de sustrato por parte de *Serio et al.* (SERIO, 2013), que trabajaron en el diseño de un reactor con microondas en el que se insertó una zona de craqueo que minimizaba la producción de líquidos y sólidos, aunque esta escala continúa estando lejos de ser considerada como planta piloto. Por otra parte, *Zao et al.* llevaron a cabo la pirólisis asistida con microondas a una escala de 30 kg de residuos agrícolas, produciéndose una gran cantidad de syngas, y demostrando ser, además, un proceso mucho más rápido y eficiente que la pirólisis convencional (ZHAO, 2010). A este mismo resultado también se llegó en otro estudio acerca del consumo energético de la torrefacción de paja en una planta piloto capaz de procesar 30 kg/h (BUDARIN, 2011), demostrando ser la torrefacción inducida por microondas 1,5 veces más eficiente que el correspondiente proceso convencional.

Como se puede comprobar a partir de las publicaciones científicas recogidas en la presente memoria, la producción de syngas a partir de residuos orgánicos se favorece enormemente gracias a la tecnología microondas. El proceso de pirólisis asistido con microondas se ha venido desarrollando desde hace años en el grupo de investigación Microondas y Carbones para Aplicaciones Tecnológicas (**MCAT**) del INCAR-CSIC. La radiación microondas aplicada a la pirólisis de residuos orgánicos ha permitido la producción de una fracción gaseosa muy apropiada para ser utilizada como sustrato en la síntesis de biopolímeros, con una composición muy diferente a su homóloga obtenida a partir de tecnologías de pirólisis convencionales.

Se puede encontrar más información acerca del uso y versatilidad de la tecnología de microondas aplicada a la pirólisis para producir syngas en el **Anexo**, donde se adjunta el capítulo *Microwave Pyrolysis of Organic Wastes for Syngas-Derived Biopolymers Production* del libro “*Production of Biofuels and Chemicals with Microwave*”.

Referencias

Bogdal, D., P. Penczek, J. Pielichowski and A. Prociak (2003). Microwave Assisted Synthesis, Crosslinking, and Processing of Polymeric Materials. Liquid Chromatography / FTIR Microspectroscopy / Microwave Assisted Synthesis, Springer Berlin Heidelberg. ***163:*** *194-263.*

Bredwell, M. D., P. Srivastava and R. M. Worden (1999). "Reactor Design Issues for Synthesis-Gas Fermentations." Biotechnology Progress ***15****(5): 834-844.*

Bridgwater, T. (2006). "Biomass for energy." Journal of the Science of Food and Agriculture ***86****(12): 1755-1768.*

Brown, R. (2007). "Hybrid thermochemical/biological processing." Applied Biochemistry and Biotechnology ***137-140****(1-12): 947-956.*

Budarin, V. L., P. S. Shuttleworth, J. R. Dodson, A. J. Hunt, B. Lanigan, R. Marriott, K. J. Milkowski, A. J. Wilson, S. W. Breeden, J. Fan, E. H. K. Sin and J. H. Clark (2011). "Use of green chemical technologies in an integrated biorefinery." Energy & Environmental Science ***4****(2): 471-479.*

Calvo, E. G., E. J. Juárez-Pérez, J. A. Menéndez and A. Arenillas (2011). "Fast microwave-assisted synthesis of tailored mesoporous carbon xerogels." Journal of Colloid and Interface Science ***357****(2): 541-547.*

Cárdenas Vargas, R. (2012). Biorefinerías para la producción de biocombustibles de segunda generación. Ingeniería y Producción Industrial, Universitat Politècnica de València - Instituto de Ingeniería Energética.

Clark, D. E., D. C. Folz and J. K. West (2000). "Processing materials with microwave energy." Materials Science and Engineering: A ***287****(2): 153-158.*

Cravotto, G., L. Boffa, S. Mantegna, P. Perego, M. Avogadro and P. Cintas (2008). "Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves." Ultrasonics Sonochemistry ***15****(5): 898-902.*

Choi, D., D. Chipman, S. Bents and R. Brown (2010). "A Techno-economic Analysis of Polyhydroxyalkanoate and Hydrogen Production from Syngas Fermentation of Gasified Biomass." Applied Biochemistry and Biotechnology ***160****(4): 1032-1046.*

Do, Y. S., J. Smeenk, K. M. Broer, C. J. Kisting, R. Brown, T. J. Heindel, T. A. Bobik and A. A. DiSpirito (2007). "Growth of Rhodospirillum rubrum on synthesis gas: Conversion of CO to H2 and poly-β-hydroxyalkanoate." Biotechnology and Bioengineering ***97****(2): 279-286.*

Domínguez, A., Y. Fernández, B. Fidalgo, J. J. Pis and J. A. Menéndez (2007a). "Biogas to Syngas by Microwave-Assisted Dry Reforming in the Presence of Char." Energy & Fuels ***21****(4): 2066-2071.*

Domínguez, A., J. A. Menéndez, Y. Fernández, J. J. Pis, J. M. V. Nabais, P. J. M. Carrott and M. M. L. R. Carrott (2007b). "Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas." Journal of Analytical and Applied Pyrolysis ***79****(1–2): 128-135.*

Doucet, J., J.-P. Laviolette, S. Farag and J. Chaouki (2014). "Distributed Microwave Pyrolysis of Domestic Waste." Waste and Biomass Valorization ***5****(1): 1-10.*

European Bioplastics (2014). Bioplastics facts and figures.

European Commission (2010). Being wise with waste: the EU's approach to waste management.

European_Bioplastics (2014). Bioplastics facts and figures. http://en.european-bioplastics.org/multimedia/, European Bioplastics.

Ferry, J. G. (1995). "Co Dehydrogenase." Annual Review of Microbiology ***49****(1): 305-333.*

Gavrilescu, M. (2010). "Environmental biotechnology: achievements, opportunities and challenges." Dynamic Biochemistry, Process Biotechnology and Molecular Biology ***4****(1): 1-36.*

Haque, K. E. (1999). "Microwave energy for mineral treatment processes—a brief review." International Journal of Mineral Processing ***57****(1): 1-24.*

Henstra, A. M., J. Sipma, A. Rinzema and A. J. M. Stams (2007). "Microbiology of synthesis gas fermentation for biofuel production." Current Opinion in Biotechnology ***18****(3): 200-206.*

Hussain, Z., K. M. Khan, S. Perveen, K. Hussain and W. Voelter (2012). "The conversion of waste polystyrene into useful hydrocarbons by microwave-metal interaction pyrolysis." Fuel Processing Technology ***94****(1): 145-150.*

Köpke, M., C. Held, S. Hujer, H. Liesegang, A. Wiezer, A. Wollherr, A. Ehrenreich, W. Liebl, G. Gottschalk and P. Dürre (2010). "Clostridium ljungdahlii represents a microbial production platform based on syngas." Proceedings of the National Academy of Sciences.

Koral, T. (2013). Considerations for Commercial Success in new RF and Microwave Industrial Heating Applications 14th International Conference on Microwave and High Frequency Heating Nottingham (UK).

Lam, S. S., A. D. Russell, C. L. Lee, S. K. Lam and H. A. Chase (2012). "Production of hydrogen and light hydrocarbons as a potential gaseous fuel from microwave-heated pyrolysis of waste automotive engine oil." International Journal of Hydrogen Energy ***37****(6): 5011-5021.*

Lara L. Madison and G. W. Huisman (1999). "Metabolic Engineering of Poly(3-Hydroxyalkanoates): From DNA to Plastic." Microbiology and Molecular Biology Reviews ***63****(1): 21-53.*

Lidström, P., J. Tierney, B. Wathey and J. Westman (2001). "Microwave assisted organic synthesis—a review." Tetrahedron ***57****(45): 9225-9283.*

Loo, C.-Y. and K. Sudesh (2007). "Polyhydroxyalkanoates: bio-based microbial plastics and their properties." Malaysian Polymer Journal ***2****(2): 31-57.*

Ludlow-Palafox, C. and H. A. Chase (2001). "Microwave-Induced Pyrolysis of Plastic Wastes." Industrial & Engineering Chemistry Research ***40****(22): 4749-4756.*

Luque, R., L. Herrero-Davila, J. M. Campelo, J. H. Clark, J. M. Hidalgo, D. Luna, J. M. Marinas and A. A. Romero (2008). "Biofuels: a technological perspective." Energy & Environmental Science ***1****(5): 542-564.*

Luque, R., J. A. Menendez, A. Arenillas and J. Cot (2012). "Microwave-assisted pyrolysis of biomass feedstocks: the way forward?" Energy & Environmental Science ***5****(2): 5481-5488.*

Menéndez, J. A., A. Domínguez, Y. Fernández and J. J. Pis (2006). "Evidence of Self-Gasification during the Microwave-Induced Pyrolysis of Coffee Hulls." Energy & Fuels ***21****(1): 373-378.*

Menéndez, J. A., A. Domínguez, M. Inguanzo and J. J. Pis (2004). "Microwave pyrolysis of sewage sludge: analysis of the gas fraction." Journal of Analytical and Applied Pyrolysis ***71****(2): 657-667.*

Menéndez, J. A., M. Inguanzo and J. J. Pis (2002). "Microwave-induced pyrolysis of sewage sludge." Water Research ***36****(13): 3261-3264.*

Menéndez, J. A., E. J. Juárez-Pérez, E. Ruisánchez, J. M. Bermúdez and A. Arenillas (2011). "Ball lightning plasma and plasma arc formation during the microwave heating of carbons." Carbon ***49****(1): 346-349.*

Miura, M., H. Kaga, A. Sakurai, T. Kakuchi and K. Takahashi (2004). "Rapid pyrolysis of wood block by microwave heating." Journal of Analytical and Applied Pyrolysis ***71****(1): 187-199.*

Mohammadi, M., G. D. Najafpour, H. Younesi, P. Lahijani, M. H. Uzir and A. R. Mohamed (2011). "Bioconversion of synthesis gas to second generation biofuels: A review." Renewable and Sustainable Energy Reviews ***15****(9): 4255-4273.*

Mujumdar, A. S. (2006). Handbook of industrial drying, CRC Press.

Munasinghe, P. C. and S. K. Khanal (2010). "Biomass-derived syngas fermentation into biofuels: opportunities and challenges." Bioresource technology ***101****(13): 5013-5022.*

Oelgeschläger, E. and M. Rother (2008). "Carbon monoxide-dependent energy metabolism in anaerobic bacteria and archaea." Archives of Microbiology ***190****(3): 257-269.*

Payakkawan, P., S. Areejit, A. Jansri, K. Klomkarn, H. Aoyama and P. Sooraksa (2012). Design and implementation of continuous microwave biomass carbonization system. Microwave and Millimeter Wave Technology (ICMMT), 2012 International Conference on.

Robinson, J. P., S. W. Kingman, C. E. Snape and H. Shang (2007) "Pyrolysis of biodegradable wastes using microwaves." Proceedings of the ICE - Waste and Resource Management ***160****, 97-103.*

Salsman, J. B. (1990). "Technique for Measuring the Dielectric Properties of Minerals as a Function of Temperature and Density at Microwave Heating Frequencies." MRS Online Proceedings Library ***189****: null-null.*

ScandinavianBiofuels. (2014). from http://www.sbiofuel.com/pyrolysis.html.

Serio, M., J. E. Cosgrove, M. A. Wójtowicz, K. Wignarajah and J. W. Fisher (2013). A Prototype Microwave Pyrolyzer for Solid Wastes. 43rd International Conference on Environmental Systems, American Institute of Aeronautics and Astronautics.

Sudesh, K., H. Abe and Y. Doi (2000). "Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters." Progress in Polymer Science ***25****(10): 1503-1555.*

Sun, Y. and J. Cheng (2002). "Hydrolysis of lignocellulosic materials for ethanol production: a review." Bioresource Technology ***83****(1): 1-11.*

Suriyamongkol, P., R. Weselake, S. Narine, M. Moloney and S. Shah (2007). "Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plants — A review." Biotechnology Advances ***25****(2): 148-175.*

SYNPOL, P. (2014). Periodic Report.

The Freedonia Group (2009). World Bioplastics.

Tirado-Acevedo, O., M. S. Chinn and A. M. Grunden (2010). Chapter 2 - Production of Biofuels from Synthesis Gas Using Microbial Catalysts. Advances in Applied Microbiology. I. L. Allen, S. Sima and M. G. Geoffrey, Academic Press. ***Volume 70:*** *57-92.*

Tompsett, G. A., W. C. Conner and K. S. Yngvesson (2006). "Microwave synthesis of nanoporous materials." ChemPhysChem ***7****(2): 296-319.*

United Nations Environment Programme (2009). Developing integrated solid waste management plan, Division of Technology, Industry and Economics International Environmental Technology Centre Osaka/Shiga, Japan. ***2****.*

Van der Drift, A. and H. Boerrigter (2006). Synthesis gas from biomass for fuels and chemicals, ECN Biomass, Coal and Environmental Research.

Wilkins, M. R. and H. K. Atiyeh (2011). "Microbial production of ethanol from carbon monoxide." Current Opinion in Biotechnology ***22****(3): 326-330.*

Zhang, X. and D. O. Hayward (2006). "Applications of microwave dielectric heating in environment-related heterogeneous gas-phase catalytic systems." Inorganica Chimica Acta ***359****(11): 3421-3433.*

Zhao, X., Z. Song, H. Liu, Z. Li, L. Li and C. Ma (2010). "Microwave pyrolysis of corn stalk bale: A promising method for direct utilization of large-sized biomass and syngas production." Journal of Analytical and Applied Pyrolysis ***89****(1): 87-94.*

Zlotorzynski, A. (1995). "The Application of Microwave Radiation to Analytical and Environmental Chemistry." Critical Reviews in Analytical Chemistry ***25****(1): 43-76.*

Capítulo 2

Objetivos

De acuerdo con las ideas presentadas en la sección de Introducción, el **OBJETIVO GENERAL** de esta Tesis Doctoral es desarrollar un ***proceso de pirólisis de residuos orgánicos inducido por microondas*** que servirá para la producción de un **syngas** adecuado para su uso como sustrato en la producción de **bioplásticos**, tal como se observa en la Figura 2.1.

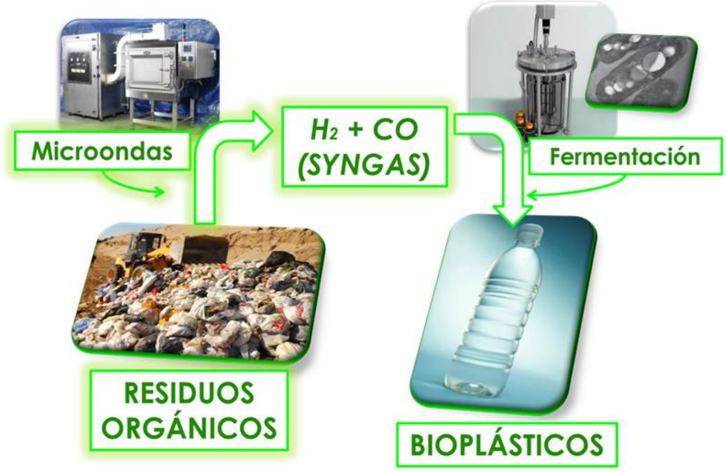


Figura 2.1 Objetivo general de la Tesis Doctoral

Para conseguir este objetivo general, se proponen los siguientes objetivos específicos:

- Seleccionar, preparar y caracterizar diferentes muestras de residuos sólidos orgánicos: residuos sólidos urbanos (fracción orgánica y fracción de plásticos), residuos agrícolas, lodos de depuradora y microalgas.

- Estudiar la producción de syngas y su composición mediante la pirólisis convencional de los residuos orgánicos.

- Estudiar la producción de syngas y su composición mediante la pirólisis inducida por microondas de los residuos orgánicos.

- Optimizar las condiciones de operación del proceso de pirólisis inducido por microondas, para obtener un gas rico en syngas adecuado para la posterior producción de bioplásticos por parte de diferentes bacterias. Las condiciones de operación estudiadas son:

    - Residuo orgánico a utilizar.
    - Temperatura.
    - Concentración del captador de microondas.
    - Humedad del residuo.
    - Gas portador del proceso de pirólisis.

- Estudiar el comportamiento dieléctrico de los residuos más apropiados para determinar los parámetros de diseño de un prototipo de reactor.

- Estudiar el crecimiento de la bacteria *Rhodospirillum rubrum* y la producción del biopolímero PHB mediante la fermentación de syngas procedente de pirólisis convencional y de pirólisis con microondas del residuo más apropiado.

Capítulo 3

Experimental

3.1 Residuos utilizados como sustratos para la pirólisis

En este apartado se describe la naturaleza de los materiales que van a ser utilizados en este trabajo para ser sometidos a procesos de pirólisis: su origen y causas de su generación, así como datos relativos a su producción y gestión. Todos los residuos proceden de la empresa *Abengoa Bioenergía Nuevas Tecnologías* (Sevilla, España), excepto las microalgas que fueron suministradas por *Exeleria S.L.* A pesar de ser sustratos con un gran potencial para la síntesis de productos de alto valor, los residuos utilizados en este trabajo no se encuentran en general lo suficientemente explotados.

3.1.1 Residuos sólidos urbanos

Los residuos sólidos urbanos (RSU) consisten en una mezcla compleja de componentes biológicos (lignina, carbohidratos, proteínas o lípidos), componentes petroquímicos (plásticos, aceites o detergentes) y algunos componentes inorgánicos (PREDA, 2007). En general, los RSU están formados por un tercio de materia compostable (como restos de alimentos de cocinas); un tercio de materia combustible (plásticos, papel, materia textil, etc.) y otro tercio de materia inerte (vidrio, materiales cerámicos, metales, etc.). Es importante tener en cuenta que las dos primeras fracciones contienen una gran cantidad de carbono que podría ser utilizado en procesos de conversión hacia bioproductos mediante el uso de procesos alternativos a la combustión.

Como regla general, se genera aproximadamente 1 kg de basura doméstica por ciudadano y día. En algunos países industrializados, este valor puede ser incluso el doble. La OCDE estima que en 2020, se podría generar un 45% más de residuos de aquellos producidos en 1995 (EUROPEAN COMISSION, 2010). La mayor parte los RSU es combustionada en incineradoras o depositada en vertederos (67%). Sin embargo, ambos métodos suponen un serio impacto medioambiental. El depósito en vertederos no sólo ocupa cada vez más espacio terrestre, sino que también produce contaminación atmosférica, en el agua y en los suelos, mediante la emisión de gases de efecto invernadero como el CO_2 y el CH_4, o la lixiviación de productos químicos tóxicos y pesticidas hacia el suelo y las aguas subterráneas. Además, si la combustión de los RSU es incompleta, se pueden liberar sustancias peligrosas como las dioxinas o gases ácidos.

En este trabajo, se han utilizado dos fracciones procedentes de RSU: una fracción orgánica y una fracción compuesta por residuos plásticos, con las siguientes características:

- La fracción orgánica de RSU (que, a partir de ahora, será llamada **MSW**) procede de un vertedero situado en Sevilla. Se llevó a cabo un pretratamiento previo a su uso como sustrato mediante el cual se redujo a un tamaño de partícula de entre 1 y 3 mm. Además, también se cuenta con una fracción derivada de la anterior, que fue sometida a un proceso de secado y a una eliminación parcial de inertes (p.e., restos de vidrios), que a partir de ahora será llamada **MSWd**.

- La fracción de residuos sólidos plásticos (a partir de ahora, será llamada **PLA**) está formada con una mezcla compleja de plásticos y procede del mismo vertedero situado en Sevilla. Se llevó a cabo un pretratamiento previo a su uso como sustrato mediante el que se redujo su tamaño de partícula a un intervalo de entre 1 y 3 mm.

3.1.2 Residuos agrícolas

La Unión Europea estima que sus estados miembros producen un total de 700 millones de toneladas de residuos agrícolas al año. Estos materiales lignocelulósicos (es decir, plantas derivadas de cultivos energéticos, residuos de actividades forestales y residuos agrícolas y vegetales) son ejemplos excelentes de materiales biomásicos con un gran potencial para la síntesis de productos orgánicos de alto valor, debido a la alta disponibilidad de biomasa y su gran contenido en carbono. Sin embargo, la conversión de materiales lignocelulósicos en biocombustibles o biomateriales mediante el proceso convencional de hidrólisis enzimática y posterior fermentación (Figura 3.1) hace que se pierda gran parte del material inicial, puesto que la lignina presente se desecha; además, las etapas de pretratamiento aumentan el coste del proceso, pero son muy necesarias debido a que permiten aumentar la producción y, en definitiva, el rendimiento de la etapa posterior de fermentación.

La <u>fracción de residuos agrícolas</u> utilizada en este trabajo (que será llamada como **STR**) procede de una planta de producción de biocombustibles situada en Salamanca. Se llevó a cabo un pretratamiento previo a su uso como sustrato mediante el cual se redujo a un tamaño de partícula de entre 1 y 3 mm.

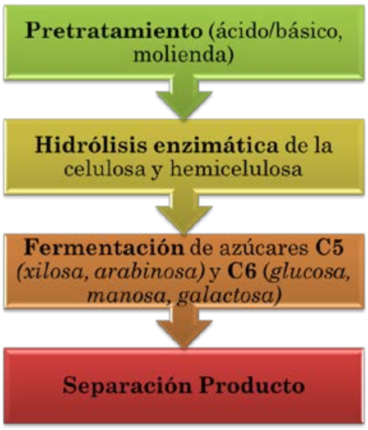


Figura 3.1 Proceso de obtención de bioproductos a partir de materiales lignocelulósicos

3.1.3 Lodos de depuradora

Los lodos de depuradora procedentes de EDAR constituyen un residuo orgánico muy complejo difícil de valorizar, ya que tienen en general un bajo contenido en carbono y una alta proporción de contaminantes. La producción de lodos ha ido incrementando en la mayoría de los estados miembros de la Unión Europea, hasta producir en España unos 1,1 millones de toneladas (en base seca) en 2012 de acuerdo al Registro Nacional de Lodos, lo cual puede ser atribuido principalmente a la implementación de la directiva sobre tratamiento de aguas residuales 91/271/EEC (GENDEBIEN, 2010). La mayor parte de estos lodos (81%) se destinó a aplicaciones agrícolas; sin embargo, los métodos principales de post-tratamiento son la incineración y el vertido en vertederos, ya que la primera alternativa presenta riesgos de contaminación en los suelos.

La fracción de lodo de depuradoras utilizada en este trabajo, que a partir de ahora será llamada **SSd**, procede de una planta de tratamiento de aguas residuales situada en Sevilla Se llevó a cabo un pretratamiento previo a su uso como sustrato mediante el cual se sometió a un secado después del tratamiento secundario de las aguas residuales y se redujo a un tamaño de partícula de entre 1 y 3 mm.

3.1.4 Microalgas

Las microalgas son microorganismos fotosintéticos que crecen rápidamente gracias a su estructura unicelular, como las algas verdes (*Chlorophyta*) y las diatomeas (*Bacillariophyta*). Son fáciles de cultivar, pueden crecer con pocos cuidados utilizando agua no apta para consumo humano y es fácil obtener sus nutrientes, por ejemplo, de aguas residuales. En la actualidad, se espera que las microalgas sean una fuente importante de productos de alto valor con aplicaciones en diferentes áreas biotecnológicas (farmacia, industria alimentaria, cosmética, etc) y, especialmente en la producción de biocombustibles (las microalgas constituyen la fuente de la llamada tercera generación de biocombustibles). El creciente interés en la aplicación de las microalgas para producir biocombustibles se debe a sus potenciales ventajas frente a otros cultivos terrestres de biomasa, como son: (1)

producción durante todo el año, lo que garantiza una mayor producción de biocombustibles; (2) uso de aguas residuales como fuente de nutrientes de las microalgas; (3) eliminación del uso de pesticidas o herbicidas; y (4) la posibilidad de cultivarlas en aguas salobres o tierras no cultivables, resultando en una minimización del impacto medioambiental. Sin embargo, resulta aún necesario reducir los costes de producción de estos biocombustibles a niveles de los combustibles fósiles.

El contenido promedio de lípidos en las microalgas alcanza el 70%. Las especies más comunes (*Chlorella, Crypthecodinium, Cylindrotheca, Dunaliella, Isochrysis, Nannochloris, Nannochloropsis, Neochloris, Nitzschia, Phaeodactylum, Porphyridium, Schizochytrium, Tetraselmis*) tienen niveles de aceite (lípidos) del 20 a 50%. También es significativa la composición en ácidos grasos, ya que pueden tener efecto en las características del biocombustible producido. De esta forma, el rendimiento en aceite de las microalgas es mucho mayor que el de los vegetales. Por ejemplo, el maíz puede producir 172 L/Ha de aceite y el girasol es capaz de producir 952 L/Ha, mientras que las microalgas pueden llegar a producir hasta 95000 L/Ha (GAO, 2012).

En esta Tesis, se ha utilizado la microalga *Scenedesmus almeriensis*, tanto en su forma original (previamente sometida a un proceso de secado), como el residuo de microalga que queda tras un proceso de extracción de lípidos, tal como se describe en la correspondiente Publicación III.

3.2 Dispositivos experimentales para llevar a cabo los procesos de pirólisis

El proceso de pirólisis de residuos orgánicos se ha llevado a cabo en un horno eléctrico y en dos hornos microondas diferentes, uno con control de temperatura y otro con control de potencia.

El horno utilizado para llevar a cabo la pirólisis convencional funciona con energía eléctrica convencional. Concretamente, es de tipo modular, cilíndrico y vertical, con una potencia de 1450 W, lo que permite alcanzar una temperatura máxima de 1100 ºC (Figura 3.2a).

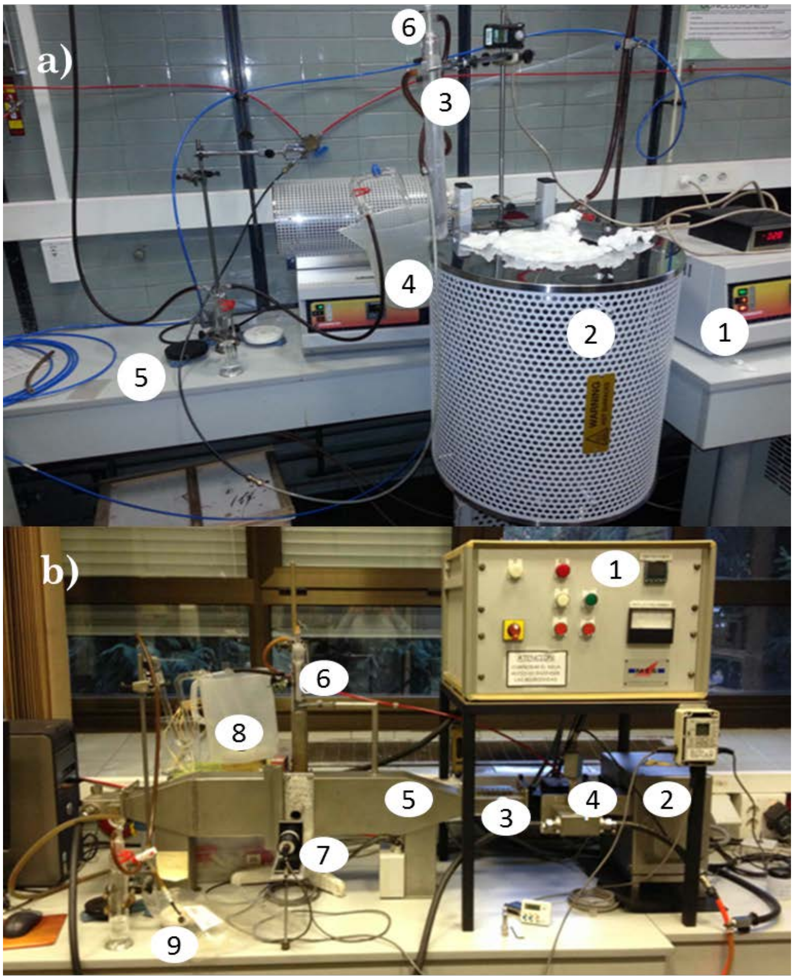


Figura 3.2 Equipamiento para llevar a cabo a) Pirólisis convencional (1. Panel de control; 2. Horno eléctrico; 3. Reactor; 4. Sistema de condensación de aceites; 5. Bolsa Tedlar; 6. Termopar); b) Pirólisis inducida por microondas con control de temperatura (1. Panel de control; 2. Magnetrón; 3. Tornillos de sintonización; 4. Disipador de ondas reflejadas y transmitidas; 5. Guía de ondas; 6.Reactor; 7. Pirómetro; 8. Sistema de condensación de aceites; 9. Bolsa Tedlar)

El horno microondas unimodo con control de temperatura (Figura 3.2b), llamado así porque únicamente trabaja en un modo de resonancia, opera a una frecuencia de 2450 MHz.

Este sistema consta de un generador de microondas, en este caso un magnetrón MES (*Microondas Énergie Systèmes*) controlado por un modulador de potencia que permite variar la potencia generada entre 0 y 1860 W, según la temperatura de trabajo deseada. Las ondas generadas se propagan a través de la guía de ondas hasta la zona de utilización. Está construida en acero inoxidable y tiene una sección rectangular en la zona en la que se sitúa la muestra de 8.5 x 14 cm^2. En su interior, la propagación de las ondas se produce por reflexiones múltiples sobre las paredes. La guía de ondas del equipo dispone de un orificio en su parte superior por el que se introduce el reactor en el que se colocará el material a tratar. El reactor posee un orificio en la parte superior que permite introducir el gas que inertiza las muestras durante la pirólisis, y otro que permite la salida de gases.

Por otra parte, la temperatura alcanzada durante los experimentos se mide con un pirómetro óptico. Éste dispone de un controlador para seleccionar y modificar los parámetros de entrada del pirómetro como la emisividad de la muestra. Para que la medida de temperatura sea eficaz, es necesario que el campo visual del pirómetro, delimitado por un orificio lateral en la guía de ondas, esté situado de frente a la muestra. También es importante determinar la emisividad de la muestra de la forma más exacta posible, para lo cual se ha optado por hacer un calibrado de emisividad con los carbonizados de los residuos que se van a emplear.

Una vez que las microondas llegan a la muestra, pueden darse varias situaciones: que sean absorbidas por el material, lo que contribuye a un aumento de su temperatura, que atraviesen la muestra sin ser absorbidas o que se reflejen cambiando su trayectoria en sentido contrario al que avanzaban. En estos dos últimos casos, la fracción no absorbida llega a dos detectores que la cuantifican y la expresan en porcentaje de potencia transmitida o reflejada, según el caso. La que se refleja es modulada por un dispositivo de orificios equipado con tornillos que permiten minimizar la potencia reflejada y evitar la entrada de las ondas en el magnetrón. Después de que la energía no absorbida pasa por los detectores, se disipa en una carga de agua, protegiendo así al magnetrón de posibles reflexiones que pudieran perjudicar su funcionamiento.

En cuanto al horno microondas unimodo con control de potencia (Figura 3.3), consiste en el mismo magnetrón que el sistema anterior, pero con una guía de ondas y una cavidad unimodo diferentes que, por su geometría, permite una absorción más eficiente de las microondas.

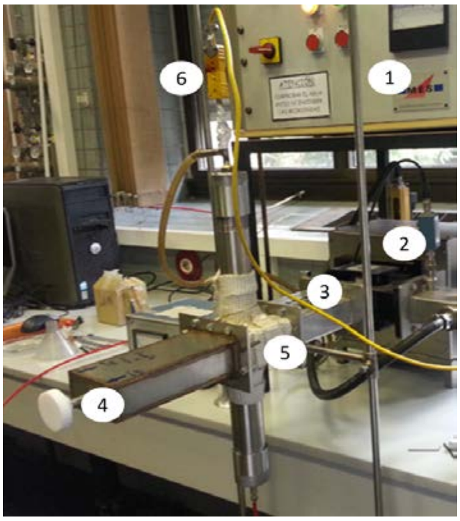


Figura 3.3 Dispositivo experimental para la pirólisis con microondas con control de potencia (1. Panel de control; 2. Magnetrón; 3. Tornillos sintonizadores; 4. Pared móvil sintonizadora; 5. Cavidad del reactor; 6. Termopar)

3.3 Técnicas experimentales

- *Análisis de los residuos y la fracción sólida*

Los análisis para caracterizar la composición de las muestras de residuos sólidos orgánicos, así como de algunas de las fracciones sólidas resultantes de la pirólisis, se llevaron a cabo en tres etapas:

1. Pretratamiento: A fin de que la caracterización entre muestras sea comparable, es necesario llevar a cabo un proceso de

molienda para reducir al mismo tamaño de partícula los diferentes sólidos. Esto se realiza mediante el uso de una trituradora de mandíbulas. Posteriormente, el sólido triturado se somete a un proceso de molienda en condiciones más controladas para reducir su tamaño a un intervalo de 1 – 3 mm mediante un molino pulverizador de anillos.

2. Análisis inmediato: Permite la caracterización del sólido en cuanto a su contenido en humedad, materia volátil y cenizas, a través del comportamiento térmico del mismo. Para ello se empleó un horno LECO TGA-601.
3. Análisis elemental: Es una técnica instrumental utilizada para obtener el contenido en C (carbono), H (hidrógeno), N (nitrógeno) y S (azufre), medido en porcentaje en masa. La técnica de análisis se basa en la combustión completa de una muestra que se somete a un tratamiento térmico a alta temperatura, aproximadamente 950 ºC, y bajo una atmósfera de oxígeno puro. Con ello, se consigue la conversión total de los elementos mencionados previamente en gases simples como CO_2, H_2O, SO_2 y NO_x, que posteriormente es reducido con Cu a N_2. Estos productos de combustión son medidos y procesados mediante un detector de conductividad térmica obteniéndose, al final, el contenido porcentual de cada elemento en la muestra analizada. El contenido en carbono, hidrógeno, nitrógeno y azufre se determinó en un microanalizador LECO-CHNS-932 mediante la combustión de aproximadamente 1 mg de muestra. El oxígeno, sin embargo, se evaluó directamente mediante microanálisis en un horno modelo LECO-TF-900. Por otra parte, también se llevó a cabo la determinación de Cl (cloro), porque representa un posible contaminante y agente corrosivo en sistemas de pirólisis, mediante un método de potenciometría y de acuerdo a un protocolo interno de la empresa suministradora de los residuos (Abengoa Bioenergía Nuevas Tecnologías).
4. Determinación de los metales presentes en las cenizas: El contenido metálico de las cenizas puede tener influencia en procesos de gasificación actuando como catalizadores. Se determinó mediante la concentración de Cu, Cd, Mn, Zn, Fe, Pb, Cr, Ni y Tl mediante espectroscopía de absorción atómica

previo tratamiento ácido de las muestras y de acuerdo a un protocolo interno de la empresa suministradora de los residuos (Abengoa Bioenergía Nuevas Tecnologías).

- *Análisis de la fracción líquida*

Para caracterizar los aceites procedentes de la pirólisis, se utilizaron dos rutas diferentes de pretratamiento previas al análisis mediante GC-MS (cromatografía de gases acoplada a espectrometría de masas):

- Para llevar a cabo la primera ruta de análisis, se añadió sulfato sódico anhidro a la fracción de aceites para eliminar las trazas de agua que pudiera contener, y se inyectó directamente en el equipo GC-MS para identificar los componentes volátiles.
- La segunda ruta de preparación consistió en una etapa de metanolisis, en la cual se adicionaron a las distintas fracciones de aceites 2 mL de una disolución de metanol con 15% de ácido sulfúrico y 0,5 mg/mL de ácido 3-metilbenzoico (patrón interno), seguido de una incubación de la mezcla a 80 ºC durante 7 h. Después de enfriar, se añadió 1 mL de agua desmineralizada y 1 mL de cloroformo, separándose la fase orgánica resultante, que fue analizada mediante GC-MS. El hecho de utilizar una etapa de metanolisis sirve para transformar compuestos no volátiles, como los ácidos grasos, en derivados de metil ésteres, que son compuestos volátiles y se pueden identificar mediante GC-MS.

Las muestras de fracciones líquidas se analizaron mediante GC-MS usando un cromatógrafo de gases *Agilent 7890A gas chromatograph* (*Agilent Technologies*, Palo Alto, California, USA) acoplado a un espectrómetro de masas Agilent 5975C (*electron ionization*, 70 eV) (*Agilent Technologies*, Palo Alto, California, USA) y equipado con una columna capilar de 30 m × 0,25 mm de diámetro interno. HP-5 (*methyl silicone bonded*) (*Agilent Technologies*). Las condiciones de operación en el caso de usar la primera ruta de pretratamiento descrita anteriormente fueron *split ratio* (50:1) y temperatura del inyector

(350 ºC). La temperatura de la columna se mantuvo durante 3 min a 40 ºC, aumentándose hasta 325 ºC a una velocidad de calentamiento de 7 ºC min^{-1}. En el caso de usar la segunda ruta de pretratamiento (metanolisis), se utilizó un *split ratio* de 20:1 y una temperatura del inyector de 350 ºC. La temperatura de la columna se mantuvo a 40 ºC durante 3 min, aumentándose hasta 325 ºC a una velocidad de calentamiento de 20 ºC min^{-1}.

Los espectros de masas resultantes y los tiempos de retención obtenidos mediante GC se utilizaron para identificar los componentes eluidos mediante comparación con los estándares encontrados en la base de datos *NIST Mass Spectral Database*. La semi-cuantificación de dichos compuestos identificados se llevó a cabo utilizando el porcentaje de área bajo cada pico respecto al área total de todos los picos de los correspondientes cromatogramas.

- *Análisis de la fracción gaseosa*

Los gases recogidos durante la pirólisis se analizaron en un cromatógrafo de gases *Varian CP3800*, provisto de un detector de conductividad térmica (TDC) y dos columnas cromatográficas conectadas en series. Una de las columnas es *Hayesep Q*, malla 80/100, de 2 m de longitud y 1/8" de diámetro y otra de tamiz molecular 13X, malla 80/100 con unas dimensiones de 1,50 m de longitud y 1/8" de diámetro. La segunda columna se encuentra en *bypass* mediante una válvula de 6 puertos para el análisis de CO_2 y de los hidrocarburos. El método cromatográfico para determinar la concentración de H_2, CH_4, CO_2, C_2H_4, C_2H_6, N_2 y CO es el siguiente: la temperatura inicial del horno es de 40 ºC, manteniéndose durante 1,2 min con un flujo continuo de 30 mL min^{-1} de helio como gas portador. Después se aumenta hasta 65 ºC con una velocidad de calentamiento de 50 ºCmin^{-1}, temperatura que se mantiene constante durante 3,7 min. Por último, se enfría el horno hasta 55 ºC a una velocidad de 20 ºC min^{-1} y dicha temperatura se mantiene durante 3,1 min. La temperatura del inyector y del detector es de 150 ºC, y el volumen de muestra inyectada de 100 µL. Previamente se hizo un calibrado a partir de mezclas de gases patrón de composición conocida y similar a la prevista en los gases a analizar.

- *Determinación de las propiedades dieléctricas de los residuos*

Para llevar a cabo la determinación de las constantes ε' y ε'' a 2.45 GHz se utilizó el siguiente procedimiento. En primer lugar, las diferentes muestras de residuos, contenidas en un tubo de cuarzo de 5 mm de diámetro interno y 43 mm de altura, se calentaron en un horno de convección GALLUR, modelo DIELKITV/DIELKITC hasta la temperatura correspondiente de medición de las propiedades dieléctricas (25, 50, 100, 200, 300, 400, 500, 600, 700, 800 y 1000 ºC) y en ausencia de oxígeno. Una vez alcanzada la temperatura, se colocaron rápidamente (máximo 3 s) en medio de una guía de ondas MICROGEM WR340, modelo NANOHOLDER, donde se determinaron los parámetros de reflexión de las ondas transmitidas (S_{11}, S_{12}, S_{21} y S_{22}) en los dos puertos de la guía mediante un analizador vectorial de redes RHODE & SCHWARZ, modelo ZVA67 (Figura 3.4). Después, el sistema se modelizó mediante el software comercial CST Microwave Studio 4.0 y, mediante una técnica inversa, se obtuvieron los valores de las permitividades a cada temperatura a partir de los parámetros de reflexión (REQUENA-PEREZ, 2006).

Figura 3.4 Guía de ondas NANOHOLDER (al frente) que contiene el tubo de cuarzo donde se inserta la muestra y analizador vectorial de redes (al fondo)

Referencias

European_Comission (2010). Being wise with waste: the EU’s approach to waste management, European Commission.

Gao, Y., C. Gregor, Y. Liang, D. Tang and C. Tweed (2012). "Algae biodiesel - a feasibility report." Chemistry Central Journal ***6****(Suppl 1): S1.*

Gendebien, A. (2010). Environmental, economic and social impacts of the use of sewage sludge on land, European Commission.

Preda, C. F. (2007). Management of municipal solid waste in Europe, Parliamentary Assembly of the Council of Europe.

Requena-Perez, M. E., A. Albero-Ortiz, J. Monzo-Cabrera and A. Diaz-Morcillo (2006). "Combined use of genetic algorithms and gradient descent optmization methods for accurate inverse permittivity measurement." IEEE Transactions on Microwave Theory and Techniques ***54****(2): 615-624.*

Capítulo 4

Resultados y Discusión: Bloque I

Producción de syngas a partir de sustratos sólidos orgánicos

Este bloque incluye los trabajos centrados en la producción de syngas a partir de residuos sólidos orgánicos de distinta naturaleza mediante la tecnología de pirólisis, tanto de forma convencional como inducida por radiación microondas.

En la Publicación I se compara el uso de diferentes sustratos orgánicos, temperaturas y métodos de calentamiento (convencional y microondas) para la producción de syngas; además, se examina la posibilidad de integrar este proceso junto a un proceso de fermentación microbiológica para la producción de bioplásticos. En la Publicación II se muestra un análisis de la fracción líquida de la pirólisis convencional y por microondas de los residuos orgánicos de la Publicación I, haciendo especial énfasis en la producción de compuestos peligrosos (PAH). La Publicación III muestra el uso de microalgas como sustrato alternativo para la producción de syngas.

4.1 Residuos orgánicos

Como se indicaba en la sección de Introducción, la producción de bioplásticos es una alternativa a los plásticos convencionales procedentes de fuentes fósiles. Sin embargo, el elevado coste de producción es uno de los principales problemas que presenta esta opción. Desde un punto de vista económico, la mayor contribución al coste total de la producción de los bioplásticos es la del sustrato carbonoso para la fermentación, habiéndose utilizado metanol, butirato, succinato, alcanoatos, glucosa o ácidos grasos (LEMOS, 1998). Para disminuir dicho coste, se están investigando diferentes estrategias como el desarrollo de cepas de bacterias recombinantes que sean capaces de utilizar fuentes de carbono más baratas como el syngas (JIN, 2014). Además, si el syngas procede de recursos renovables, esta alternativa tendría un punto a favor desde una perspectiva medioambiental. En este sentido, en la **Publicación I** se propone la producción de syngas mediante pirólisis usando residuos orgánicos complejos y heterogéneos de diferente naturaleza como son:

- Residuos sólidos urbanos (RSU), tanto la fracción orgánica (seca y húmeda) como la fracción de plásticos.
- Residuos agrícolas.
- Lodo de depuradora.

Es importante considerar que, en el caso concreto de la fermentación de syngas, las bacterias pueden utilizar H_2, CO y CO_2, por lo que este último gas también se ha incluido bajo la definición de syngas.

La Figura 4.1 muestra el esquema experimental que se siguió para la pirólisis de dichos residuos con captura de fase condensable (líquida) y gaseosa utilizando los dos dispositivos de calentamiento descritos en la sección Experimental.

Se decidió llevar a cabo la pirólisis en atmósfera de N_2, tanto convencional como con microondas, a dos temperaturas: **400 ºC** y **800 ºC**. Esta decisión estuvo basada en el comportamiento de desvolatilización de los residuos, determinado mediante la técnica de termogravimetría. En el caso de la fracción orgánica seca de RSU (Figura 4.2), la mayor generación de volátiles tiene lugar alrededor de 330 ºC (primer pico de la DTGA), finalizando esta primera etapa de desvolatilización alrededor de 400 ºC. Por otra parte, se eligió también la temperatura de 800 ºC, ya que a esta temperatura ha finalizado el proceso de desvolatilización, además de encontrarse favorecidas reacciones secundarias de gasificación y reformado de los volátiles generados (reacciones 1-4), lo cual resulta interesante de cara a favorecer la producción de syngas.

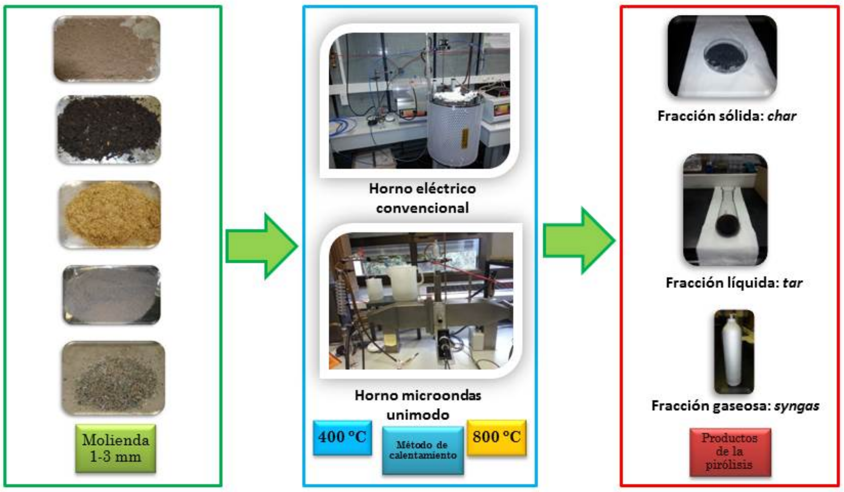


Figura 4.1 Esquema experimental del proceso de pirólisis convencional y asistida con microondas

$$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO \qquad \text{Reacción 1}$$

$$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO \qquad \text{Reacción 2}$$

$$C_nH_m + n\ CO_2 \leftrightarrow 2n\ CO + (n/2)\ H_2 \qquad \text{Reacción 3}$$

$$C_nH_m + n\ H_2O \leftrightarrow n\ CO + (n + m/2)\ H_2 \qquad \text{Reacción 4}$$

En el caso de la pirólisis con microondas, se utilizó como captador de microondas el carbonizado procedente de una pirólisis convencional de cada residuo a 800 °C, en una relación másica 0.3:1 (captador : residuo seco).

Una vez seleccionadas las temperaturas de operación y llevada a cabo la metodología experimental presentada en la Figura 4.1, se determinó el rendimiento en masa de cada fracción resultante de la pirólisis así como la **producción volumétrica** de la fracción *objetivo,* que es la gaseosa y, más concretamente, la producción en **syngas**. Así mismo, se caracterizó la **composición** de dicha fracción gaseosa.

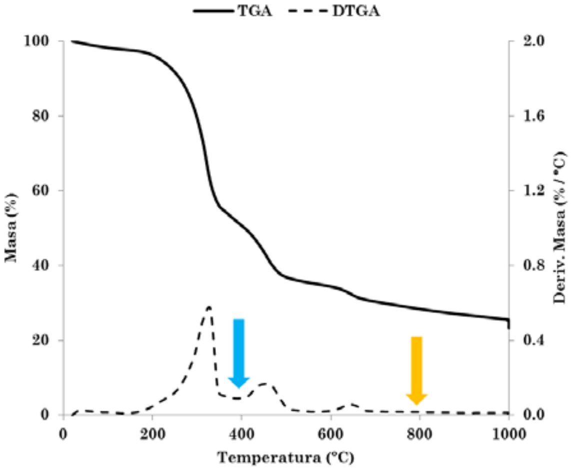


Figura 4.2 Termogravimetría de la fracción orgánica de RSU (10 °C/min; 20 mL/min N_2)

Respecto a la **pirólisis convencional**, al usar 400 °C el rendimiento en gas es extremadamente bajo; incluso en algunos casos como el de la fracción orgánica húmeda del RSU, es menor del 5% en masa. Además, el CO_2 es el gas que más se produce junto a grandes cantidades de hidrocarburos, mientras que no se detectó la presencia de H_2. Por tanto, estas condiciones no son las adecuadas para conseguir el objetivo general de este trabajo, ya que no se maximiza la producción de syngas. Por otra parte, al aumentar la temperatura hasta 800 °C, los rendimientos en gas son considerablemente más altos y la composición de las fracciones gaseosas obtenidas se acerca más a la de un syngas. Todos los residuos pirolizados produjeron más de un 20 vol% de H_2, excepto la fracción de plásticos de RSU (que tan solo generó un 9 vol%, aproximadamente). Además, se encontró que la fracción gaseosa resultante de la pirólisis de estos plásticos consistía principalmente en una mezcla de hidrocarburos y, por lo tanto, se descartó el uso de este sustrato para la producción de syngas mediante esta tecnología.

Por otra parte, la **pirólisis inducida por microondas** presentó resultados mucho más interesantes desde el punto de vista del objetivo general de esta tesis. La producción máxima de syngas fue de 0.83 $L \cdot g_{residuo}^{-1}$, correspondiente al residuo agrícola, mucho mayor que la obtenida mediante pirólisis convencional (0.44 $L \cdot g_{residuo}^{-1}$) a la misma temperatura (800 ºC). La concentración de syngas de la fracción gaseosa superó el 90 vol% en muchos casos, incluso a baja temperatura (400 ºC). Resulta especialmente atractivo utilizar como sustratos ambas fracciones orgánicas procedentes del RSU, ya que son capaces de producir concentraciones de H_2 cercanas al 50 vol% a ambas temperaturas de operación. Por tanto, la pirólisis inducida por microondas presenta la enorme ventaja de reducir el contenido en hidrocarburos en la fracción gaseosa a favor del contenido en syngas, lo que supone un syngas de mayor calidad para la fermentación. Sin embargo, tal como ocurre en el caso de la pirólisis convencional, los gases generados en la pirólisis con microondas de la fracción de plásticos de RSU, tienen una concentración de syngas relativamente baja (30-45 vol%), además de producirse gran cantidad de hidrocarburos que podrían inhibir el crecimiento posterior de las bacterias y, por tanto, la producción de bioplásticos (MUNASINGHE, 2010). Este caso tan solo ocurre usando como sustrato la fracción de plásticos de RSU.

Además, el calentamiento con microondas proporciona una mayor variedad en cuanto a la composición del syngas producido. En este sentido, se pueden obtener *ratios* H_2/CO entre 1.0 y 2.3 y *ratios* CO/CO_2 entre 0.5 y 4.5 con tan solo un cambio en las condiciones de operación y el sustrato, mientras que mediante calentamiento convencional, dichos *ratios* tan solo varían entre 0.0 y 1.0 y entre 0.1 y 1.1 respectivamente.

En cuanto al sustrato más apropiado para generar un syngas de mayor calidad (90-95 vol% de la fracción gaseosa), éstos son el residuo agrícola y, especialmente importante desde un punto de vista medioambiental, la fracción orgánica de RSU.

Los resultados obtenidos en este trabajo muestran que determinados **residuos orgánicos** podrían utilizarse en una unidad de procesamiento termoquímica para producir syngas. En concreto, la **pirólisis inducida por microondas** se perfila como un proceso muy efectivo para producir un syngas de calidad para ser usado como sustrato en la producción de bioplásticos mediante la fermentación del mismo sin la necesidad de usar ningún agente gasificante.

4.2 Análisis de los aceites

Uno de los principales problemas que presenta la tecnología de pirólisis convencional para la producción de syngas es el elevado rendimiento en aceites. Esta fracción líquida es una mezcla muy compleja de compuestos orgánicos de naturaleza muy diversa, pudiendo resultar de gran utilidad, tras un proceso de *upgrading,* como biocombustible. Sin embargo, para maximizar la producción de syngas es necesario minimizar el rendimiento de esta fracción líquida, lo cual puede tener lugar si la pirólisis se lleva a cabo mediante radiación microondas en lugar de usar un calentamiento convencional.

Por otra parte, parece ser que el mecanismo de calentamiento mediante microondas tiene gran influencia sobre la composición de la fracción de aceites. De especial interés es el análisis de la presencia de hidrocarburos aromáticos policíclicos (PAH), ya que éstos pueden llegar a ser peligrosos para la salud y el medioambiente. En este sentido, en la **Publicación II** se lleva a cabo una comparación entre la producción y composición de los aceites producidos mediante pirólisis convencional y pirólisis inducida por microondas. Para ello, se han utilizado los diferentes residuos orgánicos estudiados anteriormente para la producción de syngas en la Publicación I, habiéndose caracterizado mediante la técnica GC-MS la composición de los aceites producidos a 800 ºC, puesto que es la temperatura a la cual se maximiza la producción de syngas.

Existen algunos trabajos de investigación en los que se analiza la pirólisis con microondas de lodos de depuradora, encontrándose que se genera una menor concentración de PAH en los aceites en comparación a la producida mediante pirólisis convencional (DOMÍNGUEZ, 2005). Sin embargo, este resultado no puede ser generalizado a diferentes tipos de residuos orgánicos. Este vacío se estudia a lo largo de la Publicación II, donde se utilizan residuos de muy diferente naturaleza (fracción orgánica de RSU, lodo de depuradora, residuo agrícola y fracción de plásticos de RSU). El análisis de las fracciones de aceites concluyó que la producción de PAH es menor en el caso de la pirólisis con microondas, pero solamente en los casos de la fracción orgánica de

RSU y del lodo de depuradora. Una de las posibles causas es que la naturaleza polimérica de la fracción de plásticos de RSU y del residuo agrícola favorecen las reacciones de ciclación y condensación que producen los PAH, mientras que la naturaleza tan heterogénea de la fracción orgánica de RSU y del lodo de depuradora contiene otro tipo de componentes no tan poliméricos, por lo que las reacciones anteriormente citadas no tienen lugar en tanta extensión.

Por otra parte, es de especial interés la composición de los aceites procedentes de la pirólisis con microondas de la fracción de plásticos, puesto que dicha fracción presenta un alto contenido en aromáticos (benceno, tolueno y xilenos).

4.3 Análisis de la fracción sólida

En el caso de la pirólisis inducida por microondas, la fracción sólida presenta un papel importante, ya que puede reciclarse para ser usada como captadora de microondas en posteriores procesos de pirólisis para alcanzar la temperatura necesaria con el fin de maximizar la producción de syngas (800 ºC), como se detallará en el capítulo Resultados y Discusión: Bloque II. El hecho de usar dicha fracción como captadora de microondas presenta tres importantes ventajas: (1) La fracción sólida es un producto del propio proceso de pirólisis y, por lo tanto, no contiene ningún componente ajeno que pueda afectar a la composición de las fracciones resultantes; (2) se trata de un proceso de gestión de dicha fracción sólida; y (3) el uso de captadores de microondas permite que el consumo energético de un proceso de pirólisis inducido por microondas se pueda disminuir drásticamente, debido que aumenta la velocidad de calentamiento y el tiempo de los procesos de conversión sólido-gas es menor.

Por todo lo anterior, se analizaron las fracciones sólidas resultantes de los procesos de pirólisis inducida por microondas a 800 ºC. La Tabla 4.1 presenta los resultados. En concreto, la fracción sólida procedente del residuo agrícola es la que presenta un menor contenido en cenizas y una mayor concentración de carbono, por lo que *a priori* es la que presentará propiedades dieléctricas más favorables para convertir la energía microondas en energía térmica. Además, podría utilizarse también como combustible sólido por su contenido en carbono o como material de partida para producir adsorbentes mediante un proceso de activación física o química. Sin embargo, los carbonizados de las restantes fracciones tienen una aplicabilidad más limitada por su alto contenido en cenizas, aunque han mostrado ser efectivos para ser utilizados como captadores de microondas durante la pirólisis con microondas de las correspondientes fracciones orgánicas.

Tabla 4.1 Análisis de la fracción sólida resultante de la pirólisis con microondas a 800 ºC (resultados en base seca)

% masa	Fracción orgánica de RSU	Fracción plásticos de RSU	Residuo agrícola	Lodo de depuradora seco
Humedad	1.7	3.2	6.1	4.2
Cenizas	76.1	58.9	32.3	55.4
Materia volátil	5.1	4.3	6.2	4.0
C	21.0	36.6	64.7	39.3
H	0.2	0.5	0.5	0.6
N	0.7	0.8	0.8	3.4
S	1.1	0.8	0.2	0.1
O*	0.9	2.4	1.5	1.2

* Calculado por diferencia

Así mismo, la caracterización de las fracciones sólidas procedentes de la pirólisis convencional a 800 ºC se muestra en la Tabla 4.2. Al igual que ocurre con la caracterización de los carbonizados procedentes de la pirólisis en microondas, es el residuo agrícola el que presenta mayor concentración de carbono y menor de cenizas.

Es importante señalar que algunos trabajos enfocados en la fermentación de syngas, han utilizado la fracción sólida, sola o mezclada con la fracción líquida, como filtro del syngas producido previa introducción del mismo en el proceso de fermentación. Parece ser que dicho filtro elimina compuestos más pesados que, además, podrían ser tóxicos para las bacterias (DO, 2007).

Tabla 4.2 Análisis de la fracción sólida resultante de la pirólisis convencional a 800 ºC (resultados en base seca)

% masa	Fracción orgánica de RSU	Fracción plásticos de RSU	Residuo agrícola	Lodo de depuradora seco
Humedad	3.3	5.6	6.1	1.9
Cenizas	66.6	63.5	27.5	53.4
Materia volátil	1.7	3.2	4.3	1.8
C	30.7	28.9	67.2	41.3
H	0.1	0.3	0.8	0.5
N	1.0	0.9	1.1	4.0
S	0.7	0.9	0.2	0.1
O*	0.9	5.5	3.2	0.7

* Calculado por diferencia

Sin embargo, una de las opciones más viables e inmediatas para dar salida a esta fracción sólida es el uso de la misma como aditivo en suelos. Para ello, se llevó a cabo (en colaboración con la compañía OWS, dentro del marco del proyecto europeo SYNPOL) una serie de pruebas de ecotoxicidad agregando diferentes cantidades de carbonizado de RSU orgánico y residuos agrícolas (1% y 3%) a un suelo en el que se hizo germinar dos plantas diferentes: cebada y berro. Teniendo en cuenta que la máxima cantidad de compost que se puede añadir al suelo en Europa es del 1.14%, la concentración de carbonizado del 3% incluye un factor de seguridad 3. Además, también se llevó a cabo una prueba sin agregar carbonizado (blanco). En la Tabla 4.3 se presentan las pruebas evaluadas.

Tabla 4.3 Composición de las muestras de suelo estudiadas

Muestra de suelo	Suelo (g)	Carbonizado(g)
Blanco	180	0.0
1% RSU orgánico	180	1.8
3% RSU orgánico	180	5.4
1% Residuo agrícola	180	1.8
3% Residuo agrícola	180	5.4

De acuerdo con la normativa europea EN 13432 *Requirements for packaging recoverable through composting and biodegradation - Test* *scheme and evaluation criteria for the final acceptance of packaging* (2000), la norma americana ASTM D6400 *Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities* (2012) y la norma internacional ISO 17088 *Specifications for compostable plastics* (2012), cuando una planta se somete a un test de ecotoxicidad tras añadir compost a un suelo, la velocidad de germinación[1] y la biomasa contenida en la planta (en base fresca o seca) deberían ser mayores del 90% de las obtenidas en el correspondiente experimento en blanco.

- *Test de ecotoxidad en cebada*

Este test se realizó transcurridos 10 días. En la Tabla 4.4 se representan los resultados obtenidos en cada caso.

Tabla 4.4 Velocidad de germinación relativa y biomasa obtenida de cebada en los diferentes suelos modificados con carbonizados

Muestra de suelo	Velocidad de germinación (%)	Biomasa fresca (g)	Biomasa seca (g)	Velocidad de germinación respecto al blanco (%)	Biomasa fresca respecto al blanco (%)	Biomasa seca respecto al blanco (%)
Blanco	93.3±3.1	3.07±0.22	0.66±0.01	-	-	-
1% RSU orgánico	86.0±9.2	4.16±0.57	0.64±0.03	92.1	135.2	97.2
3% RSU orgánico	90.0±3.5	5.20±0.36	0.69±0.06	96.4	169.4	104.2
1% Residuo agrícola	82.0±6.0	5.76±0.17	0.62±0.03	*87.9*	187.5	94.4
3% Residuo agrícola	72.0±3.5	4.73±0.31	0.54±0.06	*77.1*	154.1	*81.6*

Como se observa, la velocidad de germinación está por debajo del nivel aceptable del 90% en los casos en los que se añade carbonizado del residuo agrícola. La biomasa obtenida está en general por encima del nivel del 90%, pero no en el caso de la biomasa seca al añadir un 3% de residuo agrícola.

---

[1] La velocidad de germinación relativa se determinó como el porcentaje de plantas germinadas respecto de la cantidad total de semillas añadidas inicialmente al suelo.

- *Test de ecotoxidad en berros*

Este test se realizó transcurridos 14 días. En la Tabla 4.5 se representan los resultados obtenidos en cada caso.

Tabla 4.5 Velocidad de germinación relativa y biomasa obtenida de berros en los diferentes suelos modificados con carbonizados

Muestra de suelo	Velocidad de germinación (%)	Biomasa fresca (g)	Biomasa seca (g)	Velocidad de germinación respecto al blanco (%)	Biomasa fresca respecto al blanco (%)	Biomasa seca respecto al blanco (%)
Blanco	92.0±4.4	4.13±0.39	0.23±0.01	-	-	-
1% RSU orgánico	94.3±13.7	4.29±0.16	0.26±0.01	102.5	103.7	109.2
3% RSU orgánico	94.0±3.8	4.39±0.51	0.25±0.02	102.2	106.1	105.4
1% Residuo agrícola	75.7±1.7	3.23±0.49	0.20±0.04	*82.2*	*78.3*	*87.2*
3% Residuo agrícola	83.7±12.7	3.83±0.78	0.23±0.02	90.9	92.6	97.1

Como se observa, la velocidad de germinación está en general por encima del nivel aceptable del 90%, excepto en el caso de añadir un 1% de carbonizado de residuo agrícola. La biomasa obtenida está por encima del nivel del 90%, excepto el caso de añadir también un 1% de residuo agrícola.

En vista a estos resultados, puede concluirse que el **efecto tóxico de los carbonizados en el crecimiento de las plantas es muy limitado o inexistente**.

4.4 Microalgas

El término genérico *microalgas* se refiere a un gran grupo de diversos microorganismos fotosintéticos y de dimensiones microscópicas. De entre otros tipos de biomasa, el uso de las microalgas destaca por sus múltiples ventajas, tales como su rápida velocidad de crecimiento, alta tasa de producción por unidad de superficie cultivada, alta eficiencia para capturar CO_2 o no competir con biomasa agrícola con fines alimentarios. En la Figura 4.3 se representan los principales usos de las microalgas.

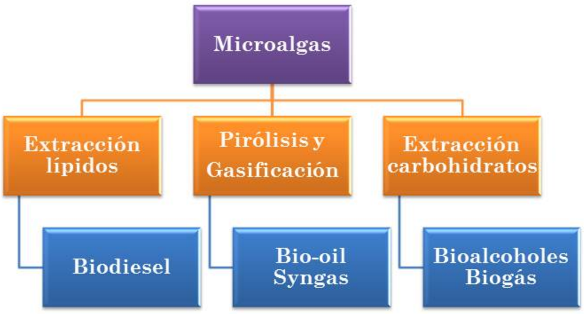


Figura 4.3 Principales aplicaciones de las microalgas

De interés para el caso concreto de esta tesis es la conversión termoquímica de las microalgas para producir syngas. Es por ello que se decidió examinar el comportamiento de la microalga *Scenedesmus almeriensis* como sustrato de pirólisis, tanto convencional como inducida por microondas, en la **Publicación III**.

En el caso de biomasa marina, existen diferentes trabajos de investigación enfocados en la pirólisis convencional para la producción de aceites (MIAO, 2004, BRENNAN, 2010, DU, 2011). Sin embargo, aunque la producción de aceites de pirólisis a partir de microalgas es superior a la obtenida con otros tipos de biomasa (TABERNERO, 2012), estos aceites se caracterizan por ser de carácter ácido, inestables y viscosos además de presentar proporciones notables de compuestos nitrogenados, lo que hace que sea necesario someterlos a un proceso de mejora para que puedan ser usados como biocombustibles. Por estas razones, la producción de syngas a partir de microalgas puede ser una alternativa prometedora a la producción de aceites.

Los resultados de la Publicación III presentan, por primera vez, la pirólisis inducida por microondas de una microalga con el objetivo de maximizar la producción de gas y, concretamente, la proporción de syngas. Además, también se estudia la pirólisis del residuo sólido de la misma microalga obtenido tras haber sido sometida a un proceso de extracción de lípidos. En la Figura 4.4 se muestra el procedimiento experimental seguido para obtener el syngas.

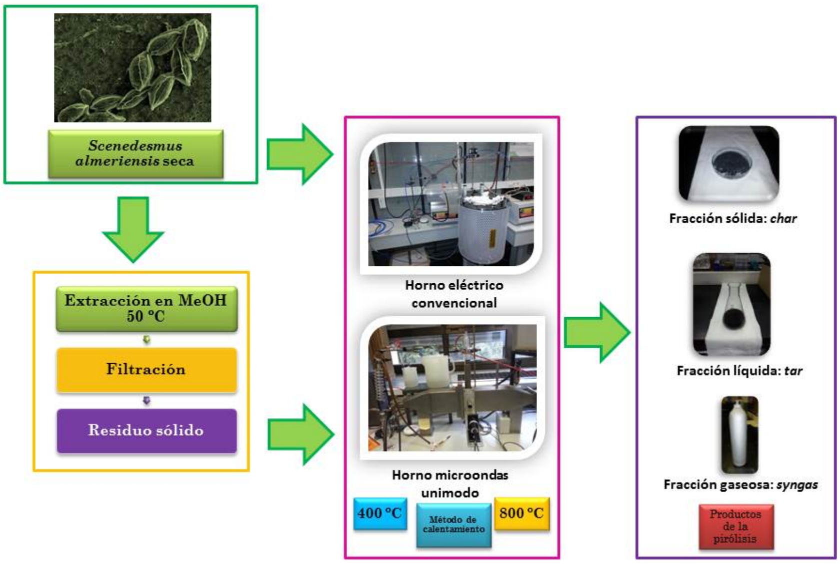


Figura 4.4 Esquema experimental del proceso de pirólisis convencional y asistida con microondas de la microalga y de su residuo de extracción

En el caso de la pirólisis con microondas, para alcanzar la temperatura de pirólisis se utilizó como captador de microondas el carbonizado procedente de una pirólisis convencional de la microalga o su residuo de extracción a 800 ºC, en una relación másica 0.3:0.7 (captador : residuo seco).

Los resultados de este trabajo indican que mediante la pirólisis inducida por microondas es posible conseguir una fracción gaseosa con un alto contenido en H_2 (50 vol%, aproximadamente) a partir de la microalga y de su residuo de extracción independientemente de la temperatura de pirólisis. Así mismo, la producción de CO se ve favorecida mediante el calentamiento con microondas en detrimento de la de CO_2 e hidrocarburos ligeros. Además, la producción de gas es mucho mayor que en el caso de la pirólisis convencional, sobre todo a baja temperatura (400 ºC). Por ejemplo, la pirólisis en microondas de la microalga a 400 ºC da lugar a una producción de gas 307% superior a la llevada a cabo de forma convencional.

Por otra parte, se ha observado que el residuo sólido de extracción de la microalga es capaz de producir una mayor concentración de syngas en todas las condiciones experimentales. Este hecho podría atribuirse a que durante el proceso de extracción en metanol, se extraen compuestos pesados como los lípidos, haciendo que la fracción líquida resultante de la pirólisis sea más fácil de craquear y reformar y se produzca una mayor cantidad de gas.

Además, se evaluó la posible actividad catalítica de los metales presentes en el carbonizado utilizado como captador de microondas, comparando la caracterización de la fracción gaseosa con aquella resultante de la pirólisis utilizando grafito como captador de microondas, ya que en otros estudios se ha observado dicho efecto catalítico (BERMUDEZ, 2014). Sin embargo, no se observaron diferencias significativas, por lo que se concluyó que los metales presentes en el carbonizado de la microalga *Scenedesmus almeriensis* no presentan actividad catalítica en el proceso de pirólisis.

Los resultados obtenidos en este trabajo muestran que las **microalgas** son un sustrato muy apropiado para la producción de syngas mediante **pirólisis inducida por microondas**. En concreto, el **residuo** sólido procedente de la **extracción** de lípidos de las microalgas es particularmente adecuado para conseguir tal fin, además de suponer una vía de gestión de un residuo procedente del proceso de obtención de biodiesel.

Referencias

*Bermudez, J. M., M. Francavilla, E. G. Calvo, A. Arenillas, M. Franchi, J. A. Menendez and R. Luque (2014). "Microwave-induced low temperature pyrolysis of macroalgae for unprecedented hydrogen-enriched syngas production." RSC Advances **4**(72): 38144-38151.*

*Brennan, L. and P. Owende (2010). "Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products." Renewable and Sustainable Energy Reviews **14**(2): 557-577.*

*Do, Y. S., J. Smeenk, K. M. Broer, C. J. Kisting, R. Brown, T. J. Heindel, T. A. Bobik and A. A. DiSpirito (2007). "Growth of Rhodospirillum rubrum on synthesis gas: Conversion of CO to H2 and poly-β-hydroxyalkanoate." Biotechnology and Bioengineering **97**(2): 279-286.*

*Domínguez, A., J. A. Menéndez, M. Inguanzo and J. J. Pis (2005). "Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge." Fuel Processing Technology **86**(9): 1007-1020.*

*Du, Z., Y. Li, X. Wang, Y. Wan, Q. Chen, C. Wang, X. Lin, Y. Liu, P. Chen and R. Ruan (2011). "Microwave-assisted pyrolysis of microalgae for biofuel production." Bioresource Technology **102**(7): 4890-4896.*

*Jin, H. and B. J. Nikolau (2014). "Evaluating PHA Productivity of Bioengineered Rhodosprillum rubrum." PLoS ONE **9**(5): e96621.*

*Lemos, P. C., C. Viana, E. N. Salgueiro, A. M. Ramos, J. P. S. G. Crespo, Reiszcorr, gt and M. A. M. (1998). "Effect of carbon source on the formation of polyhydroxyalkanoates (PHA) by a phosphate-accumulating mixed culture." Enzyme and Microbial Technology **22**(8): 662-671.*

*Miao, X., Q. Wu and C. Yang (2004). "Fast pyrolysis of microalgae to produce renewable fuels." Journal of Analytical and Applied Pyrolysis **71**(2): 855-863.*

*Munasinghe, P. C. and S. K. Khanal (2010). "Biomass-derived syngas fermentation into biofuels: Opportunities and challenges." Bioresource Technology **101**(13): 5013-5022.*

*Tabernero, A., E. M. Martín del Valle and M. A. Galán (2012). "Evaluating the industrial potential of biodiesel from a microalgae heterotrophic culture: Scale-up and economics." Biochemical Engineering Journal **63**(0): 104-115.*

Publicación I

COMPARING THE COMPOSITION OF THE SYNTHESIS-GAS OBTAINED FROM THE PYROLYSIS OF DIFFERENT ORGANIC RESIDUES FOR A POTENTIAL USE IN THE SYNTHESIS OF BIOPLASTICS

Journal of Analytical and Applied Pyrolysis

111 (55-63)

Año 2015

Journal of Analytical and Applied Pyrolysis 111 (2015) 55–63

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 22 October 2014
Accepted 13 December 2014
Available online 16 December 2014

Keywords:
Bioplastics
Polyhydroxyalkanoates
Syngas fermentation
Microwave pyrolysis
Waste valorization

ABSTRACT

In this article we propose the possibility of obtaining syngas from very different and complex organic wastes, such as municipal solid wastes, agricultural residues or sewage sludge, through microwave-induced and conventional pyrolysis at 400 and 800 °C. Microwave heating has proved to be an appropriate way to produce a syngas with $CO + H_2$ concentrations as high as 90 vol% and in large yields (up to $0.83\,L\,g^{-1}{}_{waste}$). In addition, the potential of the syngas produced by this technology as fermentation substrate for the production of bioplastics is discussed. Microwave pyrolysis seems to serve as a novel route into biorefineries to produce valuable biobased products.

1. Introduction

Plastics are widely used in almost all industries, especially in the packaging and building sectors, due to their great versatility, low weight and excellent electrical and thermal insulation properties. Although the production of plastics has grown worldwide since 1950, in the European Union, this production has remained practically constant at 55–60 million tons per year since 2000. The production process leads inevitably to the generation of large amounts of plastic waste. The slow degradation rate, the potential risk of accidental fire and the heavy metals content in plastic additives have been proposed as the potential reasons for the search for alternative means of disposal to landfill, such as re-extrusion, mechanical recycling, chemical recycling or energy recovery [1,2]. The increasing use of these technologies has led to a decrease in the amount of waste plastic sent to landfill sites since 2008. Alternatively, because of the finite sources of fossil reserves, bioplastics production is a niche industry that is being developed in an attempt to overcome the non-degradability problem of fossil-based plastics, and to help reduce the carbon footprint of products [3,4]. According to European Bioplastics (http://en.european-bioplastics.org/), bioplastics are economically innovative and have great potential for further economic growth along the value added chain.

Of special interest are those plastics that are biobased and biodegradable, such as polyhydroxyalkanoates [5] (PHA), which can be employed for short-life applications such as packaging [6], certain agricultural applications [7] and bags suitable for organic recycling, although more sophisticated uses of PHA have also recently been reported (tissue repair and regeneration, drug delivery systems or heart tissue engineering) [8,9]. Since PHA are polyesters with a highly versatile structure, their potential is immense. Their thermo-mechanical properties can even be tailored to make them comparable to those of conventional plastics [10,11]. PHA can be made by causing microorganisms to accumulate them. High-value substrates such as sucrose, methanol or vegetable oils can then be subjected to fermentation and converted into PHA. However, the cost of these carbon sources, which may amount to as much as 50% of the total production cost of PHA, is the main reason for the slow growth of the PHA industry [12]. For this reason, the use of cheaper renewable resources as substrates such as wastes from biodiesel production [13], waste plant oils [14], paper industry wastewater [15] or dairy wastewater activated sludge [16], is essential to ensure the commercial viability of the process. Another attractive alternative would be to use syngas, defined for this particular application as $CO + H_2 + CO_2$. Syngas fermentation has been

---

Abbreviations: EF, electric furnace; MIP, microwave-induced pyrolysis; MWS, municipal solid waste fraction; MSWd, dried municipal solid waste fraction; PHA, polyhydroxyalkanoates; PLA, plastic solid waste fraction; SSd, dried sewage sludge fraction; STP, standard conditions for temperature and pressure; STR, straw fraction.

* Corresponding author. Tel.: +34 985 118972; fax: +34 985 297672.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

http://dx.doi.org/10.1016/j.jaap.2014.12.011
0165-2370/

Table 1
Advantages and drawbacks of using syngas in biocatalytic processes.

Advantages	Drawbacks
Organic waste to produce syngas: abundantly available, does not require additional production costs and is a substrate that does not compete with human nutrition [37]	Mass-transfer limitations of syngas components to the fermentation medium due the low solubilities of CO and H_2 [48], although various attempts to overcome this have been reported [49]
Syngas fermentation needs low operating temperatures and pressures, reducing energy and operating costs	
Biocatalysts usually show a sulphide tolerance of ≥2% H_2S or COS [46,47]	Relatively low volumetric productivity [49]
Allows the bioreactor hydraulic retention time to be uncoupled from the substrate supply, making it possible to control substrate inhibition and product formation [42]	Some components might be inhibit the metabolism of bacteria, such as tars, SO_x and NO_x; syngas cleaning may be necessary [35,50,51]
Biological fermentation does not require a fixed H_2/CO ratio due to the specificity of enzymatic reactions [39]	

proposed as a conversion route to produce bulk chemicals such as ethanol [17], acetate [18] or butyrate [19]. The use of syngas fermentation affords significant advantages over conventional processes for producing such chemicals as shown in Table 1.

Even though more than 300 microorganisms are known to synthesize PHA [20], few of them are able to process the syngas components [21]. For instance, autotroph microorganisms can use single-carbon compounds (CO and/or CO_2) as their sole carbon source and CO and H_2 as their energy source; whereas, unicarbonotroph microorganisms are only able to use CO directly as their sole source of both carbon and energy. The use of syngas as substrate to produce PHA is a truly novel research area, and this explains why so little information is available. Do et al. studied the growth of *Rhodospirillum rubrum* on seed corn-derived syngas containing 8.8% H_2, 17.2% CO and 16.3% CO_2, which resulted in a mixture of two types of PHA (β-hydroxybutyrate and β-hydroxyvalerate) [22]. According to these authors, small quantities of H_2S in the syngas may have been responsible for increased growth rates. The results of their research were used to develop a techno-economic model to demonstrate the feasibility of PHA production from biomass-derived syngas fermentation [23]. It is with this aim that the SYNPOL project (http://www.synpol.org) is currently being developed and is expected to enable the European Union to lead the way in the field of syngas fermentation technology for waste valorization and sustainable biopolymer production.

We propose a new potential bioprocessing scheme in Fig. 1 for the production of biodegradable polyhydroxyalkanoates. As shown, the syngas stream can be obtained from renewable feedstock. The microwave pyrolysis of biomass has demonstrated its potential to maximize both the gas yield and syngas concentration, and so is the most appropriate heating method to obtain syngas for fermentation [24–29]. This process prevents the generation of wastes, e.g., by recirculating part of the solid char to the reactor as a microwave receptor material [28]. The microwave heating mechanism is volumetric and yields quite different product distributions by favoring heterogeneous reactions between the volatiles released and the carbonaceous waste. This makes it possible to increase the concentration of valuable products, such as CO, for bioplastics production. In short, microwave pyrolysis offers an excellent opportunity for diverting organic waste away from the traditional disposal methods such as landfill and incineration and the possibility of recovering commercially valuable products from wastes. Besides, the use of microwave pyrolysis to produce syngas on a large scale will probably contribute to a more environmentally sustainable and energy-efficient process compared to conventional heating processes, as has been demonstrated in a recent study in which energy efficiency of microwave pyrolysis of wheat straw was 1.5 times higher than the energy efficiency achieved by a conventional pyrolysis process [30]. Although this technology has been widely studied, it has never been previously proposed for the production of syngas for use in fermentation processes. Moreover, no studies have yet explored the possibility of applying microwave-induced pyrolysis to the biopolymer production process through syngas fermentation. Once the syngas is fermented by bacteria, PHA can be recovered by using a solvent extraction; e.g., using chloroform and methanol [31] or combining surfactant addition to break down the cell wall followed by solubilization of cell material with sodium hypochlorite [23]. This stage should be followed by the separation of the PHA-containing phase from the residual cell material by sedimentation.

In this article we offer an extensive comparative study of organic wastes and their pyrolysis-derived syngas at different temperatures and in two different heating systems for their subsequent use as feedstock for bioplastics production by means of syngas fermentation. Of particular interest is the innovative use of microwaves to achieve this goal, as this possibility to the best of our knowledge has never been considered before in the literature.

2. Material and methods

2.1. Samples preparation

Five different samples, provided by BEFESA Gestión de Residuos Industriales S.L. (Seville, Spain), were selected for this study:

1. An organic fraction from a municipal solid waste, obtained from a landfill in Seville (Spain). This fraction was subjected to a size reduction of 1–3 mm. This sample will be labelled as MSW.
2. An organic fraction from a municipal solid waste, dried and partially cleaned from inerts. This fraction was taken from the previous fraction (MSW) and subjected to removal of moisture and inert solids, such as glass or metals. After this pre-treatment, the fraction size was reduced to 1–3 mm. This sample will be labelled as MSWd.
3. A plastic fraction from a municipal solid waste. This sample, a complex mixture of plastic residues, was obtained from the same landfill in Seville. The fraction was milled to 1–3 mm and will be labelled as PLA.
4. An agricultural residue. This sample was obtained from a biodiesel production plant located in Salamanca (Spain) and is composed of straw. The sample was also milled to a size range of 1–3 mm. This sample will be labelled as STR.
5. Dried sewage sludge. This sample was collected from a wastewater plant in Seville. The sludge after being subjected to secondary treatment was dried to facilitate transportation. After being dried, the sample was milled to a size range of 1–3 mm. This sample will be labelled as SSd.

2.2. Analysis of the samples

The moisture, ash content and volatile matter data of the residues were obtained by means of a LECO TGA-601. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The micro-analyzer provides carbon, hydrogen, nitrogen, and sulfur percentage composition. The oxygen content was determined from the LECO-TF-900 furnace. The content of metals from the ashes was determined by means of atomic absorption spectroscopy using an Agilent 7700x. The

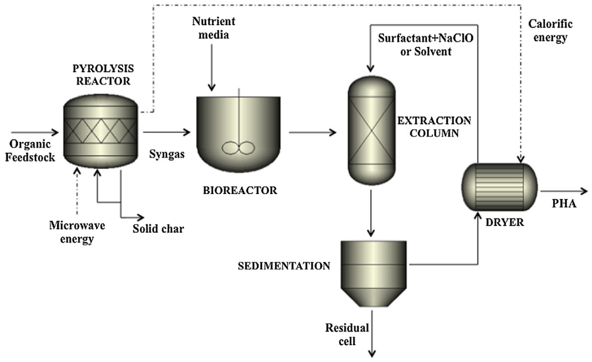


Fig. 1. Integrated microwave pyrolysis for the polyhydroxyalkanoates production process through syngas fermentation.

Table 2
Proximate and ultimate analyses of the different residues. Content of metals of the ashes.

Residue		Municipal solid waste – organic fraction	Municipal solid waste – dried and clean organic fraction	Municipal solid waste – plastic fraction	Straw	Sewage sludge (dried)
Label		MSW	MSWd	PLA	STR	SSd
Proximate analysis (wt%)	Moisture	46.3	2.8	1.3	11.5	3.4
	Ash[a]	22.6	27.7	8.9	6.3	15.4
	Volatile matter[a]	68.0	61.1	88.9	76.2	74.5
Ultimate analysis (wt%)	C	36.0	45.1	70.9	45.0	43.8
	H	5.8	5.4	9.7	5.0	6.1
	N	1.6	2.1	1.2	1.6	9.7
	S	0.2	0.4	0.5	0.0	0.1
	O	33.8	19.3	9.1	42.0	24.9
Content of metals (ppm)	Cu	24.6	44.8	50.8	0.00	153.4
	Cd	<0.1	<0.1	<0.1	0.41	2.0
	Mn	13.5	83.0	18.8	18.3	40.4
	Zn	100.5	182.9	73.2	6.6	459.8
	Fe	4880.1	8896.3	1098.8	286.9	2984.6
	Pb	17.1	30.8	4.7	<0.1	1.6
	Cr	32.0	58.7	72.5	0.0	11.7
	Ni	9.6	17.6	24.7	<0.1	2.8
	Tl	<0.1	<0.1	<0.1	0.0	0.0

[a] Dry basis.

results from this characterization are presented in Table 2. The TGA and DTGA profiles were obtained using a SDTQ600 Thermobalance (provided by TA Instruments) using a flowrate of N_2 of 20 mL/min with a heating rate of 10 °C/min up to 1000 °C. The thermogravimetric behavior of the residues is shown in the Supplementary Data (see Figs. S1–S5).

2.3. Conventional pyrolysis of samples

Conventional pyrolysis was performed at two different temperatures (400 and 800 °C) in the electric furnace (EF) shown in Fig. 2a. Approximately 4 g of sample was introduced into a quartz reactor. First, the reactor was placed outside the EF and was purged with N_2 for 30 min at a flow rate of 50 $\mathrm{mL_{STP}\,min^{-1}}$ to ensure an oxygen-free atmosphere. Meanwhile, the EF was heated up to the pyrolysis temperature. Once the reactor had been purged and the EF had reached the desired temperature, the N_2 flow was reduced to 10 $\mathrm{mL_{STP}\,min^{-1}}$ and the reactor was introduced into the EF for pyrolysis, the duration of which was 1 h. The gases evolved during pyrolysis were forced to pass through a condensing system (cooled by a cryogenic solution of water and NaCl) where the condensable compounds were removed from the gaseous fraction. Both the reactor and the condensing system were weighed before and after the pyrolysis experiment to determine the solid and liquid yields (respectively). The gas yield was determined by difference. Then, the gaseous fraction was collected in a Tedlar® bag and analysed by means of a Varian-CP3800 gas-chromatograph equipped with a TCD detector and two columns connected in series. The first column was 80/100 Hayesep Q (2 m × 1/8 in. × 2 mm) and the second column was a 80/100 Molesieve 13X (1.5 m × 1/8 in. × 2 mm). The second column was bypassed by a six-port valve for the analysis of the CO_2 and hydrocarbons. The carrier gas flow (He) was 30 mL/min. The initial oven temperature was set at 40 °C, which was maintained for 1.2 min. It was then programmed to rise from 40 to 65 °C at 50 °C/min with an isothermic step of 3.3 min. The temperature was then lowered from 65 to 55 °C at 20 °C/min and held for 2.6 min. The injector and detector temperatures were fixed at 150 °C. The TCD was calibrated using a standard gas mixture.

2.4. Microwave-induced pyrolysis of samples

Microwave-induced pyrolysis (MIP) was performed using the microwave oven shown in Fig. 2b. This system provided by MES (Microondes Énergie Systèmes) consists of a microwave magnetron

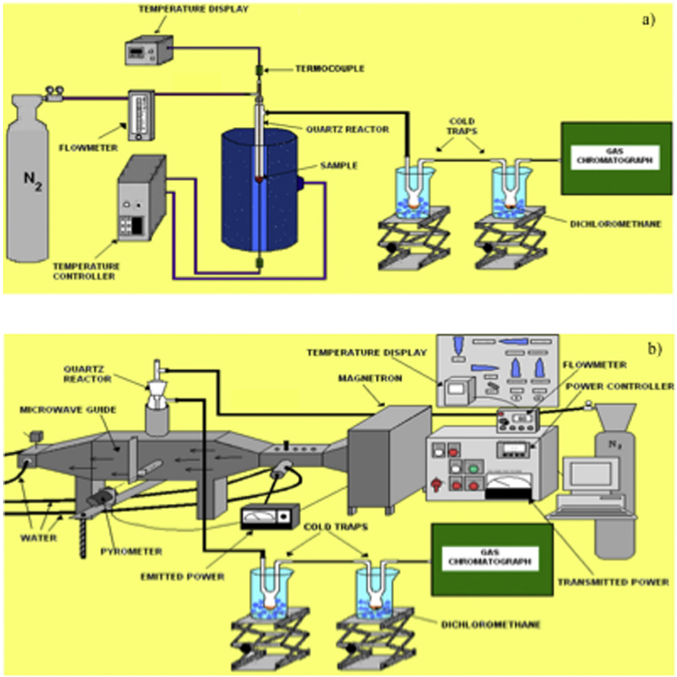


Fig. 2. Experimental set-up used: (a) conventional pyrolysis; (b) microwave-induced pyrolysis.

with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample-containing quartz reactor was placed. As in the conventional pyrolysis, the reactor was purged with N_2 for 30 min at a flow rate of 50 mL_{STP} min^{-1}. Then, the flow rate was reduced to 10 mL_{STP} min^{-1} and the microwave irradiation was switched on during 1 h. The reflected power was regulated by means of tuning screws until it reached zero. The same system as that used in conventional pyrolysis, was used to collect the liquid and gaseous fractions.

Owing to the low capacity of organic wastes used in this study to absorb microwaves, it was necessary to use a microwave receptor to induce the pyrolysis [27]. After the microwaves started to pass through the sample, they are absorbed by the receptor and the temperature increases. This allows the heat to be conducted to the waste until a temperature high enough to start the pyrolysis is reached. As the pyrolysis proceeds, the waste is carbonized and is then able to absorb microwaves, so that from that point on it can be directly heated by microwave radiation. The most appropriate material for use as microwave receptor is the char obtained from the previous pyrolysis, since it is a product of the process itself and does not contain any strange material that might influence the composition of the fractions. Nevertheless, other microwave receptor materials, such as SiC, CaO or activated carbons, could be used influencing pyrolysis reactions [32]. For this study, a receptor–to–dry feedstock mass ratio of 0.3:1 was selected. This ratio was selected after several preliminary experiments, which showed that this was the lowest ratio that would allow the biomass to be heated to the desired temperature while avoiding the thermal runaway effect which could result from microwave heating [27]. The experiments were performed in duplicate to check the repeatability. The errors came to less than 3% for the gas composition and less than 6% for the yields.

3. Results and discussion

3.1. Conventional vs. microwave-induced pyrolysis

Fig. 3 shows the specific yields from the three fractions obtained in the pyrolysis at 400 and 800 °C by conventional and microwave-induced pyrolysis. Some general trends can be clearly observed, although they are more pronounced at 400 °C than at 800 °C.

MIP enhances the gas production whereas the production of liquid is reduced in almost all cases. At 400 °C, MIP gives rise to greater gas yields than conventional pyrolysis. These consist of a percent increase from 42% in the case of SSd to more than 100% in the case of MSW and MSWd. The liquid yields are lower from MIP, with the exception of SSd and PLA. These wastes contain a larger amount of volatiles that are released at temperatures slightly higher than 400 °C compared to the other residues (see Figs. S1–S5 of ESI). Such volatiles can be removed from SSd and PLA by means of microwave heating but not by conventional heating and hence the liquid yield is increased. This ability of microwave heating to promote processes occurring at temperatures higher than the operating temperature is due to the presence of microplasmas [33,34]. These microplasmas are sparks or hot spots that last just a fraction of second and reach temperatures considerably superior to the

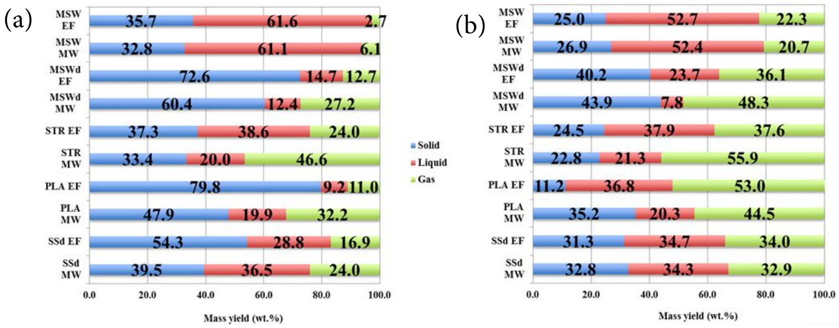


Fig. 3. Fraction yields (wt%) from the conventional (EF) and microwave-induced (MW) pyrolysis of the different residues at: (a) 400 °C; and (b) 800 °C.

Table 3
Composition of the gaseous fraction (vol%) obtained in the conventional and microwave-induced pyrolysis of the different residues.

400 °C										
	Conventional					Microwave				
	MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
H_2	0.0	0.0	0.0	0.0	0.0	51.4	46.2	9.1	32.4	21.3
CO	20.3	16.3	7.3	30.1	6.6	23.3	33.3	8.8	23.6	15.4
CO_2	48.8	37.9	28.2	48.5	47.0	19.0	11.0	14.8	33.2	22.4
Syngas	69.1	54.2	35.5	78.6	53.6	93.7	90.5	32.7	89.2	59.1
CH_4	1.2	1.1	1.2	2.2	3.0	3.9	5.1	14.1	8.6	12.9
C_2	1.0	0.7	3.2	0.9	1.7	2.4	4.4	23.8	2.3	8.1
Other[a]	28.7	44.0	60.1	18.3	41.7	0.0	0.0	29.5	0.0	20.0
H_2/CO	0.00	0.00	0.00	0.00	0.00	2.21	1.39	1.03	1.37	1.38
CO/CO_2	0.42	0.43	0.26	0.62	0.14	1.23	3.03	0.59	0.71	0.69

800 °C										
	Conventional					Microwave				
	MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
H_2	22.4	21.4	9.2	19.8	15.8	47.6	50.4	26.6	49.1	48.2
CO	24.3	25.6	9.6	31.1	18.1	33.7	36.2	11.5	37.4	22.6
CO_2	23.9	25.5	11.3	28.9	17.6	13.6	8.0	8.1	8.7	15.2
Syngas	70.6	72.5	30.1	79.8	51.5	94.9	94.6	46.2	95.2	86.0
CH_4	11.2	12.7	20.3	13.0	20.7	3.1	3.3	20.0	3.7	8.1
C_2	8.9	8.5	26.0	2.9	12.3	2.0	2.3	17.5	1.2	5.9
Other[a]	9.2	6.3	23.7	4.2	14.4	0.0	0.0	16.3	0.0	0.0
H_2/CO	0.92	0.84	0.96	0.64	0.87	1.41	1.39	2.31	1.31	2.13
CO/CO_2	1.02	1.00	0.85	1.08	1.03	2.48	4.53	1.42	4.30	1.49

[a] Higher hydrocarbons (C_3, C_4, >C_4) and aromatics.

mean temperature of the material, which remains at the operating temperature. However, temperature measurement of microplasmas is a very complex issue, although this temperature must be high enough to allow for such high H_2 and CO concentrations observed in the gas fraction during MIP as shown in Table 3. This phenomenon resembles what occurs in a lightning storm, where the rays achieve an extremely high temperature without affecting the mean temperature of the atmosphere. For this reason, microwave heating is able to extract higher amounts of volatiles [24,25,27]. These volatiles are recovered in the liquid fraction since temperatures are not high enough for further cracking into gaseous products. In the case of the MSW, although there is a small decrease in liquid production when microwave heating is used, the liquid yields are very similar in both heating devices and considerably higher than in the other wastes. This is due to the high moisture content, which mainly accumulates as water within the liquid fraction. Finally, the solid yields are lower in the MIP than in the conventional pyrolysis in all the wastes [26]. As previously mentioned, the reason for this is that at 400 °C microwaves are able to extract more volatiles than conventional heating, but cracking reactions are only slightly promoted, as a result of which only a small amount of coke is produced (Table 4, Reactions 1 and 2).

At 800 °C, the differences between both heating devices are not as great and, in some cases, the yields do not follow the same trends as in the experiments at 400 °C. In the case of the gas yields, some

Table 4
Main chemical reactions involved in pyrolysis.

Number	Reaction	$\Delta H_{298\,K}$ (kJ mol^{-1})
1	$CH_4 \leftrightarrow C + 2H_2$	76
2	$C_nH_m \leftrightarrow n\,C + (m/2)\,H_2$	
3	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	136
4	$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$	247
5	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	205
6	$C_nH_m + n\,H_2O \leftrightarrow n\,CO + (n + m/2)\,H_2$	
7	$C_nH_m + n\,CO_2 \leftrightarrow 2n\,CO + (n/2)\,H_2$	
8	$C + CO_2 \leftrightarrow 2CO$	173
9	$C + H_2O \leftrightarrow CO + H_2$	131
10	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	90

Table 5
H_2, CO, CO_2, syngas and total gas productions (on a dry basis) in the conventional and microwave-induced pyrolysis of the different residues.

400 °C											
		Conventional					Microwave				
		MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
Productions (L_{STP}/g_{waste})	H_2	0.00	0.00	0.00	0.00	0.00	0.07	0.17	0.02	0.16	0.05
	CO	0.00	0.01	0.00	0.05	0.01	0.03	0.12	0.02	0.11	0.03
	CO_2	0.01	0.02	0.01	0.08	0.04	0.03	0.04	0.04	0.17	0.05
	Syngas	0.01	0.03	0.02	0.13	0.04	0.13	0.33	0.09	0.44	0.13
	Total gas	0.02	0.04	0.05	0.16	0.08	0.14	0.36	0.26	0.50	0.22
800 °C											
		Conventional					Microwave				
		MSW	MSWd	PLA	STR	SSd	MSW	MSWd	PLA	STR	SSd
Productions (L_{STP}/g_{waste})	H_2	0.08	0.07	0.04	0.07	0.05	0.23	0.34	0.13	0.43	0.21
	CO	0.09	0.08	0.04	0.11	0.06	0.16	0.25	0.06	0.33	0.10
	CO_2	0.09	0.08	0.05	0.10	0.05	0.07	0.05	0.04	0.08	0.07
	Syngas	0.26	0.24	0.13	0.30	0.16	0.46	0.64	0.23	0.83	0.37
	Total gas	0.36	0.32	0.43	0.40	0.31	0.48	0.68	0.50	0.88	0.43

of the wastes show similar levels of gas production in both devices (MSW and SSd), which may even be lower in the MIP than in conventional pyrolysis (PLA). From the results in Table 3, it can be seen that in these cases (MSW, SSd and PLA), the gases produced in the electric furnace have considerable amounts of hydrocarbons (CH_4, C_2 and $>C_2$). These compounds, under microwave heating, can be easily cracked into smaller hydrocarbons and coke (Table 4, Reactions 1 and 2). Thus, a large amount of the gases that are produced in the EF, especially from these hydrocarbons, is deposited as coke, but to a much lesser extent than with microwave heating, which favors the formation of light gases (especially H_2 and CO). As a result, coke production from these cracking reactions leads to higher solid yields. However, the increase in the solid yield is also a consequence of the cracking of the liquid fraction compounds, so that the liquid fraction yield decreases in all cases. Only MSW (due to its high water content) and SSd show similar levels of liquid productions in MIP and conventional pyrolysis (Fig. 3). However, it is important to bear in mind that these yields are expressed in mass terms. Nevertheless, gas volumetric production (which depends on the gas yield and composition) increases in the MIP regardless of the residue and the temperature used.

The most remarkable differences between MIP and conventional pyrolysis are to be seen in the composition of the gas fractions (Table 3). Conventional pyrolysis does not produce H_2 at low temperatures (400 °C), whereas, MIP is able to produce it in high concentrations at both of the temperatures. Moreover, in conventional pyrolysis, the maximum H_2 concentration achieved is ca. 20% in the case of MSW and MSWd at 800 °C. In the case of MIP, the lowest H_2 value achieved is slightly higher than 20%, in the pyrolysis of SSd at 400 °C (with the exception of PLA, which gave the worst results irrespective of the temperature and heating device used to produce the syngas; being this due to the nature of this substrate, which is mainly composed of polymeric carbon chains with lower H/C and O/C molar ratios compared to the other residues). In terms of syngas concentration (being the sum of H_2, CO and CO_2 concentrations, which are the gases involved in fermentation processes), the results are even more favorable to MIP. As can be seen, MIP gives rise to syngas concentrations above 90 vol% in many cases, even at 400 °C. Only in the case of plastics pyrolysis, is the syngas concentration value really low for both heating devices (30–35% in the case of conventional pyrolysis and 32–46% in the case of MIP). Furthermore, owing to the high proportions of other compounds (CH_4, C_2, higher hydrocarbons and aromatics) which may damage the bacteria and inhibit the fermentation process [35], the plastic fraction from municipal solid waste can be discarded as substrate for this process. Here, MIP offers a significant advantage over conventional pyrolysis, since it is able to minimize the presence of these compounds within the gas fractions, which will favor a higher quality syngas available for fermentation with the exception of using plastic waste.

The H_2/CO and CO/CO_2 ratios of the gas fractions obtained are also shown in Table 3. The values of these parameters reveal that MIP promotes the generation of H_2 and CO over CO_2. As can be seen, these ratios are higher in microwave heating than in conventional heating.

Nevertheless, it is not only necessary to consider the composition of the gas fraction in applying pyrolysis to bioplastics production via syngas fermentation [23], but also the production of the key gases (H_2, CO, CO_2) for it is one of the parameters that determines the effectiveness of these materials as substrates for the pyrolysis. The results of the specific productions ($L_{STP}\,g^{-1}$ of residue pyrolysed) of H_2, CO, CO_2, syngas and total gas (including all the gaseous compounds) are shown in Table 5. As mentioned above, the volumetric production of gas in MIP is higher than in conventional pyrolysis in all cases. This is due to the fact that MIP favors the production of lighter gases, such as H_2 and CO, due to cracking reactions, dehydrogenating reactions (Table 4, Reaction 3), reforming reactions (Table 4, Reactions 4–7) and gasification processes (Table 4, Reactions 8–10), where CH_4, CO_2, the carbonaceous matter and steam are converted to lighter products. As already mentioned, the differences between MIP and conventional heating are apparent even at 400 °C, the production of syngas in MIP being as much as ten times higher than in the case of conventional heating. This is mainly due to the large amounts of H_2 produced by means of MIP, even at low temperatures. At 800 °C, the gap, although still wide, narrows, the syngas production in MIP being between 75 and 180% higher than in conventional heating.

In view of these results, it is clear that microwave-induced pyrolysis is a quite good technique for generating syngas from wastes without the need of a gasifying agent, as would be necessary in the case of other technologies such as gasification. This method is bound to increase the production of the key gases necessary for syngas fermentation (H_2, CO and CO_2) and PHA production.

3.2. Applicability of syngas to bioplastics production

Great efforts are being made to metabolically engineer bacteria to produce a broad variety of bulk chemicals, bioplastics and bio-

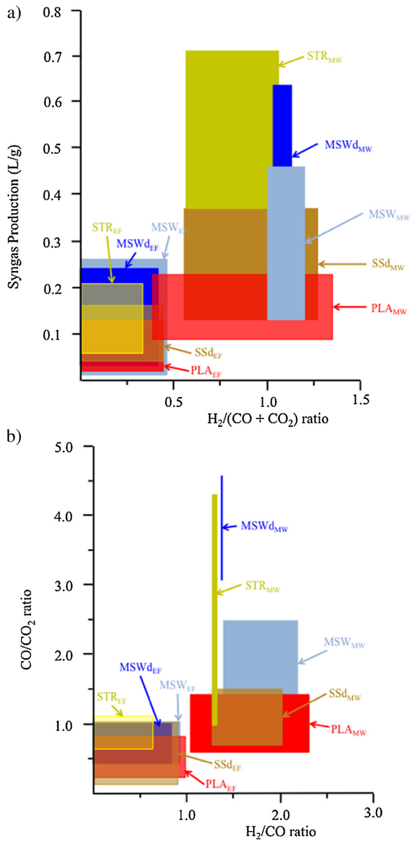


Fig. 4. (a) Syngas production versus $H_2/(CO + CO_2)$ ratio and (b) CO/CO_2 ratio versus H_2/CO ratio of the gas produced in the conventional (EF) and microwave-induced (MW) pyrolysis of the different wastes studied.

fuels [36,37] and to extend the use of substrates in the area of R&D bacterial fermentation. Researchers are strongly in favor of syngas fermentation for bioplastics production [21,38], but to date very few studies on syngas-derived biopolymers have been published. It has been widely claimed that, even though biological catalysts use a wide range of syngas H_2/CO ratios, they retain their product specificity [39]. Therefore, the syngas production process needs to be focused on the most effective means of conversion in terms of energy efficiency and production.

From the point of view of energy efficiency, it has been observed that the scaling-up of microwave-heated processes from lab to kilogram scale can be more energy efficient than conventionally heated systems [30,40]. In particular, high-temperature processing, such as pyrolysis, using powerful magnetrons over an optimized frequency range appears to be very promising. Indeed, Scandinavian Biofuel Company has already taken out a patent to perform microwave-induced pyrolysis on an industrial scale [41].

From the point of view of production, Fig. 4a evidences the superiority of MIP in terms of syngas yield, especially in the case of the STR and MSWd substrates, whose maximum values are 0.83 and 0.64 $L_{STP}\,g^{-1}{}_{waste}$, respectively. Moreover, MIP offers a wider variety since the conventional pyrolysis yields only range from 0.01 to 0.26 $L_{STP}\,g^{-1}{}_{waste}$. Although conventional pyrolysis yields a syngas composition that is richer in carbon (i.e., low values of $H_2/(CO + CO_2)$ ratio), it is important to note that the largest part is CO_2, whereas, CO is normally the preferred substrate for fermentation [21,22,42]. In this respect, MIP improves CO production and the $H_2/(CO + CO_2)$ ratio may even get to be higher than 1, so that the H_2 production would be greater than that of carbon oxides, except in the case of STR. However, neither of the organic fractions from municipal solid waste (MSW and MSWd) produce more carbon substrate ($CO + CO_2$) than H_2 in MIP.

As can be seen from Fig. 4b, microwave pyrolysis offers a wider range of syngas compositions, although it is not possible to produce syngas with H_2/CO ratios lower than 1. If necessary, conventional pyrolysis can be employed despite the serious drawback of undesired compounds (hydrocarbons and aromatics). In fact, if H_2/CO ratios greater than 1 are used for syngas fermentation, as in microwave-induced pyrolysis, an excess of hydrogen may be the result. This, however, is a highly valuable chemical that does not greatly affect the fermentation process. Indeed, in a study by *Do* et al., *R. rubrum* was cultivated on syngas to produce PHA (with ratios of $H_2/CO = 0.5$ and $CO/CO_2 = 1.1$) [22]. This gas composition was based on a typical stream from an air-blown gasifier, and therefore had not been optimized for PHA production. *R. rubrum* metabolized CO as the only substrate and produced H_2 via the biocatalytic water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) in addition to the H_2 from the syngas fed to the bioreactor. However, this should be considered an advantage, as H_2 produced by a biorefinery is a co-product that has a high market value [23].

In spite of the repeated calls in the literature for a syngas H_2/CO ratio independent of biocatalytic processes, there is some controversy surrounding this issue. Heiskanen et al. studied the effect of the syngas composition on *Butyribacterium methylotrophicum* [43]. The addition of hydrogen was reported to increase the formation of useful chemicals, such as butyric acid from *B. methylotrophicum*. In their study, they used a mixture of $H_2/CO/CO_2$ in ratios of $H_2/CO = 1.1$ and $CO/CO_2 = 1.4$, and found that *B. metylotrophicum* preferentially uses most of the CO before consuming hydrogen as reported in another study with *Eubacterium limosum* [44]. This suggests that CO_2 was not indispensable to the growth of bacteria on CO, but increased the initial growth rates of *B. metylotrophicum*, and was converted to valuable organic products in the presence of H_2 once the CO concentration reached a low enough level. Thus, the subsequent uptake of these gases should be taken into account when designing the fermentation process. In addition, Vega et al. reported the growth of *Peptostreptococcus productus* (strain U-1) on CO and CO_2/H_2 to produce acetate and found that its growth on CO_2/H_2 could not be sustained, but when CO_2 and H_2 were fed together with CO, with the resulting change in H_2/CO ratio, they contributed to the production of acetate [45]. This suggests that the composition of the syngas has an effect on the growth rate and on the products obtained from fermentation.

Whatever the case, CO is by far the most important carbon source from syngas to be used by bacteria [21] and, clearly, microwave-induced pyrolysis can provide the level of CO required by offering CO/CO_2 ratios from 0.6 to 4.5, whereas, conventional pyrolysis can only offer a range of 0.1–1.1 (Fig. 4b). Furthermore, as previously indicated, the use of microwaves allows the potential destruction of components that may be toxic to the bacteria. This is a very important advantage, since the need to remove these compounds prior to syngas use will increase the production costs that can be avoided with microwave-induced pyrolysis.

Therefore, optimization of the syngas composition should be evaluated on a case-by-case basis by metabolic engineers for possible further bioplastics synthesis, bearing in mind that microwave-derived syngas offers overwhelming advantages over traditional methods of syngas production.

4. Conclusions

Syngas fermentation is attracting widespread interest for implementation in biorefineries and great efforts are being made to metabolically engineer microorganisms for the production of specifically targeted chemicals. Organic waste has been demonstrated to have the potential for producing a high quality syngas when microwave-induced pyrolysis is used as the main thermochemical route. CO has been found to be the main carbon substrate for fermentation by bacteria and the microwave heating to be the most efficient means of producing a syngas with high CO/CO$_2$ ratios, which are even greater than 4 when straw and the organic fraction of municipal solid waste (dried and partially cleaned of inert solids) are used. The plastics fraction of the municipal solid waste has been found to be unsuitable for syngas production, since its fossil-based nature leads to significant amounts of hydrocarbons and aromatics in the composition of the gas produced, which can be highly damaging to the bacteria. Except in this case, microwaves have been demonstrated to drastically reduce the hydrocarbons and aromatics content of the syngas produced. Furthermore, the gas obtained from microwave pyrolysis contains exceptionally high H$_2$ concentrations, which amount to 49 vol% in the case of straw pyrolysis. This H$_2$ could be used by bacteria as an energy source or remain as a valuable by-product for future use. To sum up, microwave-induced pyrolysis has been confirmed to be a highly useful technology for producing syngas for use as in the production of bioplastics, due to its high gas production potential, high syngas concentration and low proportion of toxic compounds.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 311815 (SYNPOL project). D. B. also acknowledges the support received from PCTI and FICYT of the Government of the Principado de Asturias.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jaap.2014.12.011.

References

[1] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review, Waste Manage. 29 (2009) 2625–2643.

[2] T. Bhaskar, T. Matsui, J. Kaneko, M.A. Uddin, Y. Muto, A. Sakata, Novel calcium based sorbent (Ca-C) for the dehalogenation (Br, Cl) process during halogenated mixed plastic (PP/PE/PS/PVC and HIPS-Br) pyrolysis, Green Chem. 4 (2002) 372–375.

[3] R.A. Sheldon, Green and sustainable manufacture of chemicals from biomass: state of the art, Green Chem. 16 (2014).

[4] M. Guo, R.J. Stuckey, D.C. Murphy, Is it possible to develop biopolymer production systems independent of fossil fuels? Case study in energy profiling of polyhydroxybutyrate-valerate (PHBV), Green Chem. 15 (2013) 706–717.

[5] I. Keshavarz, T. Roy, Polyhydroxyalkanoates: bioplastics with a green agenda, Curr. Opin. Microbiol. 13 (2010) 321–326.

[6] C.S.K. Reddy, R. Ghai Rashmi, V.C. Kalia, Polyhydroxyalkanoates: an overview, Bioresour. Technol. 87 (2003) 137–146.

[7] S.A. Madbouly, J.A. Schrader, G. Srinivasan, K. Liu, K.G. McCabe, D. Grewell, M.R. Graves, W.R. Kessler, Biodegradation behavior of bacterial-based polyhydroxyalkanoate (PHA) and DDGS composites, Green Chem. (2014).

[8] Q. Chen, G.-Q. Wu, The application of polyhydroxyalkanoates as tissue engineering materials, Biomaterials 26 (2005) 6565–6578.

[9] S. Philip, I. Keshavarz, T. Roy, Polyhydroxyalkanoates: biodegradable polymers with a range of applications, J. Chem. Technol. Biotechnol. 82 (2007) 233–247.

[10] K. Sudesh, Y. Abe, H. Doi, Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters, Prog. Polym. Sci. 25 (2000) 1503–1555.

[11] K. Loo, C.-Y. Sudesh, Polyhydroxyalkanoates: bio-based microbial plastics and their properties, Malays. Polym. J. 2 (2007) 31–57.

[12] L. Shen, J. Haufe, M.K. Patel, In Report for European Polysaccharide Network of Excellence (EPNOE) adn European Bioplastics, (2009), p. 243.

[13] Z.T. Dobroth, S. Hu, A.G. Coats, E.R. McDonald, Polyhydroxybutyrate synthesis on biodiesel wastewater using mixed microbial consortia, Bioresour. Technol. 102 (2011) 3352–3359.

[14] I. Taniguchi, Y. Kagotani, K. Kimura, Microbial production of poly(hydroxyalkanoate)s from waste edible oils, Green Chem. 5 (2003) 545–548.

[15] Y. Jiang, L. Marang, J. Tamis, M.C.M. van Loosdrecht, R. Dijkman, H. Kleerebezem, Waste to resource: converting paper mill wastewater to bioplastic, Water Res. 46 (2012) 5517–5530.

[16] F. Bosco, F. Chiampo, Production of polyhydroxyalcanoates (PHAs) using milk whey and dairy wastewater activated sludge: production of bioplastics using dairy residues, J. Biosci. Bioeng. 109 (2010) 418–421.

[17] M.A. Griffin, D.W. Schultz, Fuel and chemical products from biomass syngas: a comparison of gas fermentation to thermochemical conversion routes, Environ. Prog. Sustain. Energy 31 (2012) 219–224.

[18] H. Younesi, A.R. Najafpour, G. Mohamed, Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, Clostridium ljungdahlii, Biochem. Eng. J. (27 2005) 110–119.

[19] I.-S. Chang, B.-H. Kim, D.-H. Kim, R.W. Lovitt, H.-C. Sung, Formulation of defined media for carbon monoxide fermentation by *Eubacterium limosum* KIST612 and the growth characteristics of the bacterium, J. Biosci. Bioeng. 88 (1999) 682–685.

[20] P. Suriyamongkol, R. Weselake, S. Narine, S. Moloney, M. Shah, Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plants—a review, Biotechnol. Adv. 25 (2007) 148–175.

[21] F.R. Bengelsdorf, P. Straub, M. Dürre, Bacterial synthesis gas (syngas) fermentation, Environ. Technol. 34 (2013) 1639–1651.

[22] Y.S. Do, J. Smeenk, K.M. Broer, C.J. Kisting, R. Brown, T.J. Heindel, A.A. Bobik, T.A. DiSpirito, Growth of Rhodospirillum rubrum on synthesis gas: conversion of CO to H$_2$ and poly-β-hydroxyalkanoate, Biotechnol. Bioeng. 97 (2007) 279–286.

[23] D. Choi, D. Chipman, R. Bents, S. Brown, A techno-economic analysis of polyhydroxyalkanoate and hydrogen production from syngas fermentation of gasified biomass, Appl. Biochem. Biotechnol. 160 (2010) 1032–1046.

[24] A. Domínguez, Y. Fernández, B. Fidalgo, J.A. Pis, J.J. Menéndez, Bio-syngas production with low concentrations of CO$_2$ and CH$_4$ from microwave-induced pyrolysis of wet and dried sewage sludge, Chemosphere 70 (2008) 397–403.

[25] R. Luque, J.A. Menendez, J. Arenillas, A. Cot, Microwave-assisted pyrolysis of biomass feedstocks: the way forward? Energy Environ. Sci. 5 (2012) 5481–5488.

[26] J.A. Menéndez, A. Domínguez, J.J. Inguanzo, M. Pis, Microwave-induced drying, pyrolysis and gasification (MWDPG) of sewage sludge: vitrification of the solid residue, J. Anal. App. Pyrolysis 74 (2005) 406–412.

[27] D. Beneroso, J.M. Bermúdez, J.A. Arenillas, A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, Bioresour. Technol. 144 (2013) 240–246.

[28] D. Beneroso, J.M. Bermúdez, J.A. Arenillas, A. Menéndez, Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste, J. Anal. App. Pyrolysis 105 (2014) 234–240.

[29] X. Zhao, Z. Song, H. Liu, Z. Li, C. Li, L. Ma, Microwave pyrolysis of corn stalk bale: a promising method for direct utilization of large-sized biomass and syngas production, J. Anal. App. Pyrolysis 89 (2010) 87–94.

[30] V.L. Budarin, P.S. Shuttleworth, J.R. Dodson, A.J. Hunt, B. Lanigan, R. Marriott, K.J. Milkowski, A.J. Wilson, S.W. Breeden, J. Fan, J.H. Sin, E.H.K. Clark, Use of green chemical technologies in an integrated biorefinery, Energy Environ. Sci. 4 (2011) 471–479.

[31] B. Kessler, R. Weusthuis, B. Witholt, G. Eggink, W. Babel, A. Steinbüchel, in: Biopolyesters, Springer Berlin Heidelberg, 2001, pp. 159–182, Chapter 5.

[32] Z. Hu, C. Ma, X. Chen, A study on experimental characteristic of microwave-assisted pyrolysis of microalgae, Bioresour. Technol. 107 (2012) 487–493.

[33] J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, A. Bermúdez, J.M. Arenillas, Ball lightning plasma and plasma arc formation during the microwave heating of carbons, Carbon 49 (2011) 346–349.

[34] J.A. Fernández, Y. Menéndez, Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes, J. Anal. App. Pyrolysis 91 (2011) 316–322.

[35] N. Nirmalakhandan, V. Arulgnanendran, M. Mohsin, F. Sun, B. Cadena, Toxicity of mixtures of organic chemicals to microorganisms, Water Res. 28 (1994) 543–551.

[36] B.P. Tracy, S.W. Jones, A.G. Fast, E.T. Indurthi, D.C. Papoutsakis, Clostridia: the importance of their exceptional substrate and metabolite diversity for biofuel and biorefinery applications, Curr. Opin. Biotechnol. 23 (2012) 364–381.

[37] M. Mohammadi, G.D. Najafpour, H. Younesi, P. Lahijani, A.R. Uzir, M.H. Mohamed, Bioconversion of synthesis gas to second generation biofuels: a review, Renew. Sustain. Energy Rev. 15 (2011) 4255–4273.

[38] M. Köpke, C. Held, S. Hujer, H. Liesegang, A. Wiezer, A. Wollherr, A. Ehrenreich, W. Liebl, P. Gottschalk, G. Dürre, Clostridium ljungdahlii represents a microbial production platform based on syngas, Proc. Natl. Acad. Sci. 107 (2010).

[39] R.C. Brown, Hybrid thermochemical/biological processing, Appl. Biochem. Biotechnol. 137–140 (2007) 947–956.

[40] C.O. Moseley, J.D. Kappe, A critical assessment of the greenness and energy efficiency of microwave-assisted organic synthesis, Green Chem. 13 (2011) 794–806.

[41] K.I. Kasin, Microwave assisted flash pyrolysis system and method using the same, US20130032464, (2013).

[42] A.M. Henstra, J. Sipma, A.J.M. Rinzema, A. Stams, Microbiology of synthesis gas fermentation for biofuel production, Curr. Opin. Biotechnol. 18 (2007) 200–206.

[43] H. Heiskanen, L. Virkajärvi, I. Viikari, The effect of syngas composition on the growth and product formation of *Butyribacterium methylotrophicum*, Enzyme Microb. Technol. 41 (2007) 362–367.

[44] M.P. Sharak Genthner, B.R. Bryant, Growth of *Eubacterium limosum* with carbon monoxide as the energy source, Appl. Environ. Microbiol. 43 (1982) 70–74.

[45] J. Vega, V. Holmberg, J. Clausen, E. Gaddy, Fermentation parameters of *Peptostreptococcus* productus on gaseous substrates (CO, H_2/CO_2), Arch. Microbiol. 151 (1988) 65–70.

[46] J.L. Vega, K.T. Klasson, D.E. Kimmel, J.L. Clausen, E.C. Gaddy, Sulfur gas tolerance and toxicity of co-utilizing and methanogenic bacteria, Appl. Biochem. Biotechnol. 24–25 (1990) 329–340.

[47] A.J. Grethlein, B.K. Soni, M.K. Worden, R.M. Jain, Influence of hydrogen sulfide on the growth and metabolism ofbutyribacterium methylotrophicum andclostridium acetobutylicum, Appl. Biochem. Biotechnol. 34–35 (1992) 233–246.

[48] K.T. Klasson, M.D. Ackerson, J.L. Clausen, E.C. Gaddy, Bioconversion of synthesis gas into liquid or gaseous fuels, Enzyme Microb. Technol. 14 (1992) 602–608.

[49] M.D. Bredwell, R.M. Srivastava, P. Worden, Reactor design issues for synthesis – gas fermentations, Biotechnol. Prog. 15 (1999) 834–844.

[50] R.M. Worden, M.D. Bredwell, A.J. Grethlein, In fuels and chemicals from biomass, Am. Chem. Soc. 666 (1997) 320–335, Chapter 18.

[51] S.K. Munasinghe, P.C. Khanal, Biomass-derived syngas fermentation into biofuels: opportunities and challenges, Bioresour. Technol. 101 (2010) 5013–5022.

Publicación II

OIL FRACTIONS FROM THE PYROLYSIS OF DIVERSE ORGANIC WASTES: THE DIFFERENT EFFECTS OF CONVENTIONAL AND MICROWAVE INDUCED PYROLYSIS

Journal of Analytical and Applied Pyrolysis

114 (256-264)

Año 2015

Journal of Analytical and Applied Pyrolysis 114 (2015) 256–264

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Oil fractions from the pyrolysis of diverse organic wastes: The different effects of conventional and microwave induced pyrolysis

D. Beneroso[a], J.M. Bermúdez[a], A. Arenillas[a], F. de la Peña[b], J.L. García[b], M.A. Prieto[b], J.A. Menéndez[a,*]

[a] *Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*
[b] *Centro de Investigaciones Biológicas, CSIC, C/Ramiro de Maeztu, 9, 28040 Madrid, Spain*

ARTICLE INFO

Article history:
Received 28 October 2014
Received in revised form 4 June 2015
Accepted 12 June 2015
Available online 18 June 2015

Keywords:
Microwave pyrolysis
Polycyclic Aromatic Hydrocarbons
Waste management
Tar reduction

ABSTRACT

Several studies have dealt with the microwave-induced pyrolysis of organic residues as an effective technology for maximizing the production of syngas at the expense of the production of oily tars. This liquid fraction is composed of a complex mixture of organic compounds making it difficult to upgrade for use as a biofuel and containing hazardous compounds such as polycyclic aromatic hydrocarbons (PAH). In this study the effect of the type of residue (municipal solid wastes, sewage sludges, plastic wastes and agroresidues) and the heating mechanism on the product distribution within the oil fraction has been investigated by means of GC–MS technique. Two different approaches have been performed: direct GC–MS analysis and methanolysed-oils GC–MS analysis, the later determining the non-volatile compounds. In general, quite different distributions are attained when microwave pyrolysis is conducted, providing lighter compounds. In some cases, such as the plastic-derived oil, microwave pyrolysis lead to a potential source of chemicals such as benzene, toluene and xylenes.

1. Introduction

Climate change and its relationship with CO_2 emissions has become an issue of major concern in recent years [1]. Although several efforts are being made to bring this phenomenon under control, the problem continues to grow. According to the World Energy Outlook of the International Energy Agency, the energy demand is expected to increase until 2035 and the associated CO_2 emissions to rise by 20% [2]. Indeed, fossil fuels will continue to be the primary source of energy generation in the short to medium term. However, in the same report this organization states that government policies can influence the pace of fossil fuel consumption. Governments have already taken concrete decisions to reduce the risks associated with fossil fuel emissions. Some examples are the Climate Action Plan in USA or the European Strategic Energy Technology Plan of the European Union [3,4]. In the case of the EU plan, one of its objectives is that 14% of the European energy mix should come from cost-competitive and sustainable bioenergy by 2020. Accordingly, technologies such as pyrolysis or gasification are going to play a key role in the development of this cost-competitive bioenergy in the near future [4].

Pyrolysis is a process in which organic matter is thermally decomposed without the use of oxidizing agents to yield three different fractions: a solid residue commonly known as char, a liquid oily fraction (tar) and a gaseous fraction. Gasification is a process which begins with a pyrolysis step that is then followed by the gasification of char and the reforming and cracking of tars and light hydrocarbons by a gasifying component, such as steam or oxygen. As a consequence, gasification usually yields higher amounts of gas than pyrolysis [5].

One of the main problems with both technologies is the production of a large amount of tars [6]. This liquid fraction is a complex mixture of organic chemicals largely composed of aromatic and polycyclic aromatic hydrocarbons that can be hazardous for health and the environment. Moreover, they can cause problems that affect the process itself including the fouling of engines and the deactivation of catalysts [7,8]. For these reasons, research into biomass pyrolysis and gasification is looking for ways to decrease the production of tars or, at least to improve their quality, by keeping the proportions of complex compounds like polycyclic aromatic hydrocarbons (PAH) down to a minimum.

For this reason, the use of microwave heating is seen as an appealing alternative since the main feature of microwave-induced

---

* Corresponding author. Fax: +34 985 297672.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

http://dx.doi.org/10.1016/j.jaap.2015.06.006
0165-2370/

pyrolysis (MIP) is its ability to maximize the production of gas and minimize that of tars [9]. This tendency has been tested with many different types of residues, including algae, municipal solid wastes, agricultural wastes, sewage sludge and automotive wastes [10–13]. However, so far the effect of microwaves upon the quality of the tars has not been given serious consideration. Some studies have pointed out that, while MIP could serve to minimize the production of PAH [14], the type of residue used might also be an influential factor. In this regard, the gaseous composition from the MIP seems to be very similar regardless of the residue pyrolysed with few exceptions [12,13,15,16], syngas ($H_2 + CO$), CO_2 and light hydrocarbons being the most common gaseous species found. On the other hand, the influence of the type of residue on oil composition is much more prominent. For this reason, the trends observed in the production of PAH by MIP in the study of Domínguez et al. [14] cannot be generalized without carrying out a deeper study of the process with several types of wastes. It is the aim of the present study to make up for this shortcoming by gaining further insight into the influence of microwave heating on the composition of the tars produced during the pyrolysis of different types of organic residues as a continuation of a previous study in which the suitability of several organic wastes was examined in order to maximize the production of syngas for further bioplastics production [17].

2. Experimental

2.1. Materials

Four different samples, provided by BEFESA Gestión de Residuos Industriales S.L. (Seville, Spain), were selected for this study:

- An organic fraction from a municipal solid waste, dried and partially cleaned from inerts, such as glass and metals. After this pre-treatment, the fraction size was reduced to 1–3 mm. This sample has been labelled MSWd.
- Dried sewage sludge. This sample was collected from a wastewater plant in Seville. The sludge, after being subjected to secondary treatment, was dried to facilitate transportation. After being dried, the sample was milled down to a size range of 1–3 mm. This sample has been labelled SSd.
- A plastic fraction from a municipal solid waste. This sample, a complex mixture of plastic residues, was obtained from the same landfill site in Seville. The fraction was milled to 1–3 mm and has been labelled PLA.
- An agricultural residue. This sample was obtained from a biodiesel production plant located in Salamanca (Spain) and is composed of straw. The sample was also milled down to a size range of 1–3 mm. This sample has been labelled STR.

The moisture, ash content and volatile matter data of the residues were obtained by means of a LECO TGA-601. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The metallic content of the ashes was determined by means of ICP-MS analysis. First, the samples were dissolved in inorganic acids (HNO_3 4N and concentrated HCl) and digested using microwave heating in a MILESTONE ETHOS 1 oven at 600 W during 35 min. Identification of the elements was carried out on an Agilent 7700*x* using a Ar plasma. An external calibration method between 0 and 1000 ppb internal standard (Sc) and a collision cell of He (to eliminate possible matrix interferences) was used to determine the concentration of metals. The results of this characterization are presented in Table 1.

2.2. Pyrolysis techniques

Conventional pyrolysis (CP) was performed at 800 °C in an electric furnace. Approximately 4 g of sample was introduced into a quartz reactor. First, the reactor was placed outside the furnace and purged with N_2 for 30 min at a flow rate of 50 mL min^{-1} to ensure an oxygen-free atmosphere. Meanwhile, the furnace was heated up to 800 °C. Once the reactor had been purged and the electric furnace had reached the desired temperature, the N_2 flow was reduced to 10 mL min^{-1} and the reactor was introduced into the furnace for pyrolysis, the duration of which was 1 h. The use of such a low flow rate favours secondary reactions of tar allowing for a maximum syngas production [17,18]. The volatiles evolved during pyrolysis were forced to pass through a condensing system (cooled by a cryogenic solution of water and NaCl) where the condensable compounds were removed from the gaseous fraction. Both the reactor and the condensing system were weighed before and after the pyrolysis experiment to determine the solid and liquid yields (respectively). The gas yield was determined by difference. Each experiment was performed in duplicate to check the repeatability and the errors came to less than 6% both for the yields and the gas composition [17].

Microwave-induced pyrolysis (MIP) was performed using a microwave oven consisting of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample-containing quartz reactor was placed. As in conventional pyrolysis, the reactor was purged with N_2 for 30 min at a flow rate of 50 mL min^{-1}. The flow rate was then reduced to 10 mL min^{-1} and the microwave irradiation was switched on and regulated until a temperature of 800 °C was reached. The reflected power was regulated by means of tuning screws until it reached zero. The same system as that used in CP was used to collect the liquid fraction.

Owing to the poor capacity of organic wastes used in this study to absorb microwaves, it was necessary to use a microwave receptor material to induce the pyrolysis [12]. For the purpose of this study, the char obtained from a previous pyrolysis at the same temperature (hence, very unlikely to release any volatiles at 800 °C) was employed as a microwave receptor at a receptor-to-feedstock mass ratio of 0.3:1.

2.3. Characterization of the oil fractions

To characterize the oils, a semi-quantitative study was carried out by calculating the percentage of area of the chromatographic peaks. Two different sample preparations were performed before the GC–MS analysis:

- In the first, anhydrous sodium sulfate (Na_2SO_4) was added to the condensed oil fraction to remove all traces of water, and injected directly into the GC–MS in order to identify the volatile compounds.
- In the second, the following methanolysis step was included. 2 mL of methanol containing 15% sulfuric acid and 0.5 mg/mL of 3-methylbenzoic acid (internal standard), was introduced, after dehydration of the oil with Na_2SO_4, followed by an incubation period of 7 h at 80 °C. After cooling, 1 mL of demineralized water and 1 mL of chloroform were added and the organic phase was analyzed by GC–MS. During the methanolysis step, the non-volatile compounds (mainly fatty acids) were turned into methyl ester derivatives, which are volatile compounds and can be easily identified by GC–MS.

All the samples were analyzed by GC–MS using an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, California, USA) coupled to an Agilent 5975C mass detector (electron ioniza-

Table 1
Chemical characteristics of the selected residues [17].

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)[a]							Metal content of ashes (mg kg^{-1})						
	MC	Ash[a]	VM[a]	C	H	N	S	O	H/C atomic	O/C atomic	Fe	Zn	Cu	Cr	Mn	Pb	Ni
MSWd	2.8	27.7	61.1	36.0	5.8	1.6	0.2	33.8	1.9	0.7	8896	183	45	59	83	31	18
SSd	3.4	15.4	74.5	43.8	6.1	9.7	0.1	24.9	1.7	0.4	2985	460	153	12	40	2	3
PLA	1.3	8.9	88.9	70.9	9.7	1.2	0.5	9.1	1.6	0.1	1099	73	51	73	19	5	25
STR	11.5	6.3	76.2	45.0	5.0	1.6	0.0	42.0	1.3	0.7	287	7	0	0	18	tr	tr

[a] Dry basis; MC: Moisture content; VM: volatile matter content; tr: traces (<0.1 mg kg^{-1}).

Table 2
Fraction yields obtained from the conventional (CP) and microwave-induced (MIP) pyrolysis of different residues at 800 °C [17].

Residue	Solid yield (wt.%)		Oil yield (wt.%)		Gas yield (wt.%)	
	CP	MIP	CP	MIP	CP	MIP
MSWd	40.2	43.9	23.7	7.8	36.1	48.3
SSd	31.3	32.8	34.7	34.3	34.0	32.9
STR	24.5	22.8	37.9	21.3	37.6	55.9
PLA	11.2	35.2	36.8	20.3	53.0	44.5

tion, 70 eV) (Agilent Technologies, Palo Alto, California, USA) and equipped with a 30 m × 0.25 mm i.d. capillary column (0.25 m film thickness) HP-5 (methyl silicone bonded) (Agilent Technologies). The working conditions for the first sample (volatile compounds) were as follows: a split ratio of 50:1 (0.02 μL of oil sample in 1 μL of dichloromethane) and an injector temperature of 350 °C; a column temperature of 40 °C for 3 min, which was then increased to 325 °C at 7 °C min^{-1}. The methanolysed samples were analyzed using the same equipment under the following working conditions: a split ratio of 20:1 (0.25 μL of oil sample) an injector temperature of 350 °C; a column temperature of 40 °C for 3 min, which was then heated to 325 °C at 20 °C min^{-1}. Blank analyses were also conducted to prevent possible procedural contaminants to be taken into account in the oil characterization.

The mass spectra and retention data were used to identify the compounds by comparing them with those of the standard in the NIST Mass Spectral Database. Those compounds were identified with a probability higher than 80%. The semi-quantification study was conducted on the basis of the percentage of area under each peak compared to the total amount of area under all the peaks in the chromatogram. The relative standard deviations obtained for testing the reproducibility for the peak areas came to less than 4% and the retention times to less than 1%.

3. Results and discussion

The data related to the ultimate composition, proximate analysis, H/C ratio and the ash metallic analysis of the different selected residues are presented in Table 1. The results reveal significant differences in the nature of the residues, which range from low carbon and high ash contents in the case of the MSW fraction, to high carbon and low ash contents, in the case of the PLA fraction. Furthermore, the straw sample and the organic fraction from the municipal solid waste have a high organic oxygen concentration. The values obtained for the H/C atomic ratio are high in the cases of MSWd, PLA and SSd fractions reflecting the marked aliphatic character of these wastes and the presence of long chains of $-CH_2-$ groups. The O/C atomic ratio values of the wastes, which range from 0.43 to 0.70, are very similar to the O/C values of the biomass samples [19], with the exception of the PLA fraction, which has quite a low ratio, which is indicative of a high heating value.

Table 2 shows the solid, oil and gas yields resulting from the residues during conventional pyrolysis and microwave pyrolysis. MIP has been reported to be an effective way to maximize the gas yield from the pyrolysis of biomass and organic wastes [12,13,15]. This finding is in agreement with the yields presented in Table 2 in the cases of MSWd and STR, with oil showing the lowest yield for all the residues subjected to MIP, the resulting values ranging between 7 and 34 wt.%. Nevertheless, the SSd and PLA fractions produce slightly more gas in the case of CP. This could be due to the fact that these fractions produce more hydrocarbons, such as CH_4, C_2H_4, C_2H_6, C_3H_8 or C_3H_6, which can be easily cracked into hydrogen, smaller hydrocarbons and coke under microwave radiation, resulting in an increase in the solid fraction yield [20], as is shown by Reactions (1) and (2) below. However, the increase in the solid yield is also a consequence of the cracking of the oil fraction components, which means that the oil fraction yield decreases in all cases.

$$CH_4 \leftrightarrow C + 2H_2 \tag{1}$$

$$C_nH_m \leftrightarrow nC + (m/2)H_2 \tag{2}$$

With respect to the composition of the oil fraction, GC–MS analysis revealed that both CP and MIP derived oils were composed of a mixture of low and high molecular weight compounds. As an example, the chromatograms of MSWd-derived oils from both preparation methods are presented in Fig. 1. In the case of chromatograms following the first preparation method (without methanolysis step), the compounds detected are listed in the Supplementary material. Fig. 2 shows the weight distribution (in molecular weight) of the compounds present in the oils, which depends on the pyrolysed residue and the heating mechanism. It should be pointed out that the values of relative abundance do not represent the real concentrations of the compounds. Rather, they indicate the different compositions of the resulting oils.

Fig. 2(a) shows that in the case of the MSWd fraction, MIP induces lesser amounts of oils in all the molecular weight intervals studied, with the exception of the 250–300 g/mol interval. During the microwave-induced pyrolysis of MSWd, it was observed that the production of volatiles was much more rapid and steeper compared to the other residues. This may have prevented the volatiles from being cracked to a certain extent, giving rise to heavier oil compounds. Nevertheless, when the results from CP and MIP are compared, the distribution shapes are very similar in both cases.

However, the distribution shapes of the different heating mechanisms are not always similar, since here the distribution also depends on the type of pyrolysed residue. In the case of the SSd fraction, according to its oil weight distribution (Fig. 2(b)), MIP produces lighter compounds as the distribution shifts to low molecular weights, in contrast to CP, which favors the production of heavier compounds, such as siloxanes, fatty acids and large amides. A similar distribution can be observed in the case of the PLA fraction, where most of the MIP oil compounds are generated in the interval 100–150 g/mol, with ethylbenzene and styrene as the main compounds. These results contrast with CP that favors the production of large-chain olefins, such as eicosadienes. In the case of the STR fraction both heating mechanisms favor lighter oil compounds, especially CP which produces large quantities of acetic acid and acetol.

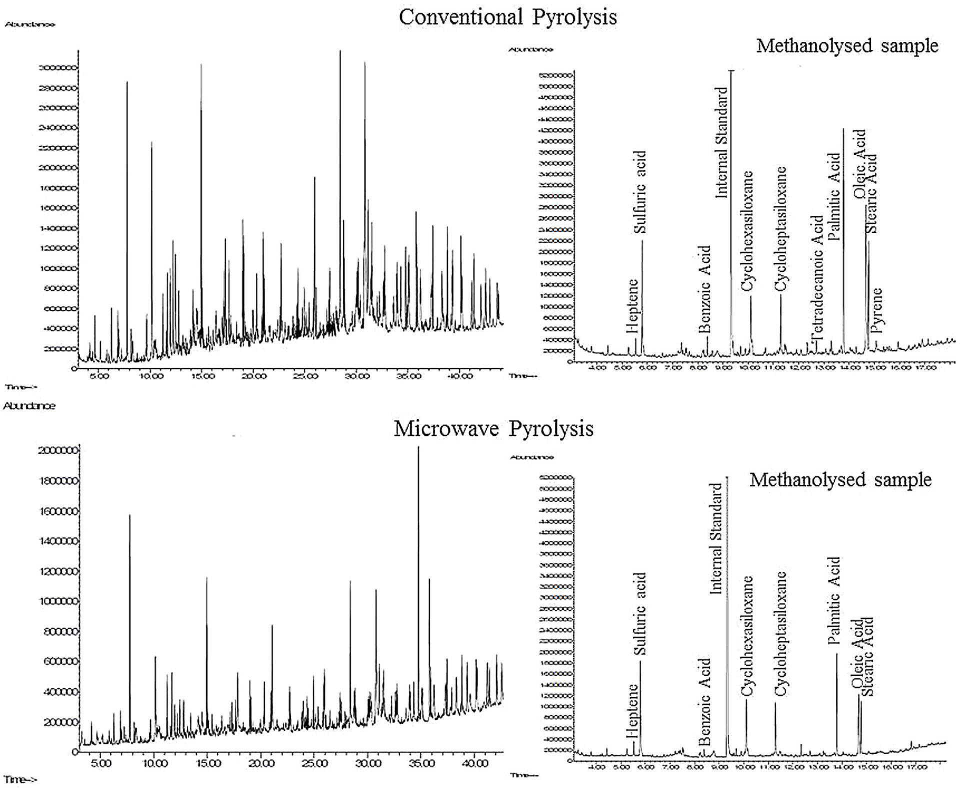
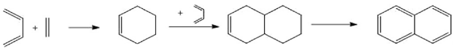


Fig. 1. Chromatograms of MSWd-derived oils from CP and MIP.

Pyrolysis oils are complex mixtures of organic compounds with a wide variety of chemical groups. To qualitatively describe their composition, the compounds identified in the oils have been grouped into the following classes: BTX (benzene, toluene, xylene and their alkyl-derivatives), PAH (polycyclic aromatic hydrocarbons), aliphatics (alkanes and alkenes), oxygenates (alcohols, ketones, esters and their derivatives), nitrogenates (amides, nitriles and N-heterocyclic compounds), fatty acids and, where applicable, siloxanes.

Fig. 3 shows the proportions of the different classes of compounds identified in the pyrolysis oils. Large amounts of BTX compounds were obtained from the SSd and PLA fractions under MIP. Of particular interest is the large amount of BTX detected in the plastic derived oil. PLA is composed basically of polymeric chains and when it was subjected to MIP, the amount of aliphatic oil was reduced compared to the oil from CP that favors the production of aromatic compounds (BTX). Aromatics are likely to be formed via Diels–Alder type secondary reactions, which involve the cyclisation of alkenes (produced from the thermal degradation of the PLA fraction) to form aromatic hydrocarbons (first step in Reaction (3), see below) [21]. These secondary reactions are likely to occur in MIP as reported in other pyrolysis processes [14,21,22]. Furthermore, the products from Diels–Alder reactions may undergo condensation to yield PAH when the temperature is high enough, ca. 700 °C (second and third steps in Reaction (3)) [22]. The increase observed in the PAH content in the PLA-derived oil under microwave pyrolysis can also be explained by Reaction (3), since microwaves generate hot spots inside the residue which locally induce temperatures much higher than 800 °C [23].


(3)

There is also an increase in the PAH content in the oil from the STR agroresidue. In this case, no polycyclic aromatic hydrocarbons were detected under CP. However, MIP generates naphthalene and low amounts of methylnaphthalene, fluorene and anthracene. These compounds have been previously detected in the oil derived from the MIP of agroresidues [11]. They are probably produced via reactions similar to Reaction (3) involving polymeric derived olefins from the lignocellulosic structures and deoxygenation reactions (carbonyl and methoxy groups are removed) that yield more stable aromatic species [24], as reported in the case of wood waste pyrolysis at high temperature [22].

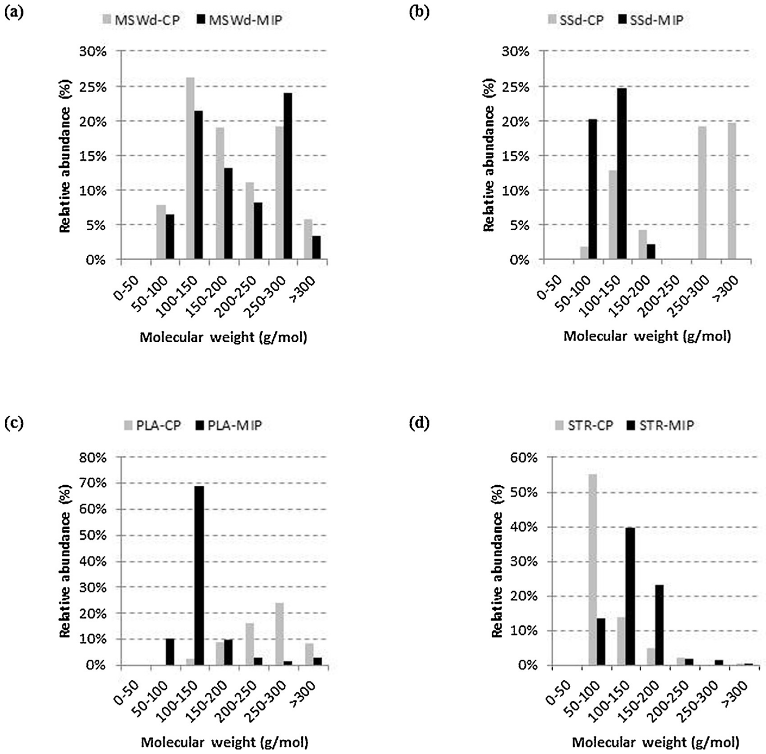


Fig. 2. Molecular weight distribution of compounds according to their relative abundances in the oil fraction obtained from (a) a municipal solid waste (MSWd); (b) a sewage sludge (SSd); (c) a plastic solid waste (PLA) and (d) agroresidues (STR).

Nevertheless, MIP does not always increase the amount of PAH and the higher local temperatures during MIP are not the only factor responsible for the production of PAH. The type of pyrolysed substrate also has an influence. Fig. 2(a) and (b) shows that both the MSWd and SSd fractions produce lower amounts of PAH under MIP than under CP. This reduction has already been reported for the MIP of different sewage sludges [25].

The differences in PAH contents depend on the type of residue. Some residues have a highly polymeric nature (e.g., plastics), and are more easily converted into dienes and olefinic structures (Fig. 4). They are able therefore to overcome Reaction (3) – type reactions that generate PAH compounds. However, this is not the case of MSWd and SSd, which are heterogeneous materials. Lignocellulosics also have a polymeric nature but in this case PAH compounds are favored by the deoxygenation of furans, phenols and cyclopentadienes during the thermal degradation of cellulose [26].

Although the PAH concentration increases in the oils from PLA and STR as a result of MIP, no PAH carcinogens, (i.e., benz[a][8]anthracene, benzo[a]pyrene and dibenz[a,h]anthracene [27]), were detected in the oil product, none of the typical fragments from those PAH within the NIST database were observed during the mass spectrometry analysis under the experimental protocol used.

With respect to the aliphatic compounds present in the oils, the total yield was very low in the case of the SSd and STR fractions. However, this value reached nearly 20% in the MSWd fraction. A common observation is that these aliphatics consist of straight long chain hydrocarbons ($>C_{10}$), which represent an potential source of kerosene and diesel. The PLA fraction shows the largest amount of aliphatics, especially from CP (40%) where the formation of alkenes is clearly promoted to the detriment of alkanes in the C_{12}–C_{20} range. During microwave pyrolysis, the aliphatics content drops to 20% in favor of aromatics.

Most of the oxygenated compounds are ketones, esters and alcohols, the concentration of which depend on the nature of the residue and the heating mechanism employed. The oxygenates present in the oil produced by conventional and microwave pyrolysis of MSWd are mainly alkyl cyclopentenones, aliphatic and aromatic ketones. However, no ketones were observed in the SSd-derived oil, the major oxygenates being esters and aromatic alcohols. Nevertheless a significant decrease in the yield of the oxygenates occurred in the case of MIP. With respect to the PLA-derived oil, CP yielded two main long chain alcohols (1-eicosanol and 1-pentacosanol), although with microwave pyrolysis the presence of oxygenates in the oil is practically excluded. In the case of the STR fraction, oxygenates are by far the most important group, especially

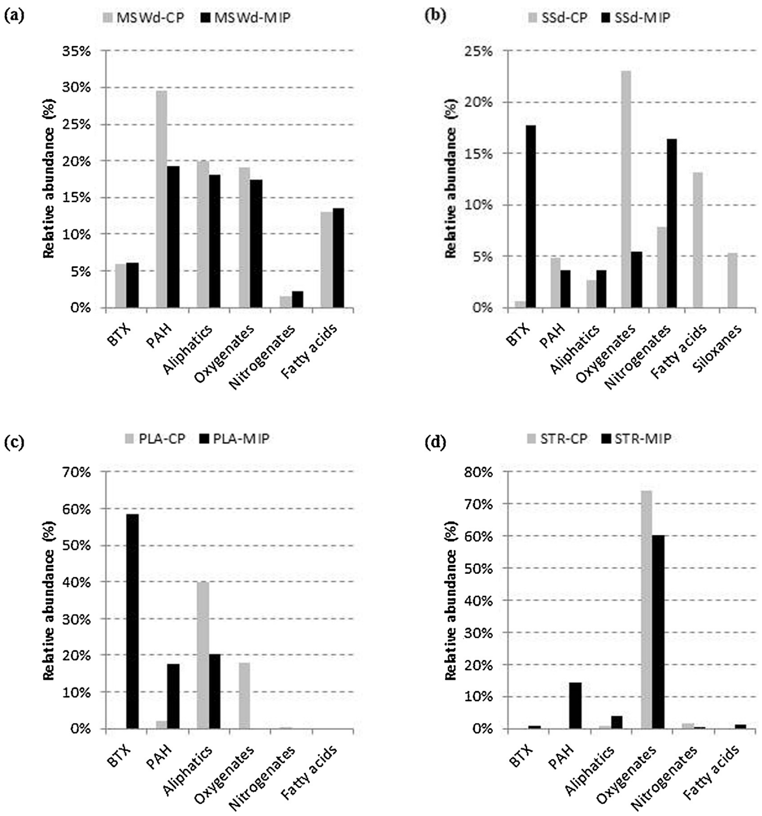


Fig. 3. Relative abundance of different groups of compounds found in the oil fraction obtained from (a) a municipal solid waste (MSWd); (b) a sewage sludge (SSd); (c) a plastic solid waste (PLA) and (d) Agroresidues (STR).

during CP, which is in accordance with the high oxygen content of lignocellulosic materials as in this case. The conventional pyrolysis of STR produces large quantities of acetic acid and ketones, whereas MIP promotes the production of phenol and phenol-derivatives. Nitrogen-containing compounds are present especially in the oils from SSd, since this fraction initially contains a large amount of nitrogen compared to the other residues. The compounds detected in the oils from SSd comprised long chain aliphatic amides in the case of CP and nitriles, pyridine, pyrrole and their derivatives in MIP. Furthermore, a large quantity of siloxanes was detected in the SSd-derived oil, as is usually the case with biogas and sewage sludges [28].

Another important constituent of the pyrolysis oils are fatty acids. It can be seen from Fig. 3, that the SSd fraction does not produce fatty acids during MIP in contrast with its high content under CP. Because fatty acids are high molecular weight long chains, a GC–MS analysis was performed after a methanolysis step in order to identify non-volatile compounds that were not detected by GC–MS. The results of these analyses for each residue derived-oil are presented in Table 3 . Within the MSWd fraction, palmitic and

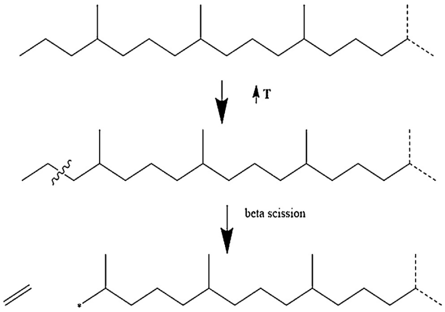


Fig. 4. A typical polymer beta scission mechanism.

Table 3
Relative abundances of compounds detected in the oil fraction by means of methanolysis.

MSWd–CP			MSWd–MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
5.54	Heptene	2.31	5.54	Heptene	3.80
8.39	Benzoic acid	2.93	8.39	Benzoic acid	2.11
10.12	Cyclohexasiloxane	11.87	10.12	Cyclohexasiloxane	16.16
11.29	Cycloheptasiloxane	7.71	11.29	Cycloheptasiloxane	16.22
12.70	Tetradecanoic acid	1.95	13.80	Palmitic acid	27.01
13.79	Palmitic acid	29.68	14.67	Oleic acid	21.28
14.68	Oleic acid	27.29	14.78	Stearic acid	13.42
14.78	Stearic acid	14.24			
15.08	Pyrene	2.02			

SSd–CP			SSd–MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
4.41	2-Butenoic acid, methyl ester	2.80	4.45	Toluene	6.90
4.60	3-Methyl butanoic acid, methyl ester	2.02	4.60	3-Methyl butanoic acid, methyl ester	2.31
5.93	2-Pentenoic acid, methyl ester	5.21	5.82	Ethyl benzene	1.82
6.19	4-Methyl Pentanoic acid, methyl ester	0.81	5.93	2-Pentenoic acid, methyl ester	7.26
7.30	Octamethyl cyclotetrasiloxane	11.37	6.19	4-Methyl Pentanoic acid, methyl ester	2.03
7.81	Succinic acid, dimethyl ester	2.02	6.98	Propyl benzene	0.79
8.09	Butanedioic acid, methyl ester	0.63	7.30	Octamethyl cyclotetrasiloxane	6.27
8.58	Benzenemethanol	1.17	7.39	Decane	0.55
8.72	Decamethyl cyclopentasiloxane	1.55	7.53	1 Methoxyethyl benzene	7.12
9.12	Phenylacetic acid, methyl ester	0.88	7.84	Succinic acid, dimethyl ester	1.20
9.26	Naphthalene	0.62	8.12	2-Methyl succinic acid, dimethyl ester	0.66
11.56	Bis (1,1 Dimethylethyl) Phenol	0.71	8.27	1-Undecene	0.78
12.69	Tetradecanoic acid, methyl ester	3.88	8.34	Undecane	0.86
13.69	Oleic acid, methyl ester	9.73	8.46	Benzoic acid, methyl ester	1.07
13.78	Palmitic acid, methyl ester	21.89	8.72	Decamethyl cyclopentasiloxane	0.65
14.28	Heptadecanoic acid, methyl ester	0.58	11.52	Dodecanoic acid, methyl ester	0.91
14.67	Oleic acid, methyl ester	22.0	12.70	Tetradecanoic acid, methyl ester	2.53
14.76	Stearic acid, methyl ester	9.71	13.05	Methyl tetradecanoic acid, methyl ester	2.81
15.66	Eicosanoic acid, methyl ester	0.65	13.10	Methyl tetradecanoic acid, methyl ester	1.26
16.50	Docosanoic acid, methyl ester	1.78	13.25	Pentadecanoic acid, methyl ester	0.83
			13.69	Palmitoleic acid, methyl ester	8.57
			13.78	Palmitic acid, methyl ester	17.91
			14.69	Oleic acid, methyl ester	16.90
			14.77	Stearic acid, methyl ester	6.77
			16.52	Tetramethyl stearic acid, methyl ester	1.25

Table 3 (*Continued*).

PLA–CP

Retention time (min)	Compound	Percentage quantified area
8.50	Benzoic acid, methyl ester	46.15
11.68	1,3-Benzenedicarboxylic acid, dimethyl ester	16.52
13.84	Palmitic acid, methyl ester	25.26
14.82	Stearic acid, methyl ester	5.99
15.97	Eicosane	6.08

PLA–MIP

Retention time (min)	Compound	Percentage quantified area
4.45	Toluene	10.92
5.39	Propyl cyclohexane	1.20
5.82	Ethyl benzene	14.86
5.93	Xylene	1.79
6.24	Xylene	4.66
6.61	Cumene	1.02
6.96	Propyl benzene	0.56
7.04	1-Ethyl, 3-Methyl benzene	0.70
7.25	1-Ethyl, 2-Methyl benzene	0.69
7.30	Octamethyl cyclotetrasiloxane	1.42
7.38	Decane	1.21
7.52	1 Methoxyethyl benzene	35.93
7.96	1 Propynyl benzene	2.01
8.19	1-Phenyl Ethanone	0.92
8.27	1-Undecene	0.71
8.33	Undecane	1.44
8.41	Benzoic acid, methyl ester	2.00
9.11	1-Dodecene	0.49
9.17	Dodecane	0.66
9.25	Naphthalene	7.02
9.93	Tridecane	0.55
10.14	1-Methyl Naphthalene	0.50
10.27	2-Methyl Naphthalene	0.53
10.73	Biphenyl	1.31
11.52	1,4-Benzenedicarboxylic acid, dimethyl ester	1.72
13.06	1-Octadecene	0.59
13.38	Phenanthrene	0.45
13.60	1-Nonadecene	0.45
13.78	Palmitic acid, methyl ester	1.47
14.67	9-Octadecenoic acid, methyl ester	1.28
14.77	Stearic acid, methyl ester	0.51
15.06	1-Docosene	0.44

STR–CP

Retention time (min)	Compound	Percentage quantified area
3.80	Butanoic acid, methyl ester	1.67
4.97	Dimethoxy-2-propanone	4.82
5.12	Trimethoxyethane	48.33
5.59	Dimethoxyacetone	15.05
6.13	Dimethoxy-tetrahydrofuran	1.34
6.30	Dimethoxy-2-propanone	5.37
6.69	Tetramethoxy ethane	1.71
6.96	Dimethoxy propanoic acid, methyl ester	2.21
7.42	Levulinic acid-methyl ester	5.38
7.60	2-Propenyl ester butanoic acid	2.02
8.30	3–Ethyl, 2–Hydroxy, 2–Cyclopentenone	5.39
8.42	2–Methy, 2–Butenedioic acid, dimethyl ester	1.56
8.76	Pentanedioic adic, dimethyl ester	3.12
10.55	2,6-Dimethoxy-phenol	2.06

STR–MIP

Retention time (min)	Compound	Percentage quantified area
5.07	Trimethoxyethane	8.24
7.41	Levulinic acid–methyl ester	6.63
8.30	3–Ethyl, 2–Hydroxy, 2–Cyclopentenone	5.74
9.29	Naphthalene	14.95
10.55	2,6-Dimethoxy-phenol	6.33
12.72	Tetradecanoic acid, methyl ester	6.92
13.81	Palmitic acid, methyl ester	29.54
14.69	Linoleic acid, methyl ester	17.60
14.79	Stearic acid, methyl ester	4.04

oleic acids were the most relevant compounds. The corresponding methyl esters were the main compounds in the oils from SSd. These compounds are of special interest owing to the fact that they can be used as source of biodiesel or even as platform molecules that can be converted into a variety of fuel additives through catalytic transformations [29]. Similar results were obtained from an analysis of the oil from the STR fraction after microwave pyrolysis. Here palmitic, linoleic, levulinic and tetradecanoic acid methyl esters made up most of the compounds detected. In the case of the oils from PLA, the resulting distributions between CP and MIP differ considerably, since the main components are benzoic and palmitic acids methyl esters in the case of conventional pyrolysis, but methoxyethyl benzene and ethylbenzene in the case of microwave pyrolysis. MIP gives rise to a wider distribution of products and generates alkyl-derivatives of BTX compounds, as can be seen from Fig. 3.

It is important to point out that the oil yield from MIP is always lower than that obtained from CP, suggesting that the production of identified chemicals can be reduced. This is the case of MSWd, for which a rough estimation predicts a yield of PAH from conventional pyrolysis of around 70 $\mathrm{mg/g_{waste}}$ against 15 $\mathrm{mg/g_{waste}}$ from MIP.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 311815 (SYNPOL project). D.B. also acknowledges the financial support received from PCTI and FICYT of the Government of the Principado de Asturias.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jaap.2015.06.006

References

[1] J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Hawthorne, Land clearing and the biofuel carbon debt, Science 319 (2008) 1235–1238.
[2] I.E. Agency, World Energy Outlook 2013 (2013).
[3] <http://www.whitehouse.gov/sites/default/files/image/president27sclimateactionplan.pdf>, 2013.
[4] <http://europa.eu/legislation_summaries/energy/european_energy_policy/l27079_en.htm>, 2007.
[5] A. Demirbaş, Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield, Energy Convers. Manage. 43 (2002) 897–909.
[6] Q. Xie, F.C. Borges, Y. Cheng, Y. Wan, Y. Li, X. Lin, Y. Liu, F. Hussain, P. Chen, R. Ruan, Fast microwave-assisted catalytic gasification of biomass for syngas production and tar removal, Bioresour. Technol. 156 (2014) 291–296.
[7] L. Devi, K.J. Ptasinski, F.J.J.G. Janssen, A review of the primary measures for tar elimination in biomass gasification processes, Biomass Bioenergy 24 (2003) 125–140.
[8] J. Han, H. Kim, The reduction and control technology of tar during biomass gasification/pyrolysis: an overview, Renew. Sustain. Energy Rev. 12 (2008) 397–416.
[9] Y. Fernández, J.A. Menéndez, Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes, J. Anal. Appl. Pyrolysis 91 (2011) 316–322.
[10] S.S. Lam, A.D. Russell, C.L. Lee, S.K. Lam, H.A. Chase, Production of hydrogen and light hydrocarbons as a potential gaseous fuel from microwave-heated pyrolysis of waste automotive engine oil, Int. J. Hydrogen Energy 37 (2012) 5011–5021.
[11] Y.F. Huang, W.H. Kuan, S.L. Lo, C.F. Lin, Total recovery of resources and energy from rice straw using microwave-induced pyrolysis, Bioresour. Technol. 99 (2008) 8252–8258.
[12] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, Bioresour. Technol. 144 (2013) 240–246.
[13] X. Zhao, Z. Song, H. Liu, Z. Li, L. Li, C. Ma, Microwave pyrolysis of corn stalk bale: a promising method for direct utilization of large-sized biomass and syngas production, J. Anal. Appl. Pyrolysis 89 (2010) 87–94.
[14] A. Domínguez, J.A. Menéndez, M. Inguanzo, J.J. Pis, Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge, Fuel Process. Technol. 86 (2005) 1007–1020.
[15] A. Domínguez, Y. Fernández, B. Fidalgo, J.J. Pis, J.A. Menéndez, Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge, Chemosphere 70 (2008) 397–403.
[16] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste, J. Anal. Appl. Pyrolysis 105 (2014) 234–240.
[17] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics, J. Anal. Appl. Pyrolysis 111 (2015) 55–63.
[18] Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Influence of carrier gas on microwave-induced pyrolysis, J. Anal. Appl. Pyrolysis 113 (2015) 153–157.
[19] P. McKendry, Energy production from biomass (part 2): conversion technologies, Bioresour. Technol. 83 (2002) 47–54.
[20] A. Domínguez, Y. Fernández, B. Fidalgo, J.J. Pis, J.A. Menéndez, Biogas to syngas by microwave-assisted dry reforming in the presence of char, Energy Fuels 21 (2007) 2066–2071.
[21] A.M. Cunliffe, P.T. Williams, Composition of oils derived from the batch pyrolysis of tyres, J. Anal. Appl. Pyrolysis 44 (1998) 131–152.
[22] P.T. Williams, S. Besler, Polycyclic aromatic hydrocarbons in waste derived pyrolytic oils, J. Anal. Appl. Pyrolysis 30 (1994) 17–33.
[23] J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, J.M. Bermúdez, A. Arenillas, Ball lightning plasma and plasma arc formation during the microwave heating of carbons, Carbon 49 (2011) 346–349.
[24] T.E. McGrath, W.G. Chan, M.R. Hajaligol, Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose, J. Anal. Appl. Pyrolysis 66 (2003) 51–70.
[25] A. Domínguez, J.A. Menéndez, M. Inguanzo, P.L. Bernad, J.J. Pis, Gas chromatographic–mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges, J. Chromatogr. A 1012 (2003) 193–206.
[26] R. Cypres, Aromatic hydrocarbons formation during coal pyrolysis, Fuel Process. Technol. 15 (1987) 1–15.
[27] W.-T. Tsai, H.-H. Mi, Y.-M. Chang, S.-Y. Yang, J.-H. Chang, Polycyclic aromatic hydrocarbons (PAHs) in bio-crudes from induction-heating pyrolysis of biomass wastes, Bioresour. Technol. 98 (2007) 1133–1137.
[28] R. Dewil, L. Appels, J. Baeyens, Energy use of biogas hampered by the presence of siloxanes, Energy Convers. Manage. 47 (2006) 1711–1722.
[29] M.J. Climent, A. Corma, S. Iborra, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, Green Chem. 16 (2014) 516–547.

Publicación III

MICROWAVE PYROLYSIS OF MICROALGAE FOR HIGH SYNGAS PRODUCTION

Bioresource Technology

144 (240-246)

Año 2013

Bioresource Technology 144 (2013) 240–246

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Microwave pyrolysis of microalgae for high syngas production

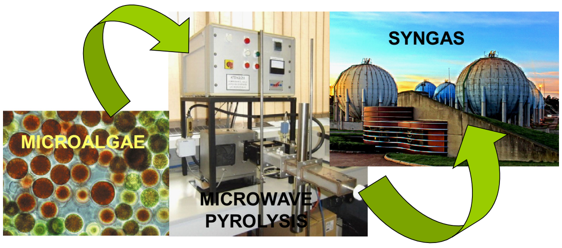
D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez *

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

HIGHLIGHTS

- Microalgae and their extraction residue are great substrates for syngas production.
- Microwave-pyrolysis produces higher syngas yields than conventional process.
- Extraction residue results in higher gas yield and syngas concentration.
- Maximum syngas production is obtained with microwave-pyrolysis at 800 °C.
- Microwave-pyrolysis leads to 1.1–2.3 H_2/CO ratios depending on operating temperature.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 May 2013
Received in revised form 23 June 2013
Accepted 25 June 2013
Available online 2 July 2013

Keywords:
Microwave
Pyrolysis
Microalgae
Bio-syngas
Bio-hydrogen

ABSTRACT

The microwave induced pyrolysis of the microalgae *Scenedesmus almeriensis* and its extraction residue was carried out at 400 and 800 °C. The results show that it is possible to obtain a gas fraction with a high content (c.a. 50 vol.%) in H_2 from both materials, regardless of the pyrolysis temperature. Furthermore, an outstanding syngas production and high gas yields were achieved. The maximum syngas concentration obtained was c.a. 94 vol.%, in the case of the pyrolysis of the residue at 800 °C, indicating that the production of CO_2 and light hydrocarbons was minimized. The same experiments were carried out in a conventional electric furnace in order to compare the products and yields obtained. It was found that microwave induced pyrolysis gives rise not only to higher gas yields but also to greater syngas and H_2 production.

1. Introduction

Microalgae are expected to become an important source of high-value products with several applications in a large number of areas of biotechnology (such as cosmetics, pharmacy and food) and, especially, in biofuels production (Brennan and Owende, 2010; Carriquiry et al., 2011; Chisti, 2007; Tabernero et al., 2012; Xu et al., 2011). The increasing interest in microalgae as a source of biofuel (the so-called third generation biofuel) is due to the several advantages that it offers over terrestrial oil crops. These advantages include: (1) an all-the-year-round production (which guarantees a considerably higher bio-oil production than oilseed crops); (2) the use of wastewater as a source of nutrients; (3) the elimination of the need for herbicides or pesticides; and (4) their possible cultivation in brackish water or non-arable land, resulting in a minimisation of the associated environmental impact (Brennan and Owende, 2010; Chisti, 2007). For these reasons and with the expected increase in liquid biofuel consumption, microalgae seem to be the only biofuel source able to completely replace conventional fuels (Chisti, 2007; Ferrel and Sarisky-Reed, 2010; Tabernero et al., 2012).

However, a number of technical and economic factors, such as species selection, photosynthetic efficiency and production costs,

---

* Corresponding author. Tel.: +34 985 118972; fax: +34 985 297672.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.06.102

have so far impeded the industrial development of biofuels from microalgae (Brennan and Owende, 2010; Carriquiry et al., 2011; Xu et al., 2011). Before it can be commercially viable, it is necessary to reduce the production costs of microalgae-based biofuels from their current levels, which far exceed the prices of petroleum fuels (Brennan and Owende, 2010; Carriquiry et al., 2011; Tabernero et al., 2012). Several economic analyses and LCA studies have been carried out with the aim of identifying weaknesses and potential improvements that could be made in the production processes in order to achieve a more sustainable and economically feasible production process (Campbell et al., 2011; Delrue et al., 2012; Ferrel and Sarisky-Reed, 2010; Harun et al., 2011; Lardon et al., 2009; Tabernero et al., 2012; Xu et al., 2011). Since Chisti proposed the application of the biorefinery concept to microalgae-based fuel production (Chisti, 2007), all of these studies have emphasized the importance of exploiting the residues generated in the production process, especially those produced after oil extraction.

Thermochemical conversion through pyrolysis has been proposed for both microalgae and their extraction residues in order to obtain three fractions: solid (bio-char), liquid (bio-oils) and gaseous (bio-gas). Conventional pyrolysis (CP) is mainly focused on the production of liquid products (Brennan and Owende, 2010; Miao and Wu, 2004; Miao et al., 2004). In the particular case of the pyrolysis of microalgae biomass, the studies performed to date have been aimed at maximising the yields of this fraction (Campanella et al., 2012; Du et al., 2011; Grierson et al., 2011; Hu et al., 2012; Miao et al., 2004; Thangalazhy-Gopakumar et al., 2012; Xu et al., 2011). However, although the pyrolysis oils obtained from microalgae are superior to those obtained from other biomass feedstocks (Du et al., 2011; Miao et al., 2004; Tabernero et al., 2012), these oils are acidic, unstable, and. viscous. Moreover, they contain solids, chemically dissolved water and significant proportions of nitrogen compounds, making it necessary to apply additional upgrading processes for the oils to be useful for biofuel production (Brennan and Owende, 2010; Campanella et al., 2012; Sanchez-Silva et al., 2013; Wang et al., 2013).

An attractive alternative for the pyrolysis of microalgae biomass could be that of bio-gas production, with the aim of obtaining the maximum possible amount of high-value components of which synthesis gas (syngas) is just one example. There have recently appeared new ways to exploit the potential of syngas from waste pyrolysis. For example, the SYNPOL project will enable the EU to take a global lead in syngas fermentation technology for waste revalorisation and the production of new materials such as biopolymers (http://www.synpol.org/). For this purpose, microwave-induced pyrolysis (MIP) seems to be the way forward. Previous studies on the MIP of biomass have shown the ability of this technology to produce higher yields of the gas fraction and a greater concentration of bio-syngas and bio-hydrogen in this gaseous product than CP (Domínguez et al., 2007; Fernández et al., 2010; Fernández et al., 2009), probably due to the presence of microplasmas and hot spots formed during microwave heating (Menéndez et al., 2011). Moreover, MIP presents several advantages over CP, such as a better control over the process, faster heating or lower temperatures (Du et al., 2011; Fernández et al., 2010; Fernández et al., 2009; Hu et al., 2012; Luque et al., 2012).

To the best of our knowledge, there have been no studies on the MIP of microalgae with the aim of maximising gas production and the proportion of high-value components, such as H_2, in the gas fraction. The novelty of the present work is to study and compare the CP and MIP of the microalga *Scenedesmus almeriensis* and its extraction residue, so as to obtain the maximum possible gas yield and the highest bio-syngas and bio-hydrogen proportions in this fraction. In addition, this is the first time that an extraction residue of microalgae has been subjected to a revalorization process for this purpose."

2. Methods

2.1. Materials

The microalga selected for this study was *Scenedesmus almeriensis*, supplied by Exeleria, S.L. The algae biomass was dried in the harvesting facilities before being supplied to the lab for the experiments. The microalga was used both as received and after being subjected to an extraction process. The extraction was carried out using methanol as solvent, at a temperature of 50 °C under magnetic stirring. After the extraction, the extract and the residue were separated by filtration. Table 1 shows the elemental and proximate analysis of the microalga and the extraction residue, which will be labelled as A and R respectively.

2.2. Experimental procedure

The pyrolysis of A and R was carried out in a conventional electrical furnace and in a single mode microwave oven at 400 and 800 °C. About 4 g of sample was placed in a quartz reactor. The reactor was purged with He for 30 min at a flow rate of 100 mL STP min^{-1}. The helium flow rate was then set to 20 mL STP min^{-1} for the pyrolysis experiments.

In the case of CP, the reactor with the sample was introduced into the conventional furnace previously heated up to the desired pyrolysis temperature, to enable the temperature of the sample to rise rapidly. In the case of MIP, the quartz reactor was placed in the centre of the microwave guide before being subjected to irradiation. Details of this experimental set-up have been described elsewhere (Domínguez et al., 2005). Since biomass is a poor microwave absorber, it is necessary to mix it with an appropriate microwave absorber to achieve the high temperatures required for pyrolysis (Domínguez et al., 2005; Fernández et al., 2009). The char obtained from the pyrolysis of the sample at 800 °C in the electrical furnace, was used as microwave absorber in an absorber: sample proportion of about 30:70 wt.%. This ratio was selected after several preliminary experiments, which showed that this was the lowest ratio that would allow the biomass to be heated to the desired temperature while avoiding the thermal runaway effect which could result from microwave heating. An additional experiment was performed with graphite dust as microwave absorber in order to study the possible catalytic effect of the char.

In the electric furnace the temperature was monitored by means of a thermocouple of type K, whereas in the microwave oven, due to the inherent difficulties involved in measuring this parameter in microwave devices (Menéndez et al., 1999), the temperature of the sample, which was regulated by manual adjustment of the microwave power (250 W and 950 W to reach 400 °C and 800 °C respectively), was monitored by means of an infrared optical pyrometer. MIP temperature was measured following a correction procedure described previously by our research group (Menéndez et al., 1999). The time-temperature profiles for the samples are included in the Supplementary Data document. In the electric furnace, the temperature started to rise as soon as

Table 1
Elemental and proximate analysis of the microalgae (A) and the extraction residue (R).

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)[a]				
	Moisture	Ash[a]	Volatile matter[a]	C	H	N	S	O[b]
A	6.5	18.1	70.7	43.8	5.7	8.1	0.6	23.6
R	5.8	19.5	69.8	42.4	5.6	8.8	0.7	23.0

[a] Dry basis.
[b] Calculated by difference.

the reactor had been placed inside the furnace, while in the microwave oven, it took about 5–7 min to start to rise, since during this time only the microwave absorber was heated by the microwave irradiation. The rest of the sample was heated by conduction as the microwave absorber temperature rose.

The experiments were labelled X–YZ, where X was the material pyrolysed (A in the case of the microalga and R in the case of the extraction residue), Y was the heating device used to carry out the pyrolysis (C for CP and M for MIP), and Z was the pyrolysis temperature (400 or 800 °C). As an example, A-M400 is the pyrolysis experiment performed on microalga by means of microwave heating at 400 °C.

The total time for the experiments was chosen on the basis of the outlet flow rate of the pyrolysis gases. The experiments were considered completed once the flow rate of the gases produced in the pyrolysis was less than 0.6 mL STP min^{-1} (i.e., 3% of the He flow rate).

The volatiles evolved from the pyrolysis of the sample were passed through a condensing system, cooled by a cryogenic solution of water and NaCl. The bio-oil fraction was recovered from the condensing system by dissolving it in dichloromethane. It was then subjected to further evaporation of the solvent at 40 °C. This fraction was not analysed, since it is was considered to be outside the scope of this work. The non-condensable gases were collected, at intervals of 10 min, in Tedlar sample bags with a polypropylene fitting for sampling and then analysed by gas chromatography. The composition of the gaseous fraction can be determined from the composition of each bag and the He flowrate (which is constant at the inlet and the outlet of the reactor because He cannot be produced or consumed in the pyrolysis process). The solid and oil fraction yields were calculated from the weight of each fraction, while the gas yield was evaluated by difference. In the case of the solid fraction, it is impossible to discern the amount of CO_2 reacting with the initial microwave absorber or the char that is being formed in the pyrolysis (which also acts as new microwave absorber). In consequence, the yield of solid fraction has been calculated assuming that the gasification of the initial microwave absorber is negligible. The experiments were performed in duplicate to check the repeatability. The errors came to less than 5% both for the yields and the gas composition.

3. Results and discussion

3.1. Gas production

As was explained in the Section 2.2., all the experiments were run until the gas produced was less than 0.6 mL min^{-1}. However, pyrolysis could be concluded before this point was reached because of the low amount of gas produced (see Fig. 1). Another possibility was to set the end of pyrolysis at a certain percentage of the maximum value of the outlet flow rate. In this study, the time selected for calculating the production, yields and gas compositions was the point at which the gas outlet flow rate had fallen to 5% of the maximum amount of gas produced during the experiment ($t_{5\%}$). Fig. 1a and b show the evolution of the outlet flow rate (L STP min^{-1} g^{-1}), normalised per gram of sample, during the pyrolysis of A and R, respectively. It can be seen that A-M400 and A-M800 yielded the highest outlet flow rate value, around 0.035 L STP min^{-1} g^{-1}.

At lower temperature (400 °C), MIP yielded a much higher outlet flow rate (Fig. 1) and gas production (Fig. 2) than CP. This outstanding result highlights the advantage of using MIP rather than CP for gas production, since it is possible to obtain much higher values of gas production at much lower temperatures due to the presence of hot spots and microplasmas in MIP. These hot spots are at much higher temperatures than the overall temperature of the system (400 °C). This phenomenon allows the development of processes that will not take place at the overall temperature of the bulk, i.e., microwave irradiation has a pseudo-catalytic effect (Menéndez et al., 2011; Zhang et al., 2003). At 800 °C, the same trend is observed although during the first 5 min of experiment A-C800, CP furnishes a slightly higher outlet flow rate, which could be attributed to the fact that the microwave heating of the sample is delayed since, initially, only the microwave absorber is heated by means of microwave irradiation.

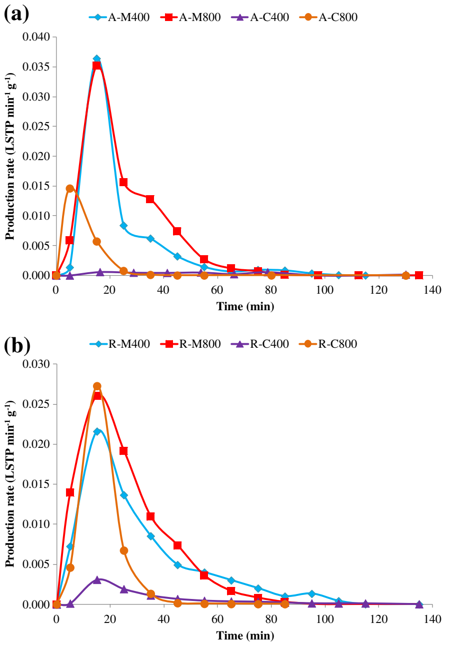


Fig. 1. Evolution of the outlet flow rate (L STP min^{-1} g^{-1}) during the different pyrolysis experiments of (a) the microalga and (b) residue.

Gas production is also affected by the temperature of pyrolysis. The higher the temperature is, the higher the production, although this difference is much less noticeable in the case of microwave heating. If both materials are compared, R shows higher gas production values than A in all cases, particularly in the CP experiments.

Although in some cases the time required for CP is less than for MIP, suggesting an *a priori* energy saving, Fig. 2 shows that the cumulative production achieved is far greater with microwave heating even at 400 °C. The $t_{5\%}$ values are indicated by arrows. In the case of A-C400, it was not possible to reduce the flow rate to 5% of the maximum flow rate after 140 min because the maximum flow rate was very low to begin with.

3.2. Product yields

The char, oil and gas yields for A and R under different pyrolysis conditions are presented in Fig. 3. From the yield data it can be seen that the distribution of products differs considerably depend-

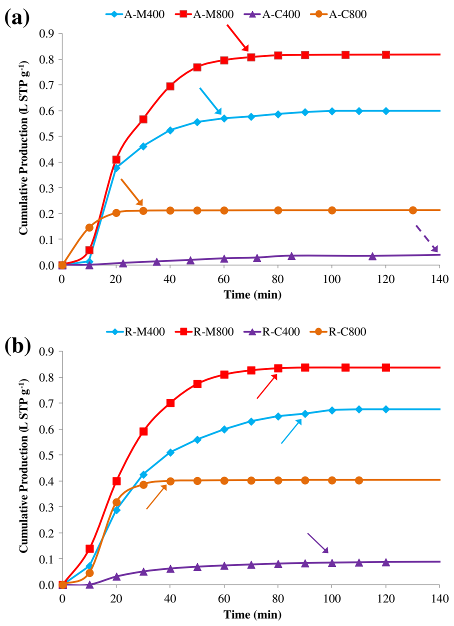


Fig. 2. Cumulative production (L STP g^{-1}) for the pyrolysis experiments of (a) the microalga and (b) residue. $t_{5\%}$ Values for each of the experiments are displayed by arrows.

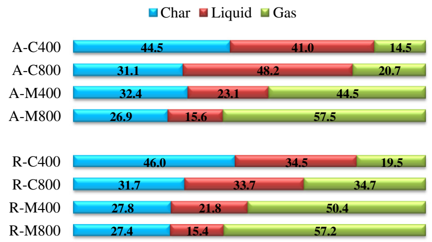


Fig. 3. Fraction yields (wt.%) from the pyrolysis of microalga and its residue as a function of the heating method and the pyrolysis temperature.

ing on several factors. With the same thermal treatment, A and R show similar yields of solids. However, the oil and gas yields are strongly dependent on the heating method and the raw material to be pyrolysed.

CP always gives higher oil yields and lower gas yields than MIP, as has been stated in other studies on biomass materials (Domínguez et al., 2007; Fernández et al., 2009). Typical oil yields of up to 75 wt.% at 500 °C have been reported for conventional biomass fast pyrolysis (Bridgwater, 2012), whereas in the experiments here reported the highest value attained in an electric furnace was around 48 wt.% at 800 °C. However, MIP always produced a greater gas yield than CP as previously demonstrated by our research group (Domínguez et al., 2007; Fernández et al., 2010; 2009).

It can be seen from Fig. 3 that the gas yield from the pyrolysis of R is much higher than for A, except in the case of experiment A-M800 where it is only slightly higher. This could be due to the fact that, with the extraction of the residue from the microalga, heavy compounds such as lipids are removed, resulting in an oil fraction which is easier to crack.

The effect of temperature was also assessed. It was observed that an increase in pyrolysis temperature leads to a decrease in the solid fraction and an increase in the gas yield. This can be attributed to an increase in the devolatilization of the organic material and the secondary cracking of pyrolysis vapours into incondensable gases. It is to be noted that at low temperature (400 °C), MIP gives rise to an exceptional gas yield compared to CP (307% higher in the case of A pyrolysis). This result highlights one of the main advantages of using microwave heating since typical gas fraction yields via conventional fast pyrolysis are about 10 wt.% (Bridgwater, 2012). Nevertheless, the gas yield difference between conventional or microwave heating decreases at the higher temperature (800 °C) although the difference is still appreciable (278% higher in the case of A pyrolysis). It should also be noted that the microalga *Scenedesmus almeriensis* utilised in this study gives a gas yield of 45 wt.% for the experiment A-M400, which is higher than that obtained with other types of microalgae such as *Chlorella* sp. when subjected to MIP at even higher temperatures (Du et al., 2011).

To sum up, these results highlight that microalgae, and particularly the residues obtained after the extraction process, are very attractive substrates for obtaining gaseous products by means of pyrolysis, especially by MIP.

3.3. Gas fraction analysis

The effects of pyrolysis temperature and heating method on the composition of the gas fraction from CP and MIP are shown in Fig. 4a and 4b respectively. The main gases obtained are H_2, CH_4, C_2H_4, C_2H_6, CO and CO_2. Thus, hydrogen is produced by the cracking of volatiles and reforming reactions; and methane, ethylene and ethane by cracking and depolymerization reactions. Finally, carbon monoxide and carbon dioxide were obtained from the depolymerisation of oxygenated organic compounds of biomass, the dehydrogenation of phenolic groups, the cracking of carbonyl groups, the rupture of oxygenated heterocycles or secondary char/hydrocarbon gasification reactions (reactions 1, 2, 4, 7, 8 and 9 in Table 2). It should be noted, too, that pyrolytic gases may participate in secondary reactions that might modify the composition of the outlet gas.”

In CP a gas rich in CO_2 is obtained at 400 °C (67% and 77% for A and R, respectively). From the results shown in Fig. 4a, it is clear that the CO_2 concentration is highly dependent on the pyrolysis temperature, since at 800 °C it is reduced to c.a. 12%. A positive effect on the total amount of gases generated is exerted when the temperature is increased, as is confirmed in Figs. 1 and 2. However, the increase in carbon dioxide produced at 800 °C is negligible compared to the other gases. There is therefore a decrease in CO_2 concentration, as has been reported for several agricultural residues (Encinar et al., 1996; Zanzi et al., 2002).

The H_2, CO, CH_4 and C_2H_4 concentrations on the other hand, increase at 800 °C. A higher temperature favours the cracking of the hydrocarbons (Table 2, reactions 3 and 6) and reforming reactions (Table 2, reactions 1, 2, 7 and 8) in the gas fraction, which leads to an increase in the yield of H_2 and CO. Hydrogen is not detected at 400 °C for any material, although it is the main gas at 800 °C with a yield at this temperature of approximately 30%. The carbon monoxide concentration starts at 9% for A and at 11% for R pyrolysis

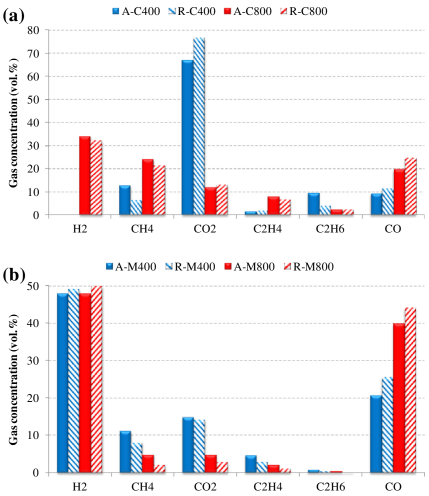


Fig. 4. Gas composition (vol.%) of the gas fraction produced from: (a) the CP and (b) MIP of A and R at different temperatures.

Table 2
Main chemical reactions involved in the pyrolysis process.

Number	Reaction	$\Delta H_{298\ K}$ (kJ mol^{-1})
1	$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO$	247
2	$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO$	205
3	$CH_4 \rightarrow C + 2\ H_2$	76
4	$CO_2 + C \leftrightarrow 2\ CO$	173
5	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	136
6	$C_nH_m \rightarrow n\ C + (m/2)\ H_2$	
7	$C_nH_m + n\ H_2O \leftrightarrow n\ CO + (n + m/2)\ H_2$	
8	$C_nH_m + n\ CO_2 \leftrightarrow 2n\ CO + (n/2)\ H_2$	
9	$C + H_2O \leftrightarrow CO + H_2$	131

and reaches a value of 20% and 25% respectively at 800 °C, which means that its concentration has approximately doubled with the doubling of the temperature. As a consequence, the best value achieved for the total concentration of CO + H_2 (syngas) by means of CP is 56.4% corresponding to R-C800.

The contribution of methane varies from 13% at 400 °C to 24% at 800 °C for A and from 6% to 21% in the case of R. The C_2H_6 concentration is reduced at 800 °C probably due to the dehydrogenation of ethane (Table 2, reactions 5). In the case of C_2H_4, although its concentration is very low at 400 °C (2% for both materials), it increases by more than three times at 800 °C.

As can be seen from Fig. 4b, the product distribution with MIP is qualitatively very different from that obtained with CP. It is evident therefore that microwave heating favours the formation of CO + H_2 (syngas). Hydrogen is the main gas produced regardless of the raw material and pyrolysis temperature. The high H_2 concentration obtained in the case of A-M400 (48%) is even higher than that obtained at 800 °C by CP (A-C800, 34%), but the concentration is greater when pyrolysing R. The highest H_2 content achieved is 50%, corresponding to the R-M800 experiment. This remarkable result can again be attributed to the presence of hot spots and microplasmas in MIP, and their pseudo-catalytic effect.

Table 3
Synthesis gas concentration and its H_2/CO ratio from the conventional and microwave pyrolysis of A and R at different temperatures.

	Microalgae				Residue of microalgae			
	A-C400	A-C800	A-M400	A-M800	R-C400	R-C800	R-M400	R-M800
Syngas (vol.%)	9.2	53.5	68.5	87.7	11.4	56.4	74.5	93.8
H_2/CO	0	1.7	2.3	1.2	0	1.3	1.9	1.1

The carbon monoxide concentration is also higher in MIP and increases with temperature, especially in the case of R. Experiment R-M400 releases a CO concentration of 26% compared to the 44% generated in R-M800. Thus, taking into account that H_2 remains practically constant for all experiments, the variability in CO leads to gas mixtures with different H_2/CO ratios, as is shown in Table 3. These results, in combination with the quicker heating rates provided by microwave heating, give MIP another advantage of MIP over CP. In MIP it is possible to increase or decrease temperatures very quickly, simply by adjusting the power emitted. This allows the composition of the syngas obtained to be easily changed from low to high values of H_2/CO or vice versa. In CP, the heating inertia rules out this possibility. With microwave heating, the H_2/CO ratio decreases when the temperature increases. The opposite occurs if heating is carried out in the conventional electric furnace. Moreover, the total concentration of syngas is much higher in the gases obtained by MIP than in CP, with values as high as 93.8% in the case of R-M800 compared to values of 56.4% for R-C800.

In contrast, the concentrations of CO_2, CH_4, C_2H_4 and C_2H_6 formed by MIP decrease with the increase in temperature. If the CO_2 concentrations resulting from the two heating methods at the same pyrolysis temperature are compared, it can be seen that the CO_2 concentrations from MIP are always lower than those from CP, and that the lower the temperature, the greater the difference. This is because the reaction between the char and CO_2 generates CO (Table 2, reaction 4) and because dry reforming reactions (Table 2, reactions 1 and 8) are favoured at high temperatures.

On the whole, the methane contents in the CP gases are higher than in the case of MIP which indicates that reforming reactions involving CH_4 (Table 2, reactions 1 and 2) are favoured in MIP (Wang et al., 2009). The presence of C_2 compounds in MIP is scarcely noticeable. In conventional heating, the heat flow goes from the walls of the reactor to the sample, so the temperature is higher in the reactor than inside the bulk sample. This creates favourable conditions for the homogeneous cracking of the liquid components, leading to an increase in the hydrocarbon content of the pyrolysis gas. In contrast, when microwave heating is used, the heat is produced by the interaction of the sample with the electromagnetic field, so the temperature is higher in the sample than in the reactor, favouring the heterogeneous catalytic decomposition of hydrocarbons (Table 2, reactions 3 and 6) (Domínguez et al., 2006). This might explain why the value of the total light hydrocarbon yield ($CH_4 + C_2H_6 + C_2H_4$) is higher in all of the experiments carried out in the electric furnace for both materials.

Regarding the influence of the extraction procedure on the gas composition, there are no big differences, possibly due to the similar proximate and ultimate compositions of the microalga and its extraction residue. Therefore the influence of pyrolysed material is not a meaningful characteristic in this sense.

3.4. Catalytic effects of the microwave absorber

Besides the pseudo-catalytic effect resulting from the microplasmas caused by microwave heating (Menéndez et al., 2011; Zhang

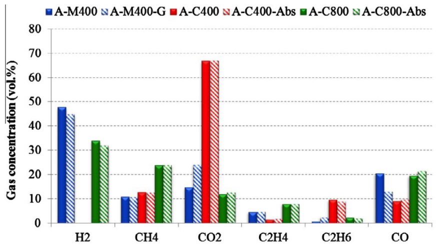


Fig. 5. Gas composition (vol.%) of the gas fraction produced in the experiments A-M400, A-M400-G, A-C400, A-C400-Abs, A-C800 and A-C800-Abs.

et al., 2003), the metallic content of the char used as microwave absorber can catalyse reforming reactions or the decomposition of hydrocarbons, and favour the generation of large amounts of hydrogen in MIP. A semiquantitative analysis of the metal content of the microwave absorber was performed using an ICP-MS 7700x Agilent, finding that the main metals present in the material are: K (3 wt.%), Mg (2 wt.%), Na (1 wt.%), Fe (7000 ppm), Sr and Mn (1500 ppm), Si (1000 ppm), Ba (300 ppm) and Cu and Zn (200 ppm). To confirm or discard this catalytic effect, three additional experiments were performed. The A-M400 experiment was repeated using graphite dust as microwave absorber (the experiment was labelled as A-M400-G) in order to study the MIP without the presence of the metallic content of the char. Experiments A-C400 and A-C800 were repeated with the addition of the char (the experiments were labelled as A-C400-Abs and A-C800-Abs), in the same proportion as in MIP, to determine whether any change occurred in the gas composition due to the presence of the metallic content of the char. The results are shown in Fig. 5. As can be seen, there are no significant differences when graphite is used as microwave absorber in the MIP or when the char is added to the CP, which suggests that the metal content of the char has no substantial catalytic effect. The only noteworthy difference is the change in the proportions of CO and CO_2 in MIP with the different absorbers. With char, the CO concentration is higher than with graphite dust, while in the case of the CO_2 the highest concentration results from mixing the microalga is achieved with a mixture of microalga and graphite dust. This may be related to the gasification of the char.

3.5. Heating values of the pyrolysis gases

Higher heating values (HHV) were calculated from the mean of the individual heating values of the compounds present in the gas fraction. Fig. 6 shows the energy content of the gas fraction per gram of pyrolysed material (E_g) under conventional and microwave heating, which was calculated from HHV. This bubble graph presents a global view of the gas yield (expressed as wt.%) and syngas content (expressed as vol.%). The size of the bubble represents E_g. It is evident from the diagram that microwave heating provides a gas with a higher E_g than in conventional heating, as in the case of the gas yield and syngas production.

The optimal conditions appear when the highest values for gas yield and syngas content are reached. These values were obtained in experiments A-M800 (57.5 wt.% of gas yield and 87.7 vol.% of syngas) and R-M800 (57.2 wt.% of gas yield and 93.8 vol.% of syngas), which gave E_g values of 3.36 and 3.15 Wh g^{-1}, respectively.

The effect of pyrolysis temperature on E_g is considerable. If the pyrolysis temperature rises, the E_g increases, especially in CP. If we compare both materials when pyrolysed by means of conventional heating, in A the E_g is almost five times higher with a rise in the pyrolysis temperature from 400 to 800 °C, whereas in R, this difference is ten times higher. However, these differences are made to appear almost insignificant when compared to the values reached by microwave heating.

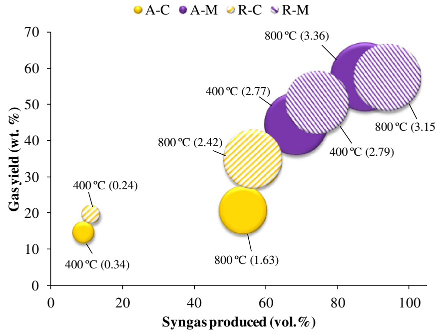


Fig. 6. Comparative diagram between the gas yield (wt.%) and syngas production (vol.%) during the pyrolysis of the microalga and its residue by CP and MIP. The size of the bubble represents the E_g values (Wh g^{-1}), which are shown between parentheses, after the pyrolysis temperature.

The E_g values obtained are rather low compared to those of other fossil fuels, such as natural gas (15.6 Wh g^{-1} gas). However, attention needs to be paid to the units in which E_g is expressed. The results in this paper have been normalized per gram of raw material instead of per gram of gas produced. In the case just metioned, the best E_g would be 5.8 Wh g^{-1} gas. Similar E_g values have been obtained with other biomass materials (Raveendran and Ganesh, 1996). Moreover, the E_g values of this study are comparable to those achieved with synthetic coal gas or blast furnace gas (Perry and Green, 1997). Nevertheless, it is important to note that the goal of the pyrolysis processes performed herein is to maximise the syngas production, which do not have particularly high energy content, but can be used for many other applications different from its use as direct fuel. These include hydrogen and methanol production, Fischer–Tropsch and synthesis of biopolymers via bacterial fermentation of syngas, among others (Bridgwater, 2012; http://www.synpol.org/).

4. Conclusions

This study has demonstrated the great potential of microalgae and their extraction residue for use as hydrogen and syngas source via microwave induced pyrolysis. The MIP of the residue at 800 °C was found to be optimal for attaining a maximum syngas concentration (93.8 vol.%), whereas the MIP of microalga at 400 °C produced the gas fraction with the highest H_2/CO ratio (2.3). The drastic differences in fraction yields and product distribution between CP and MIP in this work provide convincing evidence of the superiority of MIP for syngas and H_2 production, even at low temperatures.

Acknowledgements

Financial support from the CDTI and EXELERIA (Project CENIT-VIDA), MEC Spain INNPACTO (Project CMICROWAVES IPT-2011-0739-920000) and from the European Union Seventh Framework Programme (FP7/2007-2013) under agreement number 311815 is acknowledged. JMB also acknowledges the support received from the CSIC JAE Program.

References

Brennan, L., Owende, P., 2010. Biofuels from microalgae-A review of technologies for production, processing, and extractions of biofuels and co-products. Renewable Sustainable Energy Rev. 14, 557–577.

Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 38, 68–94.

Campanella, A., Muncrief, R., Harold, M.P., Griffith, D.C., Whitton, N.M., Weber, R.S., 2012. Thermolysis of microalgae and duckweed in a CO_2-swept fixed-bed reactor. Bio-oil yield and compositional effects. Bioresour. Technol. 109, 154–162.

Campbell, P.K., Beer, T., Batten, D., 2011. Life cycle assessment of biodiesel production from microalgae in ponds. Bioresour. Technol. 102, 50–56.

Carriquiry, M.A., Du, X., Timilsina, G.R., 2011. Second generation biofuels: Economics and policies. Energy Policy 39, 4222–4234.

Chisti, Y., 2007. Biodiesel from microalgae. Biotechnol. Adv. 25, 294–306.

Delrue, F., Setier, P.A., Sahut, C., Cournac, L., Roubaud, A., Peltier, G., Froment, A.K., 2012. An economic, sustainability, and energetic model of biodiesel production from microalgae. Bioresour. Technol. 111, 191–200.

Domínguez, A., Menéndez, J.A., Fernández, Y., Pis, J.J., Nabais, J.M.V., Carrott, P.J.M., Carrott, M.M.L.R., 2007. Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. J. Anal. Appl. Pyrolysis 79, 128–135.

Domínguez, A., Menéndez, J.A., Inguanzo, M., Pis, J.J., 2005. Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge. Fuel Process. Technol. 86, 1007–1020.

Domínguez, A., Menéndez, J.A., Inguanzo, M., Pís, J.J., 2006. Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. Bioresour. Technol. 97, 1185–1193.

Du, Z., Li, Y., Wang, X., Wan, Y., Chen, Q., Wang, C., Lin, X., Liu, Y., Chen, P., Ruan, R., 2011. Microwave-assisted pyrolysis of microalgae for biofuel production. Bioresour. Technol. 102, 4890–4896.

Encinar, J.M., Beltrán, F.J., Bernalte, A., Ramiro, A., González, J.F., 1996. Pyrolysis of two agricultural residues: Olive and grape bagasse. Influence of particle size and temperature. Biomass Bioenergy 11, 397–409.

Fernández, Y., Arenillas, A., Bermúdez, J.M., Menéndez, J.A., 2010. Comparative study of conventional and microwave-assisted pyrolysis, steam and dry reforming of glycerol for syngas production, using a carbonaceous catalyst. J. Anal. Appl. Pyrolysis 88, 155–159.

Fernández, Y., Arenillas, A., Díez, M.A., Pis, J.J., Menéndez, J.A., 2009. Pyrolysis of glycerol over activated carbons for syngas production. J. Anal. Appl. Pyrolysis 84, 145–150.

Ferrel, J., Sarisky-Reed, V., 2010. National Algal Biofuels Technology Roadmap. U.S, Department of Energy.

Grierson, S., Strezov, V., Shah, P., 2011. Properties of oil and char derived from slow pyrolysis of *Tetraselmis chui*. Bioresour. Technol. 102, 8232–8240.

Harun, R., Davidson, M., Doyle, M., Gopiraj, R., Danquah, M., Forde, G., 2011. Technoeconomic analysis of an integrated microalgae photobioreactor, biodiesel and biogas production facility. Biomass Bioenergy 35, 741–747.

Hu, Z., Ma, X., Chen, C., 2012. A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. Bioresour. Technol. 107, 487–493.

Lardon, L., Hélias, A., Sialve, B., Steyer, J.P., Bernard, O., 2009. Life-cycle assessment of biodiesel production from microalgae. Environ. Sci. Technol. 43, 6475–6481.

Luque, R., Menéndez, J.A., Arenillas, A., Cot, J., 2012. Microwave-assisted pyrolysis of biomass feedstocks: The way forward? Energy Environ. Sci. 5, 5481–5488.

Menéndez, J.A., Juárez-Pérez, E.J., Ruisánchez, E., Bermúdez, J.M., Arenillas, A., 2011. Ball lightning plasma and plasma arc formation during the microwave heating of carbons. Carbon 49, 346–349.

Menéndez, J.A., Menéndez, E.M., García, A., Parra, J.B., Pis, J.J., 1999. Thermal treatment of active carbons: A comparison between microwave and electrical heating. J. Microw. Power Electromagn. Energy 34, 137–143.

Miao, X., Wu, Q., 2004. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. J. Biotechnol. 110, 85–93.

Miao, X., Wu, Q., Yang, C., 2004. Fast pyrolysis of microalgae to produce renewable fuels. J. Anal. Appl. Pyrolysis 71, 855–863.

Perry, R.H., Green, D.W., 1997. Perry's Chemical Engineers' Handbook, seventh ed. McGraw-Hill, New York.

Raveendran, K., Ganesh, A., 1996. Heating value of biomass and biomass pyrolysis products. Fuel 75, 1715–1720.

Sanchez-Silva, L., López-González, D., Garcia-Minguillan, A.M., Valverde, J.L., 2013. Pyrolysis, combustion and gasification characteristics of *Nannochloropsis gaditana* microalgae. Bioresour. Technol. 130, 321–331.

Tabernero, A., Martín del Valle, E.M., Galán, M.A., 2012. Evaluating the industrial potential of biodiesel from a microalgae heterotrophic culture: Scale-up and economics. Biochem. Eng. J. 63, 104–115.

Thangalazhy-Gopakumar, S., Adhikari, S., Chattanathan, S.A., Gupta, R.B., 2012. Catalytic pyrolysis of green algae for hydrocarbon production using H +ZSM-5 catalyst. Bioresour. Technol. 118, 150–157.

Wang, K., Brown, R.C., Homsy, S., Martinez, L., Sidhu, S.S., 2013. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. Bioresour. Technol. 127, 494–499.

Wang, X.H., Chen, H.P., Ding, X.J., Yang, H.P., Zhang, S.H., Shen, Y.Q., 2009. Properties of gas and char from microwave pyrolysis of pine sawdust. Bioresources 4, 946–959.

Xu, L., Wim Brilman, D.W.F., Withag, J.A.M., Brem, G., Kersten, S., 2011. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. Bioresour. Technol. 102, 5113–5122.

Zanzi, R., Sjöström, K., Björnbom, E., 2002. Rapid pyrolysis of agricultural residues at high temperature. Biomass Bioenergy 23, 357–366.

Zhang, X., Hayward, D.O., Mingos, D.M.P., 2003. Effects of microwave dielectric heating on heterogeneous catalysis. Catal. Lett. 88, 33–38.

Capítulo 5

Resultados y Discusión: Bloque II

Parámetros influyentes en la pirólisis con microondas

Este bloque incluye los trabajos centrados en la influencia de los parámetros de operación sobre el proceso de pirólisis con microondas para la producción de syngas. La temperatura de pirólisis es uno de dichos parámetros; sin embargo, su efecto en la producción de syngas ya ha sido analizado por conveniencia en las publicaciones presentadas en el Bloque I.

En la Publicación IV se analiza el efecto de la potencia de microondas y la proporción de captador añadida al sustrato en la producción de syngas. La Publicación V muestra la influencia de la humedad del sustrato en la producción de syngas mediante pirólisis inducida por microondas. En la Publicación VI se analiza el posible efecto del gas portador ya que, en principio, podría afectar a la naturaleza de los microplasmas generados al aplicar las microondas sobre el captador, haciendo que la producción de syngas pudiera verse afectada. Por último, en la Publicación VII se analiza el comportamiento dieléctrico (es decir, la capacidad de absorción de microondas y conversión en energía térmica) de los residuos en función de la temperatura, y cómo este hecho influye en la eficiencia energética del proceso de pirólisis.

Para el desarrollo de este Bloque II, se seleccionó como sustrato la fracción orgánica de RSU, ya que proporcionó unos resultados muy prometedores en cuanto a producción de syngas, tal y como se ha presentado en el Bloque I. Además, esta fracción de RSU resulta ser un sustrato muy novedoso respecto a su aplicación en un proceso de pirólisis inducido por microondas, ya que apenas existen referencias bibliográficas acerca del mismo.

5.1 Captador de microondas

Como se adelantó en la sección de Introducción, para conseguir una temperatura lo suficientemente alta como para que tenga lugar la pirólisis de un material transparente a la radiación microondas, es decir, con malas propiedades dieléctricas, resulta necesario añadir captadores de microondas al residuo a pirolizar, tales como el propio carbonizado de dicho residuo. La influencia del captador es uno de los principales factores que afecta a la pirólisis con microondas, ya que dependiendo de su naturaleza, y por tanto de sus propiedades dieléctricas, tiene lugar un perfil de temperatura determinado. De esta forma, los captadores de microondas que sean susceptibles de provocar velocidades de calentamiento y temperaturas altas favorecerán la producción de gases, lo que implica cambios en la distribución de productos y, por tanto, en la proporción de syngas.

En este sentido, la temperatura alcanzada en un proceso de calentamiento con microondas parece depender de las propiedades dieléctricas del captador, mientras que la velocidad de calentamiento parece estar más relacionada con la composición química y la estructura física del mismo. Sin embargo, no solo es importante la naturaleza del captador de microondas (ZUO, 2011), sino también su concentración en el medio de reacción. Sin embargo, el efecto este parámetro en la producción de syngas no ha sido estudiado en los trabajos de investigación que pueden encontrarse en la literatura; por el contrario, la mayoría de estudios acerca del efecto de la concentración del captador de microondas se ha centrado en la producción de aceites (SALEMA, 2011, SALEMA, 2012, ABUBAKAR, 2013). Dicho parámetro debe ser optimizado, ya que no solo mejora la concentración de syngas, sino que también puede permitir una reducción notable en el consumo energético del proceso de pirólisis inducido por microondas. Con este objetivo se presenta la **Publicación IV**, cuyo procedimiento experimental se resume en la Figura 5.1.

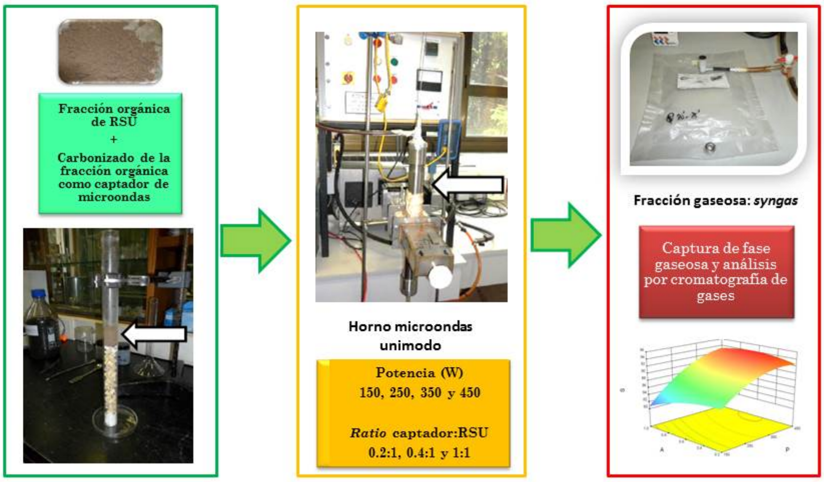


Figura 5.1 Esquema experimental del estudio de optimización de potencia y concentración de captador de microondas en la pirólisis de la fracción orgánica de RSU

Para llevar a cabo el estudio de optimización, se empleó un diseño experimental sobre el cual se aplicó la metodología de superficies de respuesta a través de la interacción entre el factor **potencia** y el factor ***ratio* captador:RSU**. De esta forma, se observó que la contribución de la potencia de radiación microondas a la producción de syngas es mucho más significativa que la concentración de captador de microondas. Este resultado era de esperar, puesto que al aumentar la potencia se genera una mayor potencia volumétrica que hace que la velocidad de calentamiento sea mayor, favoreciendo la producción de gas, que resulta ser casi el doble al pasar de 150 W a 450 W, pero penalizando el consumo energético.

Sin embargo, la presencia del carbonizado como captador de microondas también parece tener un efecto significativo, aunque en menor grado que la potencia. De esta forma, es posible obtener una fracción gaseosa con una concentración en syngas de entre 80 y 94 vol% a bajas potencias. El valor mínimo del *ratio* captador:RSU fue 0.2:1, ya que por debajo de este valor no fue posible llevar a cabo la pirólisis debido a la transparencia del residuo a las microondas. Este resultado es de extrema importancia, ya que incluso utilizando altas potencias (450 W) es absolutamente necesaria la adición de captador al residuo para llevar a cabo la pirólisis en microondas.

Además de ser necesario un *ratio* captador:RSU mínimo, se encontró que, precisamente, este valor fue el más óptimo para maximizar la concentración y producción de syngas a partir de la fracción orgánica de RSU seca. Este efecto ya ha sido descrito por otros autores, indicando que, posiblemente, cuando se utiliza una alta concentración de captador de microondas, la temperatura final del proceso puede ser menor debido a que el captador se calienta de forma muy localizada y la transferencia de calor hacia el residuo a pirolizar no es tan eficiente (SALEMA, 2012). Realmente, este hecho podría entenderse como un efecto mixto entre la cantidad de captador y el diseño geométrico del reactor.

Por otra parte, se analizó el efecto de la concentración de captador de microondas en el caso de usar la fracción orgánica de RSU **húmeda**. En este caso, las tendencias observadas fueron diferentes. El vapor de agua generado a partir de la humedad parece participar en reacciones de gasificación, que estarían más favorecidas en el caso de disponer de una mayor concentración de captador carbonizado, como se muestra en las reacciones 5-6. Así mismo, las reacciones 2 y 4 también estarían favorecidas. De esta forma, podría explicarse la mayor producción de gas (en base seca de residuo) y de H_2 y CO_2 que tienen lugar en el caso de utilizar la fracción húmeda.

$$C + H_2O \leftrightarrow H_2 + CO \qquad \text{Reacción 5}$$

$$C + 2\ H_2O \leftrightarrow 2\ H_2 + CO_2 \qquad \text{Reacción 6}$$

Los resultados obtenidos en este trabajo sugieren que la utilización de un material captador de microondas resulta esencial para llevar a cabo la pirólisis inducida por microondas, y que el carbonizado resultante de la propia pirólisis del residuo es muy adecuado para ser utilizado como captador. Además de conseguir la temperatura de pirólisis necesaria, es una forma de aprovechar la fracción sólida del proceso de pirólisis sin introducir un material ajeno al propio proceso. Por otra parte, hay que remarcar que el contenido en humedad del residuo a pirolizar favorece la producción de gas. Este resultado abre la puerta al diseño de una unidad que podría integrar los procesos de secado y pirólisis para favorecer la producción de syngas. Esta posibilidad ha sido investigada y los resultados obtenidos se presentan a continuación en la **Publicación V**.

5.2 Humedad

Una alternativa para mejorar la eficiencia de una planta consiste en la integración de procesos. En este sentido, la incorporación de diferentes procesos físico-químicos en una misma unidad de proceso resulta especialmente atractiva. La **Publicación V** se basa en este concepto con el fin de desarrollar una metodología que permita un tratamiento de valorización de residuos sólidos urbanos.

La humedad se encuentra presente en los residuos urbanos en un porcentaje aproximado del 40% en masa, si bien es cierto que puede oscilar en el intervalo 25 - 60%. Esta característica debe de ser tenida en cuenta en los procesos de compresión de residuos, producción de lixiviados, transporte, procesos de transformación, tratamientos de incineración o de recuperación energética, y procesos de separación de residuos en la correspondiente planta de reciclado. En procesos de conversión termoquímica, no es deseable un contenido en humedad alto porque la eficiencia del proceso disminuye, ya que se necesita una gran cantidad de energía para convertir el agua líquida en vapor (NIU, 2013), además de producir gases combustibles de menor poder calorífico y aumentar los costes de transporte. Sin embargo, el efecto de la presencia de humedad durante un proceso de conversión termoquímica asistido con microondas puede ser diferente, ya que el agua es un buen captador de microondas y se pueden favorecer reacciones heterogéneas con vapor de agua como agente gasificante.

De esta forma, en la Publicación V se propone la integración de tres procesos (secado, pirólisis y gasificación) de la fracción orgánica de RSU en un reactor calentado por microondas, con el objetivo de producir syngas. Para ello, se ha utilizado la fracción orgánica de RSU con diferentes grados de humedad, habiéndose sometido la fracción húmeda, que posee un 45% de humedad, a secados parciales en una estufa para obtener diferentes contenidos de humedad (0%, 12% y 34%), tal y como se muestra en la Figura 5.2.

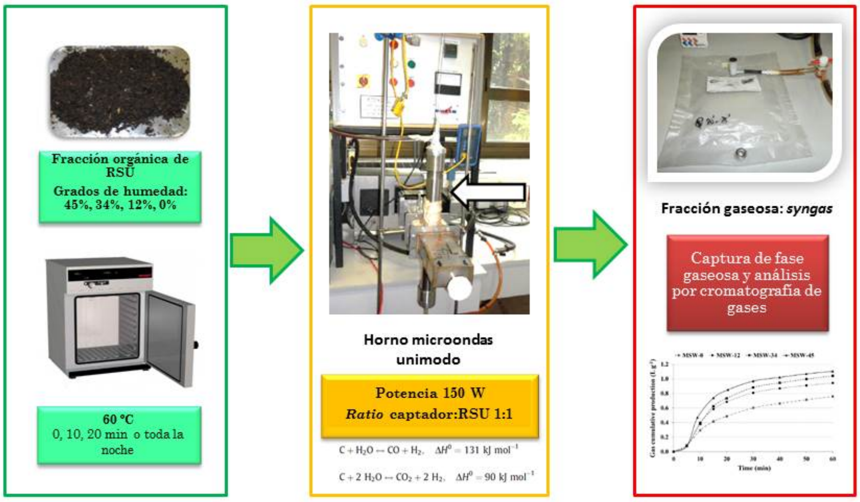


Figura 5.2 Esquema experimental del estudio de la influencia de la humedad en la pirólisis de la fracción orgánica de RSU

Se escogió una potencia de 150 W para estudiar con más claridad el efecto de la humedad, ya que en la anterior Publicación IV se observó que a una densidad de potencia elevada, el efecto de la humedad en la producción de syngas es menor. Por otra parte, el *ratio* captador:RSU fue 1:1, ya que en la misma Publicación IV se mostró que con un residuo húmedo, un *ratio* elevado proporciona una mayor concentración de syngas, ya que hay mayor cantidad de carbono susceptible de ser gasificado con el vapor generado a partir de la humedad del residuo.

Los resultados obtenidos en este trabajo sugieren que existe un **contenido en humedad óptimo** para la producción de syngas (**12%**), debido probablemente a que el calentamiento se ve favorecido con microondas, teniendo lugar una absorción de microondas más eficiente; sin embargo, a mayores contenidos en humedad, la producción comienza a caer. Además, se ha confirmado que la producción gaseosa se ve favorecida a mayor contenido de humedad del residuo, lo cual puede ser atribuible a las reacciones de gasificación en las que participa el vapor de agua. De esta forma, se ha encontrado un entorno en el cual es favorecedora la integración del secado con los procesos de pirólisis y gasificación para la producción de syngas, ya que además todo parece indicar que el consumo energético podría disminuir respecto a la pirólisis del residuo seco (SERIO, 2012).

5.3 Gas portador

Durante el calentamiento con microondas de materiales carbonosos, se producen microplasmas (MENÉNDEZ, 2011). En este sentido, se ha encontrado que en reacciones heterogéneas asistidas con microondas tiene lugar una mejora de la actividad catalítica, habiéndose atribuido a la existencia de dichos microplasmas, ya que en estos puntos existe una temperatura mucho mayor que la temperatura media del lecho catalítico (ZHANG, 2003). De hecho, se ha sugerido que los microplasmas pueden provocar cambios en las constantes de equilibrio, por lo que se suele hablar de que los microplasmas producen un efecto *pseudo-catalítico* durante el calentamiento con microondas. En el contexto de un proceso de pirólisis inducido por microondas, son los microplasmas los que permiten facilitar la extracción de volátiles y que las reacciones heterogéneas entre el sólido carbonoso y los volátiles para producir syngas se vean favorecidas.

Existen algunas evidencias de que uno de los factores que influyen directamente en la generación de estos microplasmas es la atmósfera gaseosa que los rodean. Así, la presencia de H_2 durante el reformado seco de gas de coquería asistido con microondas parece ser la responsable de obtener unos microplasmas de mayor temperatura que los que se producen en el reformado seco de metano (BERMÚDEZ, 2012).

Por otra parte, existen algunos trabajos acerca de la influencia del gas portador en el proceso de pirólisis con microondas, pero siempre enfocados hacia la influencia del tiempo de contacto entre la materia a pirolizar y dicho gas. Sin embargo, no existen en la literatura trabajos enfocados en la influencia de la composición de dicho gas portador en la distribución de productos de la pirólisis. En este sentido, en la **Publicación VI** se analiza el efecto que tiene utilizar como gases portadores N_2 y He sobre la producción de syngas, así como el hecho de no utilizar ningún gas portador.

Los resultados obtenidos en este trabajo indican que la pirólisis inducida por microondas de residuos puede llevarse a cabo **sin utilizar un gas portador**, si previamente se ha inertizado el reactor, lo que supone un menor coste operacional. Por otra parte, el hecho de utilizar

N_2 o He como gas portador parece no afectar significativamente a la producción de syngas.

5.4 Propiedades dieléctricas

Para llevar a cabo el diseño y escalado de procesos que hagan uso de la tecnología de calentamiento con microondas, resulta esencial seleccionar el tipo de cavidad adecuada. Para ello, tanto los requerimientos del proceso como las propiedades directamente relacionadas con el calentamiento con microondas, deben conocerse en detalle. En este sentido, se deben conocer las propiedades dieléctricas de los materiales procesados en función de la temperatura del proceso, puesto que serán determinantes a la hora de evaluar la eficiencia del proceso en términos de potencia absorbida por la carga.

En la **Publicación VII**, se determina la respuesta dieléctrica de la fracción orgánica de RSU en función de la concentración de captador de microondas añadida (relaciones másicas captador:RSU 0:1, 0.3:1, 0.6:1 y 1:0) y de la temperatura de pirólisis. Dicha respuesta se ha evaluado a diferentes temperaturas durante el proceso de pirólisis en términos de la constante dieléctrica ε', el factor de pérdidas dieléctrico ε'' y la distancia de penetración en el material. Para ello, se ha utilizado una metodología inversa (Figura 5.3), basada en un método de optimización que permite obtener las propiedades dieléctricas mediante la comparación entre los coeficientes de reflexión de ondas derivados del material real y del material simulado (S_{11}, S_{12} y S_{22}) (REQUENA-PEREZ, 2006). Estos coeficientes dependen de la capacidad de absorción de microondas de los materiales y, por tanto, de ε' y ε''.

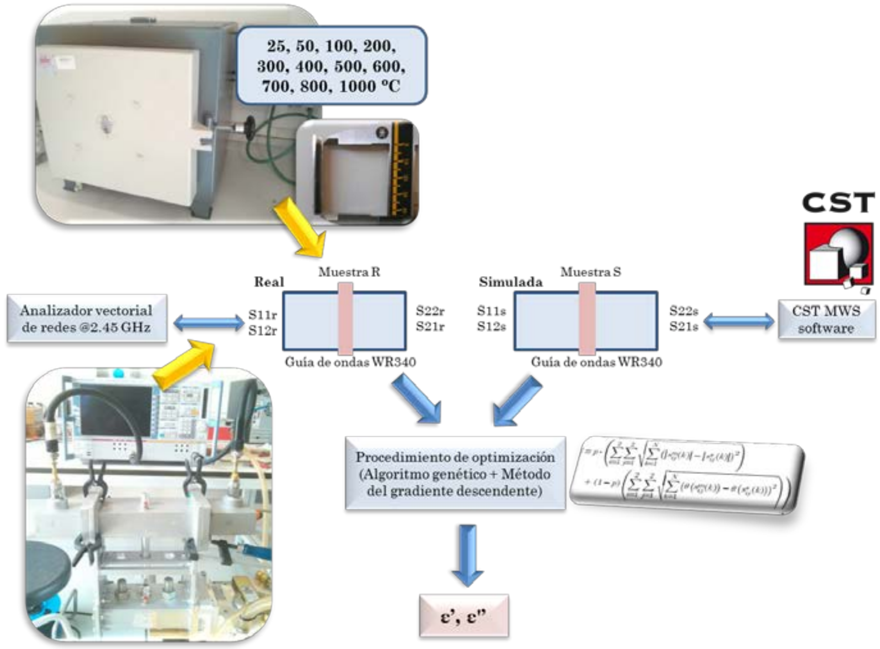


Figura 5.3 Esquema experimental utilizado para la determinación de las propiedades dieléctricas de los residuos

En la Figura 5.4 se representa, a modo de ejemplo, la variación de la constante dieléctrica con la temperatura, ε', de la mezcla captador: residuo en una proporción másica 0.3:1. Así mismo, en la Figura 5.5 se representa la variación del factor de pérdidas dieléctricas con la temperatura, ε'', y en la Figura 5.6 la variación de la tangente de pérdidas dieléctricas. Todas las propiedades mencionadas se mantienen aproximadamente constantes, con tendencia a disminuir al acercarse a los 400 °C, siendo la absorción de microondas muy moderada. Sin embargo, a partir de 500 °C, el comportamiento del residuo es completamente diferente: la tangente de pérdidas dieléctricas aumenta de forma considerable hasta un máximo de 1.7, valor que se corresponde con la pirólisis a 800 °C. A esta temperatura tiene lugar, por tanto, la máxima conversión de energía electromagnética microondas en energía térmica debido al incremento de la densidad de electrones deslocalizados en la estructura carbonosa como consecuencia de la pérdida de volátiles, tal como se explicó en el capítulo de Introducción.

Por otra parte, la constante dieléctrica crece continuamente hasta 1000 ºC, mientras que el factor de pérdidas dieléctricas muestra un pico a 800 ºC, el cual se puede asociar a un fenómeno de polarización interfacial, indicando que tiene lugar un cambio estructural en el material (PENG, 2012).

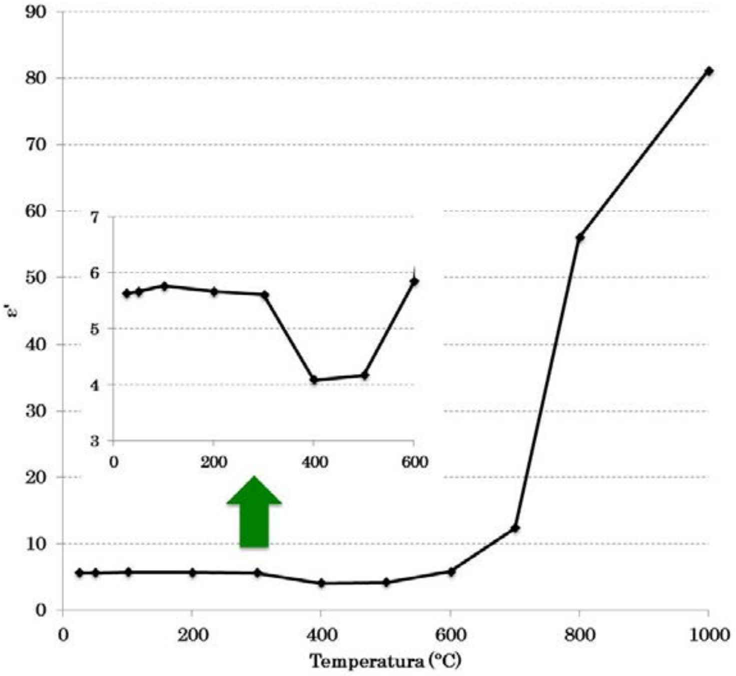


Figura 5.4 Constante dieléctrica del captador + residuo (0.3:1) en función de la temperatura a 2.45 GHz

Además, como consecuencia del incremento de la absorción de microondas al aumentar la temperatura, la distancia de penetración de las mismas se ve reducida a partir de 400 ºC hasta 800 ºC, temperatura a la que dicha distancia es mínima, por lo que el resto del material se calentaría por transferencia de calor (Figura 5.7). Este aspecto es fundamental a tener en cuenta en el diseño y modo de operación de un prototipo de reactor para llevar a cabo la pirólisis a mayor escala. En este sentido, se está comenzando a trabajar en novedosos diseños como la pirólisis inducida por microondas utilizando un lecho fluidizado, lo que evitaría los problemas de dispersión de ondas en un lecho fijo por encontrarse el material compactado (XIE, 2014).

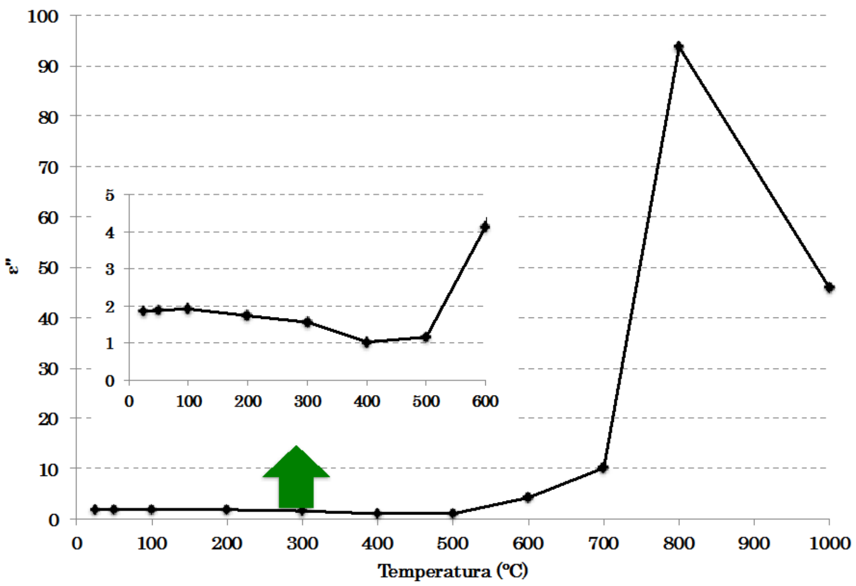


Figura 5.5 Factor de pérdidas dieléctricas del captador + residuo (0.3:1) en función de la temperatura a 2.45 GHz

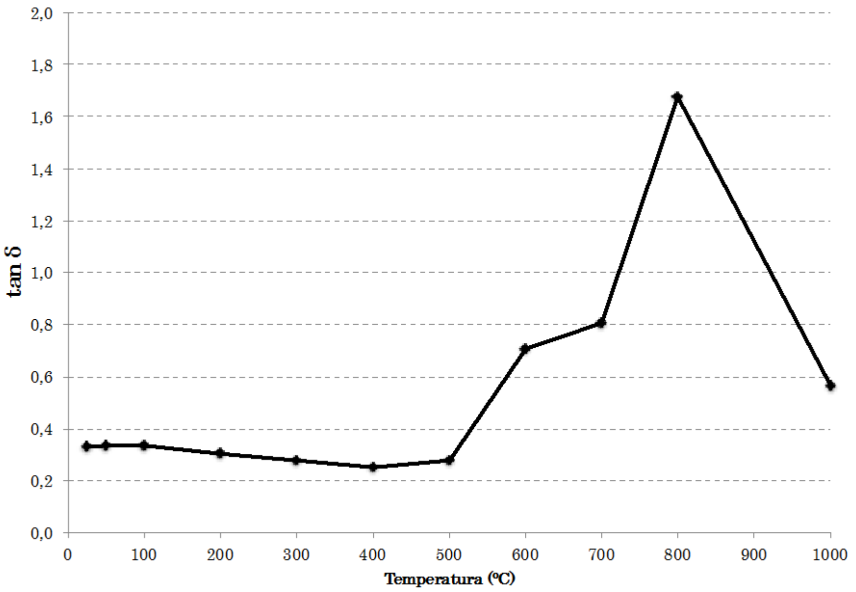


Figura 5.6 Tangente de pérdidas dieléctricas del captador + residuo (0.3:1) en función de la temperatura a 2.45 GHz

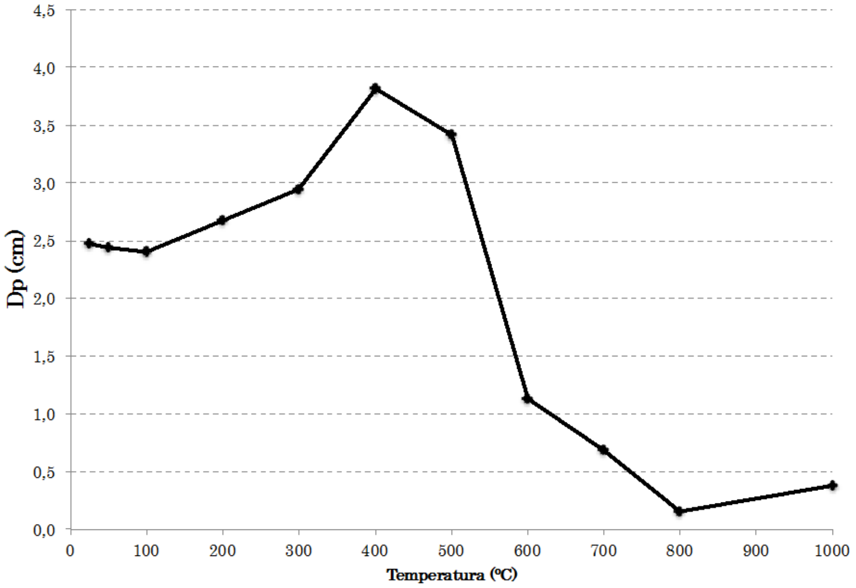


Figura 5.7 Distancia de penetración de las microondas en la mezcla captador + residuo (0.3:1) en función de la temperatura a 2.45 GHz

Gracias al valor del parámetro *tan δ*, se ha podido determinar que la **eficiencia** de la conversión de energía microondas en calor es casi **20 veces superior cuando se añade captador al RSU** a temperatura ambiente. Esta diferencia ha resultado ser incluso mayor en el intervalo 600 – 800 ºC, lo cual es muy prometedor en procesos de pirólisis.

Además, cuanto mayor es la concentración de captador añadido, el efecto de *thermal runaway* (mediante el cual, la energía de las microondas se concentra en un material absorbente cuya velocidad de absorción aumenta con la temperatura dando lugar a un crecimiento exponencial de la velocidad de calentamiento) ocurre a más baja temperatura, aunque el calentamiento es más heterogéneo y la distancia de penetración de las microondas es menor. Por tanto, la **composición** de la **mezcla** de **partida influirá** en gran medida en el **comportamiento dieléctrico** al aumentar la temperatura a pesar de que el producto final sea el mismo (char).

Por lo tanto, existen dos efectos contrapuestos al añadir captador de microondas que deberían ser tenidos en cuenta para conseguir un proceso de pirólisis con microondas más eficiente, tal y como se muestra en la Figura 5.8.

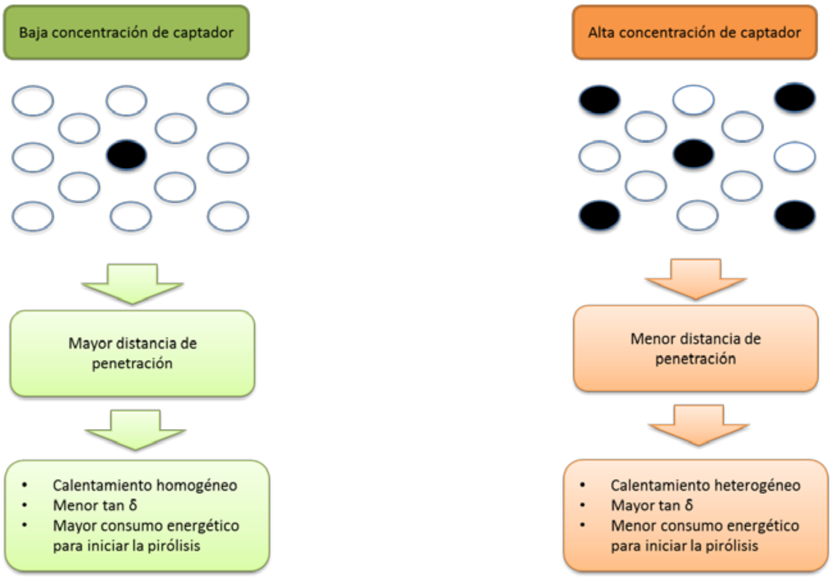


Figura 5.8 Efecto de la concentración de captador (círculos oscuros) en el calentamiento con microondas. Los círculos blancos representan el residuo orgánico transparente a las microondas

Evidentemente, el consumo energético del proceso de pirólisis inducida por microondas también dependerá del **diseño geométrico** del reactor además de las propiedades dieléctricas de los residuos. A modo de referencia, en un estudio reciente en el que se llevó a cabo la pirólisis de residuos sólidos urbanos con microondas a mayor escala (20 kW), los autores reportaron consumos energéticos del orden de **0.5 – 0.7 kWh/kg** (LI, 2011).

Referencias

Abubakar, Z., A. A. Salema and F. N. Ani (2013). "A new technique to pyrolyse biomass in a microwave system: Effect of stirrer speed." Bioresource Technology ***128****(0): 578-585.*

Bermúdez, J. M., A. Arenillas and J. A. Menéndez (2012). "Microwave-assisted CO_2 *reforming of coke oven gas: An exception to the general rule?" Afinidad* ***69****(559): 185-190.*

Li, X.-y., J. Yan, H. Yang, T. Peng and Q.-c. Yang (2011). Study on processing technology for microwave pyrolysis of municipal solid waste. Materials for Renewable Energy & Environment (ICMREE), 2011 International Conference on.

Menéndez, J. A., E. J. Juárez-Pérez, E. Ruisánchez, J. M. Bermúdez and A. Arenillas (2011). "Ball lightning plasma and plasma arc formation during the microwave heating of carbons." Carbon ***49****(1): 346-349.*

Niu, M., Y. Huang, B. Jin and X. Wang (2013). "Simulation of Syngas Production from Municipal Solid Waste Gasification in a Bubbling Fluidized Bed Using Aspen Plus." Industrial & Engineering Chemistry Research ***52****(42): 14768-14775.*

Peng, Z., J.-Y. Hwang, B.-G. Kim, J. Mouris and R. Hutcheon (2012). "Microwave Absorption Capability of High Volatile Bituminous Coal during Pyrolysis." Energy & Fuels ***26****(8): 5146-5151.*

Requena-Perez, M. E., A. Albero-Ortiz, J. Monzo-Cabrera and A. Diaz-Morcillo (2006). "Combined use of genetic algorithms and gradient descent optmization methods for accurate inverse permittivity measurement." Microwave Theory and Techniques, IEEE Transactions on ***54****(2): 615-624.*

Salema, A. A. and F. N. Ani (2011). "Microwave induced pyrolysis of oil palm biomass." Bioresource Technology ***102****(3): 3388-3395.*

Salema, A. A. and F. N. Ani (2012). "Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer." Journal of Analytical and Applied Pyrolysis ***96****(0): 162-172.*

Serio, M., J. Cosgrove, M. Wójtowicz, K. Wignarajah and J. Fisher (2012). Pyrolysis Yields from Microwave-Assisted Heating of Solid Wastes. 42nd International Conference on Environmental Systems, American Institute of Aeronautics and Astronautics.

Xie, Q., F. C. Borges, Y. Cheng, Y. Wan, Y. Li, X. Lin, Y. Liu, F. Hussain, P. Chen and R. Ruan (2014). "Fast microwave-assisted catalytic gasification of biomass for syngas production and tar removal." Bioresource Technology ***156****: 291-296.*

Zhang, X., D. Hayward and D. M. Mingos (2003). "Effects of Microwave Dielectric Heating on Heterogeneous Catalysis." Catalysis Letters ***88****(1-2): 33-38.*

Zuo, W., Y. Tian and N. Ren (2011). "The important role of microwave receptors in bio-fuel production by microwave-induced pyrolysis of sewage sludge." <u>Waste Management</u> ***31****(6): 1321-1326.*

Publicación IV

INFLUENCE OF THE MICROWAVE ABSORBENT AND MOISTURE CONTENT ON THE MICROWAVE PYROLYSIS OF AN ORGANIC MUNICIPAL SOLID WASTE

Journal of Analytical and Applied Pyrolysis
105 (234-240)
Año 2014

Journal of Analytical and Applied Pyrolysis 105 (2014) 234–240

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

ARTICLE INFO

Article history:
Received 30 September 2013
Accepted 17 November 2013
Available online 23 November 2013

Keywords:
Microwave absorbent
Pyrolysis
Municipal solid waste
Syngas
Waste valorisation

ABSTRACT

Microwave pyrolysis is presented in this study as a recycling approach for municipal solid waste treatment. The process is based on the conversion of solid waste to syngas ($CO + H_2$) by means of a microwave absorbent. Experiments to characterise the syngas produced were performed using the char obtained from the pyrolysis of a municipal solid waste as microwave absorbent in the microwave power range of 150–450 W and in an absorbent-to-waste ratio range of 0.2:1 to 1:1 (wt.%:wt.%). A rich-syngas fraction with a high H_2 content (c.a. 50–55 vol.%) was obtained and analysed by means of response surface methodology through the interaction between the microwave power and absorbent-to-waste ratio. Moreover, a positive effect of the moisture content on gas production is attained since gasification of the char occurs. Thus, the simple use of a cheap waste-derived char leads to a reduction in the microwave power and economic cost of the process.

1. Introduction

Municipal solid waste (MSW) consists mainly of waste from households (60–90%), though similar wastes from other sources such as commerce or public institutions are also included. According to Eurostat, which is the statistical body of the EU, MSW generation in Europe has remained stable at about 260 Mt per year since 2002 [1]. Various management alternatives are available for the treatment of MSW such as landfilling, incineration, recycling or composting. In recent years, recycling has increased, although landfilling still remains the most widely used method of disposal, in spite of its several drawbacks, such as the leaching of dangerous chemicals into the soil and the release of methane to the air. However, this gap has narrowed in the last few years. In the EU the landfill/recycling MSW weight ratio was 56/17 in 2001 compared to 37/25 in 2011 [2].

Pyrolysis technology has emerged not only as a very effective way of MSW disposal but also as an attractive technology for valorising these residues by producing fuels or precursors of valuable chemicals, such as syngas ($CO + H_2$). As an example, the SYNPOL project [3] aims to produce new biopolymers via the fermentation of syngas from waste materials.

Several studies have been carried out on MSW pyrolysis [4–7]. In general, the syngas content of the gas fraction produced in pyrolysis processes is not very high, since it is mixed with large amounts of CO_2, CH_4 and light hydrocarbons. As a way to improve the syngas concentration and, especially, the H_2 content, several researchers have proposed catalytic pyrolysis. In such cases, the role of the catalyst, such as dolomite [4], is to crack the heavy compounds in order to obtain lighter gases. However, the same effect can be achieved by means of microwave irradiation, without the need to add a catalyst to the system, as demonstrated in previous studies [8–10]. Microwaves are able to generate microplasmas, which promote heterogeneous catalytic reactions, but not all materials can be heated by means of microwave irradiation, since some materials are transparent to microwaves. To solve this problem, the addition of carbon-rich materials has been proposed to absorb microwaves [11–14]. The material to be pyrolysed is then heated by conduction. Use of the char obtained from MSW pyrolysis process, as microwave absorbent is an attractive solution since it avoids the addition of materials that might increase the cost of the process.

The microwave pyrolysis of MSW has been performed previously by Gedam and Regupathi [15], but it is still at an early stage of development. In the study of Gedam and Regupathi, both the microwave power and irradiation time were varied. Although a minimum value of power was required to carry out the pyrolysis of MSW, the addition of different carbon materials that served as microwave absorbents allowed the pyrolysis to proceed at a lower microwave power. Surprisingly, no hydrogen was produced other than trace concentrations, providing a gas rich in CO, CO_2 and CH_4. So far the effect of the amount of microwave absorbent on MSW pyrolysis has not received much attention. However, this parameter has been studied in relation to other materials. The microwave

---

* Corresponding author. Tel.: +34 985 118972; fax: +34 985 297672.
E-mail addresses: angelmd@incar.csic.es, jmbermen@gmail.com (J.A. Menéndez).

0165-2370/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jaap.2013.11.009

induced pyrolysis (MIP) of microalgae with various microwave absorbents, such as activated carbon, CaO, SiC or microalgae char has been carried out by Hu et al. [16]. These authors found that there was a specific proportion of absorbent-to-microalga at which the liquid fraction was maximised, depending on the absorbent used. Oil palm shell biomass was recently subjected to MIP in a study by Salema and Ani [17], which showed the importance of the quantity of microwave absorbent added to the oil palm shell as a method of controlling the pyrolysis temperature in an overhead stirrer reactor. The authors reported that an increase in microwave absorbent led to a decrease in the pyrolysis temperature and in turn in to higher solid fraction yields. All of these studies were focused on maximising the liquid fraction yield. However, to the best of our knowledge, no studies have been aimed at maximising the gas fraction yield.

Herein, we report for the first time on a statistical model based on response surface methodology (RSM) designed to assess the combined effect of microwave power and ratio of microwave absorbent-to-waste upon the amount and characteristics of the syngas generated from MIP. In addition, the effect of moisture content of the MSW is evaluated.

2. Materials and methods

2.1. Materials

The sample selected for this study was an organic fraction from a municipal solid waste, supplied by BEFESA *Gestión de Residuos Industriales* S.L. (Seville, Spain) in two forms: wet (with a moisture content of c.a. 45 wt.%) and dry (with a moisture content of c.a. 1.5 wt.%). The dry and wet fractions will be labelled as *D* and *W*, respectively. Proximate and ultimate analyses were performed to characterise the composition of the feedstock samples. The moisture, ash content and volatile matter data (from a LECO TGA-601) are summarised in Table 1 together with the ultimate analysis results (a LECO-CHNS-932 micro-analyser and LECO-TF-900 furnace were used). Metallic content of the ashes from the organic MSW was determined by means of atomic absorption spectroscopy.

The gases were analysed in a Varian-CP3800 gas-chromatograph equipped with a TCD detector and two columns connected in series. The first column was 80/100 Hayesep Q (2 m × 1/8 in. × 2 mm) and the second column was 80/100 Molesieve 13× (1.5 m × 1/8 in. × 2 mm). The second column was bypassed by a six-port valve for the analysis of CO_2 and hydrocarbons. The TCD was calibrated with a standard gas mixture.

2.2. Microwave induced pyrolysis

The pyrolysis of *D* and *W* was carried out in a microwave oven which consisted basically of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample was irradiated using powers ranging from 150 to 450 W. The single mode cavity allows a well-defined electric field in a relatively small volume due to the superposition of incident and reflected waves, and causes the microwave field to focus on a given location [18]. The reflected power is regulated until it is reduced to zero by means of stub tuners. About 3 g of sample (on a dry basis) was placed on an inert bed inside a quartz reactor. The reactor was purged with N_2 for 30 min at a flow rate of 50 mL_{STP} min^{-1}. The N_2 flow rate was then set to 10 mL_{STP} min^{-1} for the pyrolysis experiments in order to ensure an oxygen-free atmosphere.

As mentioned in previous studies on microwave induced pyrolysis of biomass, it is also necessary to mix the MSW fraction with an appropriate microwave absorbent to achieve the high temperatures required for pyrolysis [11–14]. The char obtained from the prior pyrolysis of *D* and *W* at 800 °C in an electrical furnace was used as microwave absorbent in different absorbent-to-waste ratios (0.2:1, 0.4:1 and 1:1), in order to evaluate the influence of this parameter on the characteristics of the syngas. Preliminary experiments showed that lower values of absorbent-to-waste ratio prevented the pyrolysis of the MSW fraction.

The experiments lasted 1 h, but the time chosen for the calculation of the parameters was 40 min, since by this time all the MIP experiments would have reached 90% of total syngas production.

The volatiles released from the pyrolysis of both organic fractions were passed through a condensing system cooled by a cryogenic solution of water and NaCl. The liquid fraction was recovered from the condensing system by dissolving it in CH_2Cl_2. It was then subjected to further evaporation to remove the solvent at 40 °C. The non-condensable gases were collected at intervals of 10 min in Tedlar sample bags and then analysed by gas chromatography. The composition of the gaseous fraction was determined from the composition of each bag and the N_2 flow rate.

2.3. Statistical model

RSM is a widely used technique for the optimisation of a set of parameters. This methodology assesses the combined effect of a set of independent variables on response variables by means of three-dimensional surface plots. The experimental response variables are fitted to a mathematical model by multiple regression analysis, which is then subjected to statistical evaluation by means of the analysis of variance (ANOVA) in order to determine whether the model and model parameters are significant on the basis of the *p*-value to within a certain level of confidence, e.g. at 95%. In the field of MIP, only a few studies employ RSM [19,20], but none of them are focused on the influence of the microwave power or on the effect of the microwave absorbent on the syngas produced.

As mentioned at the end of Section 1, three factors were selected as the independent variables used to model the characteristics of the gas obtained from the MIP of the organic fraction of municipal solid waste: the microwave power (*P*, expressed in Watts), the absorbent-to-waste ratio (*A*, wt.%:wt.%) and the moisture content (*M*, wt.%). The values of *P* ranged from 150 W to 450 W and those of *A* from 0.2:1 to 1:1. Additional experiments were performed on the *W* fraction (45 wt.% of moisture) to evaluate the influence of the water content on the pyrolysis process.

In order to model the gas fraction evolved during the MIP, the following response variables were characterised: the syngas concentration, i.e. $CO + H_2$ concentration in the pyrolysis gases (S, vol.%); the syngas production (SP, $L_{STP}\,g_{MSW}{}^{-1}$) and the H_2, CO, CO_2 and CH_4 concentrations in the gas fraction (vol.%). The experimental design is shown in Table 2.

The experimental results for *D* and *W* were fitted using a polynomial quadratic equation (Eq. (2.1)) by means of Design Expert® software to correlate the response variables $R(P, A)$ to the independent variables *P* and *A* within the model parameters: the offset term (α), the linear effects (β, γ) the squared effects (δ, ε) and the interaction term (ζ):

$$R(P,\ A) = \alpha + \beta P + \gamma A + \delta P^2 + \varepsilon A^2 + \zeta PA \qquad (2.1)$$

3. Results and discussion

3.1. Syngas production models

The main objective of this study is to characterise the syngas generated by the microwave induced pyrolysis of municipal solid waste and determine its composition and production. The

Table 1
Proximate and ultimate analyses of the organic fraction from MSW and metal content of the ashes.

Proximate analysis (wt.%)			Ultimate analysis (wt.%)[a]					
Moisture	Ash[a]	Volatile matter[a]	C	H	N	S	Cl	O[c]
1.5[b]	30.3	61.1	39.4	5.2	1.5	0.4	0.9	22.3

Metal content of ashes (mg_{metal}/kg_{MSW})						
Fe	Zn	Mn	Cr	Cu	Pb	Ni
8896	183	83	59	45	31	18

[a] Dry basis.
[b] Moisture content of *D*. In the case of *W*, moisture content is 45 wt.%.
[c] Calculated by difference.

relationships between the factors *P* and *A* and the responses S and SP are illustrated in Fig. 1(a)–(b). Qualitatively, an increase in the microwave power directed at the sample leads to a higher syngas concentration and production. Factor *A* seems to have only a slight effect on the responses studied. The regression models calculated to predict S (vol.%) and SP ($L_{STP}\,g_{MSW}{}^{-1}$) are expressed as follows:

$$S = 75.247 + 0.087P - 0.787A + 0.024PA - 1.171 \times 10^{-4}P^2 - 7.885A^2 \quad (3.1)$$

$$SP = 0.039 + 1.765P - 0.393A + 3.395 \times 10^{-5}PA - 1.870 \times 10^{-6}P^2 + 0.253A^2 \quad (3.2)$$

To statistically quantify the influences of the *P* and *A* factors, ANOVA tests were performed. In Table 3, the model *p*-values $\ll$0.05 suggest that both models are significant to within a 95% confidence level. In the case of the syngas concentration model (Eq. (3.1)), the linear term for microwave power (*P*) has the greatest effect on the H_2 + CO content due to the extremely low *p*-value (<0.0001). In contrast, the influence of the microwave absorbent quantity, although significant, is not as great. The term for the absorbent-to-waste ratio (*A*) has a significant effect on S with a *p*-value of 0.0012. In the case of the syngas production model, the terms *P* and *A* were found to be significant factors too.

From the surface plots of the regression models (Fig. 1(a)–(b)), it is possible to determine the effect exerted by *P* and *A* on the response variables in the experimental space studied. At a low microwave power (150, 250 and 350 W), a high *A* leads to a decrease in both the syngas concentration and production, although at 450 W the trend of S seems to change, since a maximum appears at *A* = 0.4:1. Anyway, the concentration of syngas in the gas fraction obtained over the entire range of experimental conditions studied is considerable (>80 vol.% in all the cases). In short, the MIP of MSW is very selective towards syngas.

Table 2
Experimental design for the MIP of organic MSW.

Experiment	*P* (W)	*A* (wt.% absorbent:wt.% residue)	*M* (wt.%)
1	150	0.2:1	1.5
2	150	0.4:1	1.5
3	150	1:1	1.5
4	250	0.2:1	1.5
5	250	0.4:1	1.5
6	250	1:1	1.5
7	350	0.2:1	1.5
8	350	0.4:1	1.5
9	350	1:1	1.5
10	450	0.2:1	1.5
11	450	0.4:1	1.5
12	450	1:1	1.5
13	150	0.2:1	45
14	150	1:1	45
15	450	0.2:1	45
16	450	1:1	45

To investigate the fit of the model, the *R*-squared and Adjusted *R*-squared values were evaluated. As can be observed in Table 3, the S model has an R^2 value of 0.989, indicating that the model variation of 98.9% for the syngas concentration is attributable to the independent variables and only 1.1% of the total variation could not be explained by the model. The value of Adj-R^2 is also very high, lending further support to the high significance of the model proposed. In the case of the SP model, similar conclusions can be drawn.

Of the two factors (i.e. microwave power and the absorbent-to-waste ratio), microwave power plays the more important role

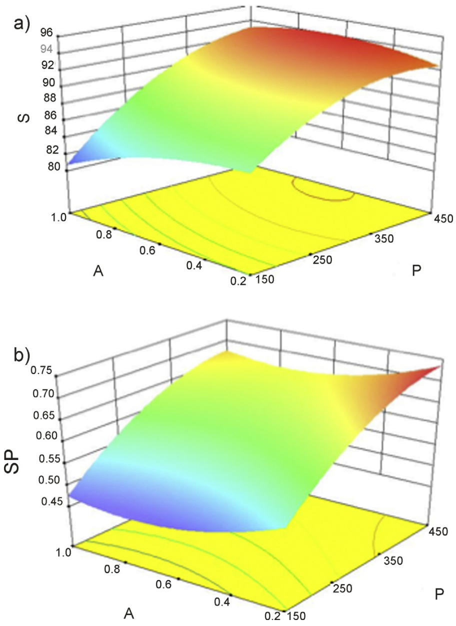


Fig. 1. Response surface plots based on syngas concentration (S, vol.%) (a), and syngas production (SP, $L_{STP}\,g_{MSW}{}^{-1}$) (b), as a function of microwave power (*P*) and absorbent-to-waste ratio (A).

Table 3
ANOVA for the syngas models (S and SP).

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value	Significance (to within a 95% confidence level)	R^2 Adj-R^2
Response: syngas composition (S, vol.%)							
Model	179.697	5	35.939	109.125	<0.0001	Significant	0.989
P	145.264	1	145.264	441.072	<0.0001	Significant	0.980
A	10.904	1	10.904	33.109	0.0012	Significant	
PA	10.359	1	10.349	31.423	0.0014	Significant	
P^2	16.450	1	16.450	49.948	0.0004	Significant	
A^2	2.204	1	2.204	6.692	0.0414	Significant	
Response: syngas production (SP, $L_{STP}\,g_{MSW}{}^{-1}$)							
Model	0.068	5	0.014	52.400	0.0010	Significant	0.985
P	0.062	1	0.062	235.94	<0.0001	Significant	0.966
A	0.005	1	0.005	17.78	0.014	Significant	
PA	1.932×10^{-5}	1	1.932×10^{-5}	0.074	0.799	Not significant	
P^2	0.003	1	0.003	10.770	0.031	Significant	
A^2	0.001	1	0.001	5.700	0.075	Not significant	

in MIP. Nevertheless, it is important to emphasise that without the presence of a microwave absorbent, it would be impossible to carry out the MIP experiments and that its presence allows the microwave power to be reduced, as mentioned by Gedam and Regupathi [15]. These authors found that with a single mode cavity, the MIP of MSW was not possible without the addition of a microwave absorbent, unless the microwave power was higher than 450 W. However, the addition of carbonaceous absorbents such as charcoal with an A value of 0.5:1 allowed MSW to be pyrolysed even at 100 W. In a more recent study by Hu et al. [16], the authors performed the MIP of microalgae without any absorbents but at powers higher than 750 W. They also found that the addition of small amounts of solid residue obtained from the microalgae promoted gas production.

3.2. Gas component models

The response surface models corresponding to the major components of the gas fraction (i.e. H_2, CO, CO_2 and CH_4) are shown in Fig. 2(a)–(d). From the trends of these models, it can be seen that the concentrations of the most valuable components (H_2 and CO) were favoured by the power irradiated at the sample. As observed by Hu et al. [16], the higher the microwave power is, the higher the temperature reached inside the bulk, since both the microwave density and the microwave energy absorbed by the bulk increase. As a consequence, the endothermic reactions leading to the formation of syngas are favoured [9]. On the other hand, the addition of absorbent to MSW seems to have little effect on the gas concentrations. To assess the effects of both factors more effectively, the following regression models for H_2, CO, CO_2 and CH_4 (vol.%) were obtained:

$$H_2 = 42.367 + 0.048P + 8.242A + 6.475 \times 10^{-3}PA - 6.183 \times 10^{-5}P^2 - 8.162A^2 \tag{3.3}$$

$$CO = 32.870 + 0.039P - 9.013A + 0.018PA - 5.533 \times 10^{-5}P^2 + 0.271A^2 \tag{3.4}$$

$$CO_2 = 9.114 - 0.019P + 2.693A \tag{3.5}$$

$$CH_4 = 9.768 - 0.039P + 1.524A - 0.015A + 6.508 \times 10^{-5}P^2 + 2.667A^2 \tag{3.6}$$

ANOVA tests were carried out as in Section 3.2. The model p-values $\ll$0.05 (Table 4) imply that all the models are significant to within a confidence level of 95%. In the case of the hydrogen concentration model (Eq. (3.3)), the only significant term is the microwave power linear term (P) since its p-value is 0.0029. No significance was found for the other terms. In the case of the CO model (Eq. (3.4)), both the P and the A terms have significance, their p-values 0.0028 and 0.0310 being respectively. For CO_2, a linear model was found to be the most accurate (Eq. (3.5)). Both linear terms were found to be significant for the CO_2 model. However, the trend of the CO_2 model was the opposite to that of the CO model. This is because CO and CO_2 are related by Boudouard's equilibrium (Eq. (3.7)):

$$C + CO_2 \leftrightarrow 2CO, \quad \Delta H^0 = 173\ \mathrm{kJ\,mol^{-1}}. \tag{3.7}$$

From Fig. 2(b) and (c) it can be observed that the maximum CO_2 concentration corresponds to the conditions at which the CO concentration is minimised (low power and a high quantity of microwave absorbent) and vice versa. This behaviour could be due to the fact that, as A increases, the bulk temperature decreases as stated in another study by Salema and Ani [17] and that the lower power leads to lower temperatures, shifting Eq. (3.7) to the side of reactants since it has an endothermic enthalpy (173 kJ mol^{-1}).

Finally, in the CH_4 model (Eq. (3.6)), P is the only significant factor since it has p-value of 0.0044, and its trend is similar to that of the CO_2 model. Endothermic reforming reaction of methane (Eq. (3.8)) is favoured at high power and so CO and H_2 production from these reactions is greater.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO, \quad \Delta H^0 = 247\ \mathrm{kJ\,mol^{-1}}. \tag{3.8}$$

From the mathematical models presented above (Eqs. (3.3)–(3.6)), it can be seen that the microwave power has a positive effect on H_2 and CO production, but a negative effect on the production of CO_2 and CH_4. Moreover, the addition of larger quantities of absorbent to MSW inhibits the production of CO but favours the production of CO_2. Table 4 shows that factor A has no significance for the H_2 and CH_4 response variables in the experimental set-up employed in this study. Anyway, it would seem that the hydrogen model would not represent the physical process very well since the absorbent would modify the pyrolysis temperature and, hence, affect the production of hydrogen. As scale-effects may be masking this point, larger scale experiments are being carried out by our research group.

An interesting point in relation to the quality of the syngas produced is the H_2/CO ratio, especially in regard to its future use. For example, in the case of methanol synthesis from syngas, a H_2/CO ratio of around 2 would be the ideal [21]. In this work, it was found that from the microwave pyrolysis of MSW, this parameter does not vary appreciably. H_2/CO ratios between 1.3 and 1.5 were obtained over the entire experimental space analysed.

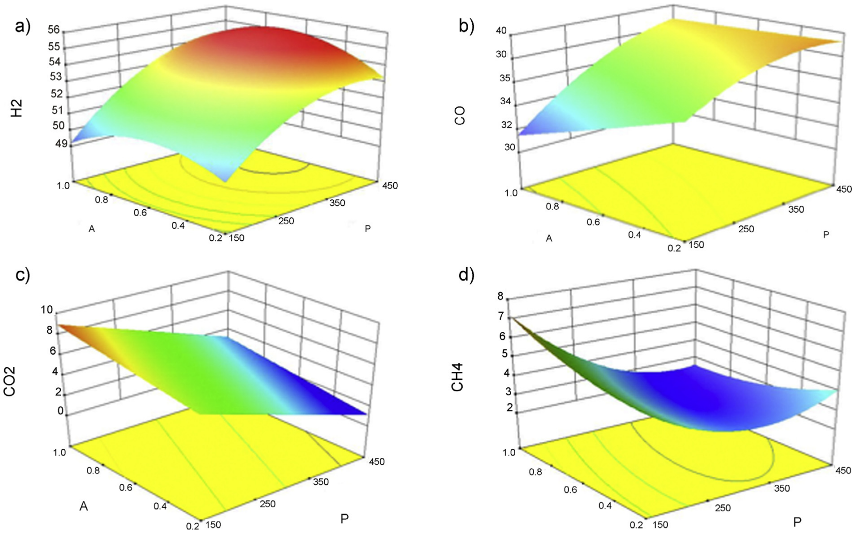


Fig. 2. Response surface plots based on H_2 (a), CO (b), CO_2 (c) and CH_4 (d) concentrations (vol.%) in the gas fraction as a function of microwave power (*P*) and absorbent-to-waste ratio (*A*).

3.3. Effect of the moisture content of the MSW

Since the wet fraction has a large moisture content (*M*), H_2O might be expected to play an important role in the pyrolysis process via the gasification reactions of the char (Eqs. (3.9) and (3.10)) and the reforming reactions (Eqs. (3.11) and (3.12)), leading to an enrichment in H_2, CO or CO_2 depending on the experimental conditions.

$$C + H_2O \leftrightarrow H_2 + CO, \quad \Delta H^0 = 131\,\text{kJ}\,\text{mol}^{-1} \tag{3.9}$$

$$C + 2H_2O \leftrightarrow 2H_2 + CO_2, \quad \Delta H^0 = 90\,\text{kJ}\,\text{mol}^{-1} \tag{3.10}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO, \quad \Delta H^0 = 205\,\text{kJ}\,\text{mol}^{-1} \tag{3.11}$$

Table 4
ANOVA for the gas fraction component models.

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*p*-Value	Significance (to within a 95% confidence level)	R^2 Adj-R^2
Response: hydrogen concentration (H_2, vol.%)							
Model	37.809	5	7.562	5.726	0.0277	Significant	0.827
P	30.811	1	30.811	23.330	0.0029	Significant	0.682
A	0.195	1	0.195	0.148	0.7138	Not significant	
PA	0.727	1	0.727	0.550	0.4862	Not significant	
P^2	4.588	1	4.588	3.474	0.1116	Not significant	
A^2	2.361	1	2.361	1.788	0.2297	Not significant	
Response: carbon monoxide concentration (CO, vol.%)							
Model	62.265	5	12.453	6.967	0.0175	Significant	0.853
P	42.210	1	42.210	23.615	0.0028	Significant	0.731
A	14.045	1	14.045	7.857	0.0310	Significant	
PA	5.566	1	5.566	3.114	0.1281	Not significant	
P^2	3.674	1	3.674	2.055	0.2016	Not significant	
A^2	0.003	1	0.003	0.002	0.9708	Not significant	
Response: carbon dioxide concentration (CO_2, vol.%)							
Model	63.830	2	31.910	50.230	<0.0001	Significant	0.918
P	53.770	1	53.770	84.640	<0.0001	Significant	0.899
A	10.050	1	10.050	15.830	0.0032	Significant	
Response: methane concentration (CH_4, vol.%)							
Model	20.628	5	4.126	6.032	0.0246	Significant	0.834
P	13.455	1	13.455	19.672	0.0044	Significant	0.695
A	0.146	1	0.146	0.213	0.6606	Not significant	
PA	3.706	1	3.706	5.419	0.0588	Not significant	
P^2	5.083	1	5.083	7.431	0.0344	Significant	
A^2	0.252	1	0.252	0.369	0.5661	Not significant	

Table 5
Comparison of the gas fraction from the MIP of the dry fraction (*D*) and the wet fraction (*W*) with different *A* ratios (0.2:1 and 1:1) at 150 W and 450 W.

	A = 0.2:1		*A* = 1:1	
	D	*W*	*D*	*W*
P = 150 W				
H_2 (vol.%)	49.37	53.40	48.94	57.03
CO (vol.%)	36.89	33.72	31.46	23.45
CO_2 (vol.%)	6.52	7.62	9.59	15.33
CH_4 (vol.%)	5.43	3.99	7.70	3.05
S (vol.%)	86.26	87.12	80.40	80.48
Gas production (L_{STP} g_{MSW})[a]	**0.64**	**0.92**	**0.58**	**1.06**
SP (L_{STP}/g_{MSW})[a]	0.55	0.73	0.47	0.85
P = 450 W				
H_2 (vol.%)	53.54	53.10	54.30	53.61
CO (vol.%)	38.60	37.42	38.66	41.13
CO_2 (vol.%)	2.17	5.17	3.50	3.77
CH_4 (vol.%)	4.22	2.50	2.50	1.01
S (vol.%)	92.14	90.52	92.96	94.74
Gas production (L_{STP} g_{MSW})[a]	**0.79**	**0.94**	**0.73**	**1.10**
SP (L_{STP}/g_{MSW})[a]	0.73	0.85	0.68	1.05

[a] Calculated on a dry basis.

$$C_nH_m + nH_2O \leftrightarrow (n + m/2)H_2 + nCO \tag{3.12}$$

The MIP experiments on *W* were conducted at both low and high power (150 W and 450 W). In addition, the quantity of microwave absorbent was evaluated along with *M*, using *A* ratios of 0.2:1 and 1:1, as shown in Table 2. The results of the analysis of the gas fraction for these cases are reported in Table 5. As might be expected from Eq. (3.10), the H_2 and CO_2 concentrations obtained from the wet fraction at 150 W are greater than those obtained from the dry fraction. In fact, water condenses at the top of the reactor, which is at a much lower temperature than the sample. In other words, there is a water reflux effect which favours a vapour-rich atmosphere and the gasification of the char. However, when the power is increased to 450 W, there are no appreciable differences in the gas composition of W and *D*. Therefore, Eq. (3.9) might be taking place to a much greater extent than Eq. (3.10), since the endothermic character of Eq. (3.9) is favoured by the higher temperatures. Moreover, *M* also affects the CH_4 concentration in the gas fraction by reducing its content. This may be due to the steam reforming reaction of methane (Eq. (3.11)). At 450 W the higher temperature would favour the thermal cracking and the steam reforming reaction of CH_4 much more than at 150 W. Finally, it could be remarkable that the percentage of syngas within the gas fractions seems to be similar regardless the moisture content. However, this behaviour might not be generalised yet.

Also important is the effect of moisture on syngas production. At 450 W, the *W* fraction produces 35% more syngas than the *D* fraction when a ratio 1:1 is employed, but their values converge at a ratio of 0.2:1, there being a difference in this case of around 15%. There is also a marked difference between these values at 150 W, since the *W* fraction produces much more syngas than fraction *D* (45% higher) when a 1:1 ratio is employed. Once more, these values converge at a ratio of 0.2:1, the wet fraction producing 25% more syngas than the dry fraction. This suggests that moisture content favours the production of a greater amount of gas, an impression that is confirmed by the results in Table 5. This is an interesting point since it implies that the drying and pyrolysis processes of MSW could be integrated in the MIP process to increase the production of gas.

Both the quantity of absorbent and the moisture content influence the gas composition. However, in the case of the wet fraction the amount of absorbent added has a much greater influence. Hence gasification of the char from the wet fraction is bound to occur. At 150 W, a greater increase in H_2 and CO_2 is observed at a ratio of 1:1 than at 0.2:1. However, at 450 W the CO_2 concentration decreases as CO is produced due to the increase in the quantity of absorbent. Thus, it may be assumed that the Boudouard equilibrium (Eq. (3.7)) is controlling the process in these conditions. In contrast, the syngas production results reported in the above paragraph suggest that the addition of more microwave absorbent to the wet fraction improves the production of syngas, which is not the case with the dry fraction. Once more, this evidences the importance of the char gasification reactions.

4. Conclusions

This study has demonstrated the possibility of recycling the char obtained from municipal solid wastes for use as microwave absorbent in the microwave pyrolysis process. Although microwave power is the most important factor for controlling the pyrolysis, since higher power allows better conversion to syngas and syngas production, the presence of the char in the material subjected to microwave pyrolysis is of overwhelming importance. This allows a rich syngas (CO + H_2) fraction (c.a. 80–94 vol.% of the gas fraction) to be obtained with a low microwave power. A minimum *A* ratio of 0.2:1 was found to be necessary to induce the microwave pyrolysis process. In addition, low ratios seem to be more suitable for obtaining a higher concentration and production of syngas. Moisture also plays an important role, as it favours H_2 and CO_2 production, especially at low power, in addition to improving the syngas production process.

List of abbreviations

A	absorbent-to-waste ratio (kg:kg)
ANOVA	analysis of variance
D	dry fraction from organic municipal solid waste
MIP	microwave induced pyrolysis
MSW	municipal solid waste
P	microwave power (watts)
RSM	response surface methodology
S	syngas concentration (vol.%)
SP	syngas production (L_{STP} $g_{MSW}{}^{-1}$)
W	wet fraction from organic municipal solid waste

Acknowledgment

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 311815 (SYNPOL project).

References

[1] http://epp.eurostat.ec.europa.eu/cache/ITY_OFFPUB/KS-SF-11-031/EN/KS-SF-11-031-EN.PDF (accessed 28.10.13).

[2] http://epp.eurostat.ec.europa.eu/cache/ITY_PUBLIC/8-04032013-BP/EN/8-04032013-BP-EN.PDF (accessed 28.10.13).

[3] http://www.synpol.org/ (accessed 28.10.13).

[4] M. He, B. Xiao, S. Liu, Z. Hu, X. Guo, S. Luo, F. Yang, Syngas production from pyrolysis of municipal solid waste (MSW) with dolomite as downstream catalysts, J. Anal. Appl. Pyrol. 87 (2010) 181–187.

[5] F. Ateş, N. Miskolczi, N. Borsodi, Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I. Product yields, gas and pyrolysis oil properties, Bioresour. Technol. 133 (2013) 443–454.

[6] I. Velghe, R. Carleer, J. Yperman, S. Schreurs, Study of the pyrolysis of municipal solid waste for the production of valuable products, J. Anal. Appl. Pyrol. 92 (2011) 366–375.

[7] W.K. Buah, A.M. Cunliffe, P.T. Williams, Characterization of products from the pyrolysis of municipal solid waste, Process Saf. Environ. 85 (2007) 450–457.

[8] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, Bioresour. Technol. 144 (2013) 240–246.

[9] A. Domínguez, J.A. Menéndez, Y. Fernández, J.J. Pis, J.M.V. Nabais, P.J.M. Carrott, M.M.L.R. Carrott, Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas, J. Anal. Appl. Pyrol. 79 (2007) 128–135.

[10] Y.F. Huang, W.H. Kuan, S.L. Lo, C.F. Lin, Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis, Bioresour. Technol. 101 (2010) 1968–1973.
[11] J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, J.M. Bermúdez, A. Arenillas, Ball lightning plasma and plasma arc formation during the microwave heating of carbons, Carbon 49 (2011) 346–349.
[12] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Process. Technol. 91 (2010) 1–8.
[13] A. Domínguez, J.A. Menéndez, M. Inguanzo, J.J. Pis, Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge, Fuel Process. Technol. 86 (2005) 1007–1020.
[14] Y. Fernández, A. Arenillas, M.A. Díez, J.J. Pis, J.A. Menéndez, Pyrolysis of glycerol over activated carbons for syngas production, J. Anal. Appl. Pyrol. 84 (2009) 145–150.
[15] V. Gedam, I. Regupathi, Pyrolysis of municipal solid waste for syngas production by microwave irradiation, Nat. Resour. Res. 21 (2012) 75–82.
[16] Z. Hu, X. Ma, C. Chen, A study on experimental characteristic of microwave-assisted pyrolysis of microalgae, Bioresour. Technol. 107 (2012) 487–493.
[17] A.A. Salema, F.N. Ani, Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer, J. Anal. Appl. Pyrol. 96 (2012) 162–172.
[18] E.T. Thostenson, T.W. Chou, Microwave processing: fundamentals and applications, Compos. A: Appl. Sci. Manuf. 30 (1999) 1055–1071.
[19] M.A. Jamaluddin, K. Ismail, M.A. Mohd Ishak, Z. Ab Ghani, M.F. Abdullah, M.T.-u. Safian, S.S. Idris, S. Tahiruddin, M.F. Mohammed Yunus, N.I.N. Mohd Hakimi, Microwave-assisted pyrolysis of palm kernel shell: optimization using response surface methodology (RSM), Renew. Energy 55 (2013) 357–365.
[20] R. Zhou, H. Lei, J. Julson, The effects of pyrolytic conditions on microwave pyrolysis of prairie cordgrass and kinetics, J. Anal. Appl. Pyrol. 101 (2013) 172–176.
[21] X. Yin, D.Y.C. Leung, J. Chang, J. Wang, Y. Fu, C. Wu, Characteristics of the synthesis of methanol using biomass-derived syngas, Energy Fuels 19 (2004) 305–310.

Publicación V

INTEGRATED MICROWAVE DRYING, PYROLYSIS AND GASIFICATION FOR VALORISATION OF ORGANIC WASTES TO SYNGAS

Fuel

132 (20-26)

Año 2014

Fuel 132 (2014) 20–26

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Integrated microwave drying, pyrolysis and gasification for valorisation of organic wastes to syngas

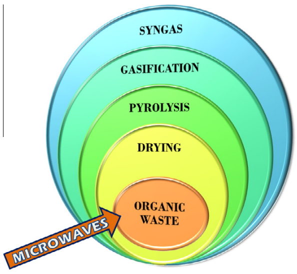
D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez [*]

Instituto Nacional del Carbón, CSIC, Apartado 73, Oviedo 33080, Spain

HIGHLIGHTS

- Drying of organic waste can be co-integrated with microwave pyrolysis (MIP).
- Moisture promotes the gasification of char and favours gas production.
- There exists an optimal moisture content which maximises the syngas concentration.
- The specific energy efficiency of MIP can be improved at higher scale.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 20 March 2014
Accepted 17 April 2014
Available online 2 May 2014

Keywords:
Microwave pyrolysis
Drying
Municipal solid waste
Syngas
Energy efficiency

ABSTRACT

The development of integrated platforms is desirable in order to improve the efficiency of biorefineries. This study deals with an innovative *all-in-one* thermochemical process (drying, pyrolysis and gasification) based on the use of microwave energy, which could eliminate the need to pre-dry municipal solid waste in order to produce a high quantity of synthesis gas. Depending on the initial moisture content and pyrolysis time, it is possible to obtain different syngas compositions but only during the first 20 min. Beyond this time the syngas composition remains almost constant. In addition, the moisture content was found to improve the volumetric gas production by almost 50%. The energy consumption of this *all-in-one* process is discussed by comparing it with the scarce information available in the literature concerning the scaling-up of microwave-assisted processes, which may be more cost-effective at a higher scale.

1. Introduction

The concept "biorefinery" refers to a processing plant where biomass feedstock is converted into valuable products by means of a combination of biological, thermal and chemical processes. The resulting high-value products, such as chemicals and new materials, derived-fuel and the additional power and heat production may well help to lower energy costs and reduce greenhouse gas emissions produced by traditional power facilities.

Nonetheless, there remain a number of barriers related to the implementation and commercialization of the biorefinery that need to be overcome. Apart from non-technical barriers, such as restrictions on use of land or the environmental effects of large areas of feedstock monoculture, reliable equipment designs for the thermochemical conversion of organic feedstock need to be extensively demonstrated on a larger scale [1]. To this end, integrated process platforms appear the most promising way forward.

---

[*] Corresponding author. Tel.: +34 985 118972; fax: +34 985 297662.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

http://dx.doi.org/10.1016/j.fuel.2014.04.064

In general, the drying of biomass materials before their introduction into the conversion units is desirable, since high moisture contents are known to produce fuel gas of lower effective heating value and lead to higher transportation costs, although a large amount of energy is consumed to remove the moisture. Dryers are designed taking into consideration that the wet material must be heated from the inlet temperature up to the wet bulb temperature in order to produce a driving force for surface water to be removed from the material. Afterwards, the material must be heated to drive water from the inside of the biomass to the surface so that it can evaporate. Nevertheless, the benefits provided by the drying of organic feedstock must be balanced against the increased operating and capital cost [2].

Pyrolysis and gasification are the main thermochemical conversion processes that have been developed within the biorefinery concept to produce synthesis gas (or syngas). Both technologies need an external source of heating to yield gaseous and oily products, whose characteristics depend on feedstock composition, temperature, reactor configuration, gasifying agent, etc. Pyrolysis may be defined as the regime in which the organic matter is degraded by thermal reactions in the absence of oxidizing agents. A gasification process, however, begins with a pyrolysis step followed by the gasification of char and reforming reactions of tar and light hydrocarbons through the addition of a gasifying component such as steam. As a result, gasification usually yields higher amounts of gas fraction than pyrolysis [3]. In order to develop an integrated platform of these processes in a biorefinery, microwave heating should also be considered as an attractive alternative. This method is very tolerant of water compared to conventional pyrolysis and is suitable for most biomass types without pre-drying [4]. Owing to its volumetric nature and high heating rates, a large quantity of steam is generated from the moisture content at the temperatures at which gasification and reforming reactions take place. As a consequence, drying, pyrolysis and gasification processes of wet organic feedstock could all be integrated together in a single microwave induced process (MIP). This method has already been demonstrated by our research group to be a feasible option [5]. In that particular case, it was used to demonstrate a new alternative for wet sewage sludge management which resulted in a gas fraction rich in CO and H_2, making this approach interesting for further production of valuable chemicals [6]. In the previous study, conventional and microwave heating techniques were compared, it being concluded that higher gas yields could be obtained with conventional heating, though the gas from microwave heating was richer in syngas. It should be pointed out however, that the gas yields were expressed in terms of weight percentage of the initial sewage sludge mass, which could be misleading for the evaluation of gas production. For instance, a gas fraction richer in hydrogen would result in a lower mass of gas due to the low molecular weight of hydrogen, which does not mean a lower volumetric gas production. An alternative more accurate way to calculate gas production might be based on the volume of gas produced per unit of feedstock mass. Results from the literature show that the production of syngas from biowaste microwave pyrolysis by means of this alternative approach is far higher than that from conventional heating [7].

The influence of the moisture content, and the need for feedstock pre-drying, on the gas characteristics from pyrolysis and gasification has been evaluated in several studies, even though further research is still needed. Xiong et al. performed the pyrolysis of different sewage sludges by conventional heating [8]. The steam-rich atmosphere generated by the moisture content of the sludge was found to favour the steam reforming reactions of volatile compounds as well as the gasification of solid char, which in turn improved the gas weight yields and the H_2 content. Xie et al. reported that an increase in the moisture content in sewage sludge improved the contents of CO_2, CH_4 and H_2 and reduced the tar yield under air gasification, but they provided no results on gas production [9]. Niu et al. simulated the gasification of municipal solid waste with different moisture contents. A higher heat input to the gasifier for turning liquid water into superheated steam and a lower gasification efficiency were the effects of the high moisture contents, suggesting that the input feedstock stream should be predried to ensure an optimal gasification performance [10]. Moreover, the H_2 concentration increased slightly in spite of a noticeable drop in CO content. Domínguez et al. observed that the influence of sewage sludge moisture on the gas products from microwave pyrolysis was negligible, but only a wet and a dried samples were used [11]. However, they attributed this to the fact that water was eliminated very quickly from the reactor and did not have to time to participate in gasification reactions. This problem could have been resolved by using a better reactor design, to enhance the extent of these reactions. Since microwave heating is driven volumetrically, heterogeneous reactions between the water released and the organic waste are much more favored than under conventional heating, which may lead to an increase in the yield of valuable products. Wang et al. recently conducted sewage sludge microwave pyrolysis at 850 °C in a single mode reactor and observed an increase in the H_2 and CO concentrations at higher moisture contents while the CO_2 and CH_4 concentrations decreased [12]. Interestingly, CO production seemed to increase with moisture if microwave heating was applied instead of conventional heating. The results obtained were substantially higher than under conventional pyrolysis.

Syngas production by means of microwave heating in the presence moisture has been widely discussed. The question that still remains to be answered is whether the presence of moisture improves gas production from the microwave pyrolysis of organic residues. If so, this introduces the possibility of creating a new efficient integrated platform for the green disposal of municipal solid wastes through the integration of the drying step into the pyrolysis reactor. The aim of this work is to demonstrate the feasibility of this alternative.

2. Methods

2.1. Materials

The sample selected for this study was a wet organic fraction from a municipal solid waste, supplied by BEFESA *Gestión de Residuos Industriales* S. L. (Seville, Spain) with a moisture content of 45 wt.%. This fraction was deposited in three vessels and subjected to partial drying in a stove at 60 °C over different drying times (10 min, 20 min and overnight), resulting in three fractions with moisture contents of 34, 12 and 0 wt.%. The samples were immediately stored in a freezer to preserve their moisture content. The samples will be labelled as MSW-*X*, where *X* is the moisture. To corroborate the effect of moisture on the pyrolysis gas from other residues, two fractions (dry and 60 wt.% of moisture) from a sewage sludge, SS-0 and SS-60, and two other fractions from straw residues (dry and 11 wt.% of moisture), ST-0 and ST-11, were also subjected to MIP. The moisture, ash content and volatile matter data (from a LECO TGA-601) are summarised in Table 1 together with the ultimate analysis results (a LECO-CHNS-932 micro-analyser and LECO-TF-900 furnace were used). The metallic content of the ashes was determined by means of atomic absorption spectroscopy.

2.2. Methods

The pyrolysis was carried out in a microwave oven which consisted of a microwave magnetron with a maximum output power

Table 1
Proximate and ultimate analyses of the organic wastes and metal content of the ashes.

Feedstock	Proximate analysis (wt.%)			Ultimate analysis (wt.%)[a]				
	Moisture	Ash[a]	Volatile matter[a]	C	H	N	S	O
MSW	46.3	22.6	68.0	36.0	5.8	1.6	0.2	33.8
SS	60.0	15.4	74.5	43.8	6.1	9.7	0.1	24.9
ST	11.5	6.4	76.2	45.0	5.0	1.6	0.1	41.9
	Fe	Zn	Mn	Cr	Cu	Pb	Ni	Cd
Metal content of ashes (mg_{metal}/kg)								
MSW	8896.3	182.9	82.9	58.7	44.8	30.8	17.6	<0.1
SS	2984.6	459.8	40.4	11.7	153.4	1.6	2.8	1.9
ST	286.9	6.6	18.3	0.0	0.0	<0.1	<0.1	0.4

[a] Dry basis.

of 2 kW operating at 2450 MHz and a single mode cavity where the sample was irradiated using 150 W of emitted microwave power (representing approximately 225 W of consumed power). The reflected power was regulated until reduced to zero by means of stub tuners. About 3 g of sample (on a dry basis) was placed on an inert bed inside a quartz reactor. The reactor was purged with N_2 for 30 min at a flow rate of 50 mL_{STP} min^{-1}. The N_2 flow rate was then set to 10 mL_{STP} min^{-1} for the pyrolysis experiments in order to ensure an oxygen-free atmosphere. The sample was mixed with an appropriate microwave absorbent to induce the thermochemical process, as organic residues are transparent to microwaves. The char obtained from the pyrolysis of previous performed in the same microwave reactor was used as the microwave absorbent in an absorbent-to-sample ratio of 1:1, since a previous study had shown that in the case of the wet fraction from the same organic residue, a higher amount of microwave absorbent would enhance the gasification of the char and, in turn the production of gas [13]. Each experiment lasted 1 h and was repeated twice. The results from the experiments were calculated as the average of the repetitions. Details of the experimental set-up used to collect the oils and gas can be found elsewhere [13].

The gases were analysed in a Varian-CP3800 gas-chromatograph equipped with a TCD detector and two columns connected in series. The first column was 80/100 Hayesep Q (2 m × 1/8 in. × 2 mm) and the second column was a 80/100 Molesieve 13X (1.5 m × 1/8 in. × 2 mm). The second column was bypassed by a six-port valve for the analysis of the CO_2 and hydrocarbons. The carrier gas flow (He) was 30 mL/min. The initial oven temperature was set at 40 °C, which was maintained for 1.2 min. It was then programmed to rise from 40 to 65 °C at 50 °C/min with an isothermic step of 3.3 min. The temperature was then lowered from 65 to 55 °C at 20 °C/min and held for 2.6 min. The injector and detector temperatures were fixed at 150 °C. The TCD was calibrated using a standard gas mixture.

3. Results and discussion

3.1. Gas production

The gas productions from the wet fractions from the MSW (calculated on a dry basis) have been normalized to the gas production from the dry fraction (MSW-0), as shown in Fig. 1. Two stages can be clearly identified during the gas production: the first from the initial time to ca. 20 min when production increases, and the second stage from ca. 20 min until the end of the pyrolysis experiment. There is a very large peak of volatiles production at ca. 15 min, during the first stage. From this point, the differences between the gas productions for different moisture contents become more pronounced. Afterwards, the production rate slows down and the differences diminish. Since the relative production is higher than 1 for all the wet samples studied after 5 min, a higher gas production than that corresponding to the dry sample is bound to occur. Furthermore, it can be seen that the higher the moisture content is, the greater the gas production. Fig. 2(a) depicts the absolute values of gas production (L g_{MSW}^{-1} on a dry basis). The main reason for this is the gasification reaction of the microwave absorbent and the char formed during the pyrolysis as a result of which syngas and CO_2 are produced:

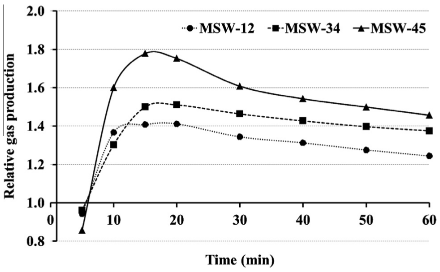


Fig. 1. Relative gas production (L g_{MSW}^{-1} on a dry basis) at different moisture contents in MSW relative to dry MSW gas production.

$$C + H_2O \leftrightarrow CO + H_2, \quad \Delta H^0 = 131 \text{ kJ mol}^{-1}$$

$$C + 2\ H_2O \leftrightarrow CO_2 + 2\ H_2, \quad \Delta H^0 = 90 \text{ kJ mol}^{-1}$$

As can be seen, the solid fraction yields decrease with the moisture content (Table 2), confirming that the initial water present in the samples has a positive effect on the gasification of char.

If the trends in Fig. 2(a) are compared, a noticeable gap can be observed between MSW-0 and MSW-12 (MSW-12 is a 24% higher). However, the differences between MSW-12, MSW-34 and MSW-45 are smaller, which suggests that a small amount of water favours the production of gas, although a large quantity does not significantly improve it.

3.2. Gas composition

The gas composition of each MSW fraction is depicted in Fig. 2(b)–(f). As pointed out by Domínguez et al. [11], the gas composition remains essentially the same regardless of the moisture content, once the second stage (>20 min) has been reached. In fact, there appears to be a value of moisture content value at which the steam generated reaches a saturation point preventing further gasification reactions. This possibility has also been suggested in another study based on the conventional pyrolysis of sewage

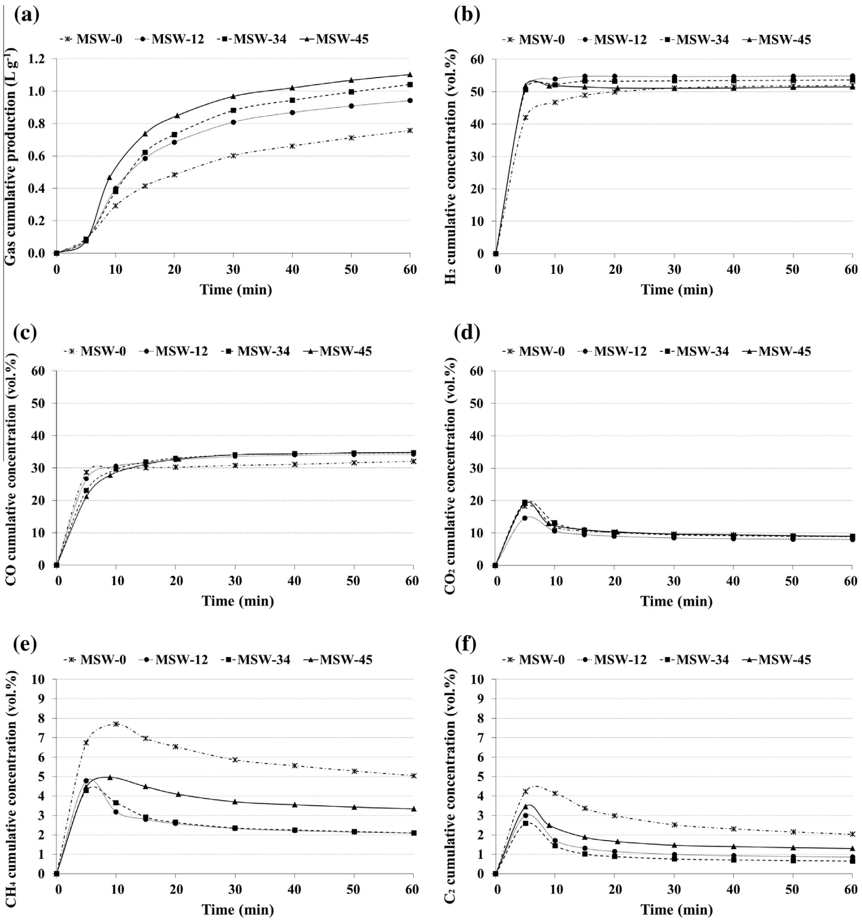


Fig. 2. (a) Total cumulative gas production (on a dry basis) and cumulative concentration of (b) H_2, (c) CO, (d) CO_2, (e) CH_4 and (f) C_2 hydrocarbons at different moisture contents in MSW.

Table 2
The effect of moisture content on the solid MSW pyrolysed.

Moisture content (wt.%)	Solid residue yield (wt.%)[a]
0	68
12	61
34	58
45	48

[a] Solid yield is expressed as the ratio of final solid residue mass to the initial load mass (MSW + microwave absorbent).

sludge [8], in which a moisture content of ca. 50 wt.% is proposed as being the critical value in the production of hydrogen. Nevertheless, with microwave heating this saturation point seems to be reached at lower moisture contents, at least in the case of the organic MSW used in the present study, since at the end of the experiments the difference in hydrogen concentrations among the wet fractions was less than 7 vol.%, whereas in the study of *Xiong*, it reached ca. 40 vol.%. Besides, both the hydrogen (Fig. 2(b)) and syngas concentrations (Fig. 3) are greater in the case of MSW-12, hence 12 wt.% can be assumed to be the critical moisture content in these cases. Nevertheless, during the first 5 min, MSW-45 is the fraction which gives off more hydrogen. In the case of CO (Fig. 2(c)), although the differences are also very small, it can be seen that the presence of moisture slightly improves the CO produced, but only after 10 min, perhaps due to the prolongation of char gasification. However, at the beginning of the process, the CO concentration is 50% greater in the case of the dry fraction

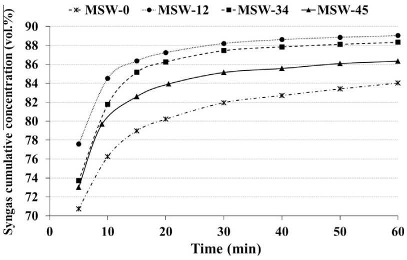


Fig. 3. Syngas concentration (vol.%) from the MIP of the MSW as a function of the moisture content and the pyrolysis time.

MSW-0. In the case of CO_2, the profiles depicted in Fig. 2(d) show a common trend. Thus, the water gas shift reaction, as illustrated below, which should lead to a higher CO_2 concentration with moisture, cannot be taking place to any significant degree:

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^0 = -41\ \text{kJ mol}^{-1}$$

As for the CH_4 concentration, the MSW-0 sample generates more methane and the differences between the wet fractions are more pronounced. For instance, MSW-0 produces ca. 130% more than MSW-12 and MSW-34. This marked difference could be due to a mixed effect of the dilution of methane at a higher moisture content and the reforming reactions of hydrocarbons. However it has not been possible so far to elucidate which explanation is more plausible.

The syngas concentration has been plotted in Fig. 3 as a function of the moisture content and the pyrolysis time and ranges from 70 to 88 vol.%. It is clear that the syngas concentration is significantly enhanced with time at the expense of higher energy consumption. This is because more thermal cracking takes place, enhancing the conversion of volatiles to H_2 and CO, as occurs when microwave heating is used [6,14]. The highest moisture contents (34 and 45 wt.%) seem to disfavour the syngas content compared to MSW-12. Interestingly, the dry fraction MSW-0 produces the smallest syngas concentration at the expense of hydrocarbon (CH_4 and C_2) production. This indicates that MSW-12 is the most appropriate fraction for maximising the syngas concentration.

Fig. 4(a)–(b) shows the quality of the gas fraction in terms of H_2/CO and CO/CO_2 ratios. At the very beginning of the first pyrolysis stage, the highest H_2/CO ratio corresponds to MSW-45 (2.44), but there is a significant decrease affecting all the wet fractions from that point, especially during the first stage (<20 min). This is due to the increased CO production as can be seen in Fig. 2(c). However, for MSW-0 the opposite tendency was found with H_2 production increasing in the first stage and reaching its highest H_2/CO value (1.62) at 60 min. It can be concluded therefore that the moisture content improves the gas quality towards H_2 if the pyrolysis time is not extended beyond 10 min. The H_2/CO ratio will then remain constant at approximately 1.5–1.6 regardless of the moisture content. In the case of the CO/CO_2 ratio, a rising tendency with time is observed, which may indicate that CO_2 is being converted to CO, as can be observed from Fig. 2(d), where there is a progressive fall in the CO_2 concentration pattern from the very beginning of the process. MSW-12 shows the highest CO/CO_2 ratio over the entire experiment. This sample, which displays the critical moisture content, gives rise to the greatest extent of gasification reactions.

In order to check whether the moisture content affects the gas production in a positive way with different organic feedstocks, two other residues (sewage sludge and agricultural straw residue) were subjected to microwave pyrolysis under the same experimental conditions as the MSW. The results from these experiments are presented in Table 3. In all the cases, a significant reduction in solid yield is observed at the expense of an improvement in the gas yield, as occurred with MSW, especially in the case of the wet sewage sludge, SS-60, which yielded 60 wt.% of gas fraction. With respect to the gas composition (values are reported at 60 min), differences are more appreciable in SS and ST, particularly in the case of hydrocarbons content (HC). This is due to the fact that moisture content favours the gasification of tar and light hydrocarbon gases. The gas fraction from the pyrolysis of the straw residue was clearly the fraction most affected by moisture content. For this reason, feeding wet feedstock to a full-scale pyrolysis reactor would promote syngas production considerably. Anyway, from these results it can be concluded with a fair degree of certainty that regardless of the moisture content which is bound to improve gas production, the type of feedstock is of extreme importance for gas production as previously reported by our research group [15].

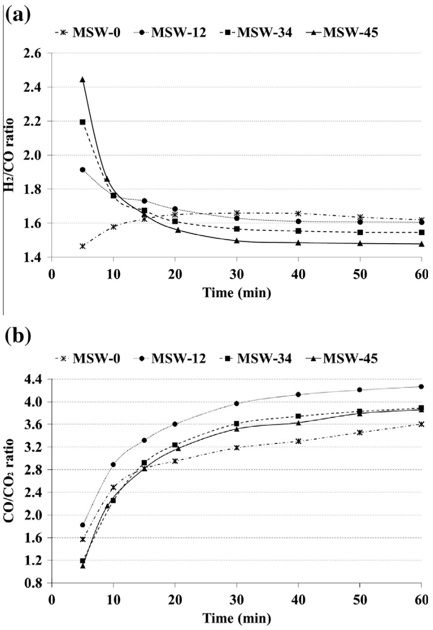


Fig. 4. (a) H_2/CO and (b) CO/CO_2 ratios from the MIP of the MSW as a function of the moisture content and the pyrolysis time.

3.3. Energetic considerations

A lower energy consumption is usually stated as one of the main advantages of microwave heating. However, this aspect in relation to the scaling-up of microwave pyrolysis has not been dealt with in depth in the literature. Only one study on low temperature pyrolysis of wheat straw deals with the energy requirements when the feedstock mass to be pyrolysed is increased from a few grams up to 200 g [4]. In that case, it can be observed that there exists a critical mass at which the specific energy con-

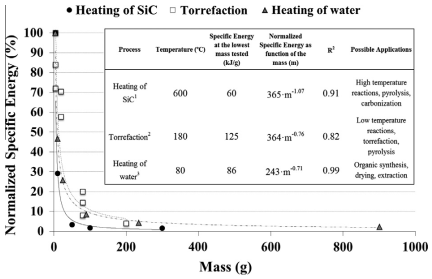
Table 3
Characteristics from the MIP of MSW, SS and ST at different moisture contents.

Feedstock	Solid yield (wt.%)	Liquid yield (wt.%)[a]	Gas yield (wt.%)	[H_2] (vol.%)	[CO] (vol.%)	[CO_2] (vol.%)	[CH_4] (vol.%)	[HC][b] (vol.%)
MSW-0	68	6	26	52.0	32.1	8.9	5.0	2.0
MSW-45	48	4	48	51.5	34.9	9.0	3.3	1.3
SS-0	64	9	27	35.5	23.0	6.2	3.5	31.8
SS-60	34	6	60	38.8	32.1	4.6	3.5	21.0
ST-0	68	4	28	42.0	27.1	11.4	3.5	16.0
ST-11	59	3	38	53.1	34.9	8.6	2.7	0.7

[a] The liquid yield is calculated on a dry basis.
[b] Hydrocarbons concentration (C_2 and higher).

sumption needed to achieve the desired temperature falls drastically; i.e., energy consumption in lab-scale experiments can lead to wrong conclusions, since the specific energy needed for a few grams is much higher than that needed for a larger quantity of feedstock. To corroborate whether this also happens in other microwave heating processes, Fig. 5 shows the corresponding trends for two other very different processes: the heating of SiC samples up to 600 °C and of pure water up to 80 °C. As can be seen, regardless of the type of process and targeted temperature, there is always a critical mass and a hyperbolical trend with increasing mass. For example, the microwave heating of 5 g of pure water requires ca. 85 kJ g^{-1} to reach 80 °C and for this temperature to be held for 15 min, whereas only 4.25 kJ g^{-1} are necessary for 300 g to reach the same temperature, representing a reduction in specific energy of 95%.

Presumably, in our microwave pyrolysis–gasification process, a similar behaviour can be expected when scaling-up. As 3 g of MSW was used in this study, the energy consumption corresponding to 225 W during a 1 h experiment was 270 kJ g^{-1} (810 kJ). Therefore, a reduction in consumption of more than 90% could be achieved by increasing the residue mass to beyond 200 g. However, it is necessary to take into account the moisture content since the latent heat of evaporation of water (2.257 kJ g^{-1}) cannot be ignored. At a small scale (as in our MSW pyrolysis experiments), since there is a very high specific consumption, the energy required to evaporate the water is relatively small. For example, 2.46 g of water were present in the MSW-45 pyrolysis and only 5.55 kJ in 810 kJ were theoretically necessary to evaporate the moisture, which is less than 1% of the total amount of energy. Nonetheless, at higher scales the situation is completely different. For example, to pyrolyse 200 g of MSW-45 using the same input power as at lab-scale, it would be necessary to evaporate 90 g of water, representing 203 kJ or 25% of the total amount of energy, the remaining energy being left to overcome the pyrolysis. However, this would lead to a poorer syngas quality, since the power density would be lower. Ultimately, although the integration of the drying step into our microwave pyrolysis–gasification process might be feasible, an economic assessment of the consumption of the microwave scaled-up process and the value of the final products would help to decide whether this process could become cost-effective.



Process	Temperature (°C)	Specific Energy at the lowest mass tested (kJ/g)	Normalized Specific Energy as function of the mass (m)	R^2	Possible Applications
Heating of SiC[1]	600	60	$365 \cdot m^{-1.07}$	0.91	High temperature reactions, pyrolysis, carbonization
Torrefaction[2]	180	125	$364 \cdot m^{-0.76}$	0.82	Low temperature reactions, torrefaction, pyrolysis
Heating of water[3]	80	86	$243 \cdot m^{-0.71}$	0.99	Organic synthesis, drying, extraction

Fig. 5. Normalized specific energy dependence on the mass to achieve the desired temperature (i.e., the energy per unit of mass divided by the energy required for the lowest mass tested) in three different microwave induced processes. References: [1]Electromagnetic simulations in MW and RF processing. AMPERE short course given by Dr. Eng. Paolo Veronesi from Department of Engineering "Enzo Ferrari" (Modena, Italy) on 16th September 2013; [2]Ref. [4]; [3]Experiments performed in our laboratory.

4. Conclusions

This paper has dealt with the integration of the drying step of organic waste into a microwave pyrolysis reactor, as an alternative process for syngas production. This would make it unnecessary to install a previous dryer to the pyrolysis reactor and also allows the *in situ* gasification of the solid waste, improving the gas yield regardless of the organic waste.

This is the first time that the influence of the moisture content on microwave pyrolysis of municipal solid waste has been studied in a systematically way, having found out that there appears to be an optimal moisture content which maximises the syngas. In this study, 12 wt.% of moisture in MSW was found to be the saturation point (yielding ca. 90 vol.% of syngas) beyond which syngas concentration started to fall.

Nevertheless, despite these advantages, the energy required to evaporate the moisture is high, which could be a limiting factor for the energy balance of a successful prototype design.

Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under Grant Agreement No. 311815 (SYNPOL project). D. Beneroso also acknowledges the financial support received from the PCTI and FICYT of the Government of the Principado de Asturias (Spain).

References

[1] Fatih Demirbas M. Biorefineries for biofuel upgrading: a critical review. Appl Energy 2009;86(Supplement 1):S151–61.
[2] Amos WA. Report on biomass, drying technology, in, 1998.
[3] Demirbaş A. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. Energy Convers Manage 2002;43:897–909.
[4] Budarin VL, Shuttleworth PS, Dodson JR, Hunt AJ, Lanigan B, Marriott R, et al. Use of green chemical technologies in an integrated biorefinery. Energy Environ Sci 2011;4:471–9.
[5] Menéndez JA, Domínguez A, Inguanzo M, Pis JJ. Microwave-induced drying, pyrolysis and gasification (MWDPG) of sewage sludge: vitrification of the solid residue. J Anal Appl Pyrolysis 2005;74:406–12.
[6] Menéndez JA, Domínguez A, Inguanzo M, Pis JJ. Microwave pyrolysis of sewage sludge: analysis of the gas fraction. J Anal Appl Pyrolysis 2004;71:657–67.
[7] Luque R, Menendez JA, Arenillas A, Cot J. Microwave-assisted pyrolysis of biomass feedstocks: the way forward? Energy Environ Sci 2012;5:5481–8.

[8] Xiong S, Zhuo J, Zhang B, Yao Q. Effect of moisture content on the characterization of products from the pyrolysis of sewage sludge. J Anal Appl Pyrolysis 2013;104:632–9.

[9] Xie L-P, Li T, Gao J-D, Fei X-N, Wu X, Jiang Y-G. Effect of moisture content in sewage sludge on air gasification. J Fuel Chem Technol 2010;38:615–20.

[10] Niu M, Huang Y, Jin B, Wang X. Simulation of syngas production from municipal solid waste gasification in a bubbling fluidized bed using aspen plus. Ind Eng Chem 2013;52:14768–75.

[11] Domínguez A, Fernández Y, Fidalgo B, Pis JJ, Menéndez JA. Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge. Chemosphere 2008;70:397–403.

[12] Wang X-L, Deng W-Y, Yu W-C, Su Y-X. Hydrogen-rich gas formation characteristics during microwave-induced high temperature pyrolysis of sewage sludge. J Fuel Chem Technol 2013;41:243–51.

[13] Beneroso D, Bermúdez JM, Arenillas A, Menéndez JA. Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste. J Anal Appl Pyrolysis 2014;105:234–40.

[14] Domínguez A, Menéndez JA, Inguanzo M, Pís JJ. Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. Bioresour Technol 2006;97:1185–93.

[15] Fernández Y, Menéndez JA. Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes. J Anal Appl Pyrolysis 2011;91:316–22.

Publicación VI

INFLUENCE OF CARRIER GAS ON MICROWAVE-INDUCED PYROLYSIS

Journal of Analytical and Applied Pyrolysis
113 (153-157)
Año 2014

Journal of Analytical and Applied Pyrolysis 113 (2015) 153–157

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Influence of carrier gas on microwave-induced pyrolysis[☆]

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

ARTICLE INFO

Article history:
Available online 10 December 2014

Keywords:
Microwave pyrolysis
Carrier
Microplasmas
Syngas

ABSTRACT

Interest in microwave-induced pyrolysis has increased in recent years due to its several advantages over conventional pyrolysis. Most of these advantages are related to the presence of microplasmas in microwave heating, since the pyrolysis reactions that take place in a plasma atmosphere generally produce light molecules, such as H_2 and CO. Although the exact nature of these plasmas is as yet unknown, it is likely to be dependent on the ionization of the surrounding gases. For this reason, the influence of different carrier gases (N_2, He or no carrier gas) on microwave-induced pyrolysis was chosen as the subject of this study. It was found that microwave-induced pyrolysis can be used to obtain equally good gas compositions and yields after the reactor has been inertized, without the need for a carrier gas.

1. Introduction

Microwave heating has attracted increasing attention as an energy source for pyrolysis processes over the last decade [1]. This interest stems from the advantages that microwave heating offers over conventional heating, including higher heating rates, volumetric and selective heating, shorter operation times and a quick start–stop capability [2,3]. In the specific case of pyrolysis, microwave heating has been demonstrated to produce extraordinary gas yields, especially, of syngas [1,4,5]. This has promoted interest in microwave-induced pyrolysis (MIP) as a means of converting organic feedstock in biorefineries into energy, fuels or materials [6,7]. Apart from parameters, such as the operating conditions or the type of feedstock used in the process [1,8,9], the main reason for this high productivity seems to be the presence of microplasmas during microwave heating [2,10].

These plasmas are hot spots that are confined to a very tiny space and last only a fraction of a second. The temperature at these points is significantly higher than the mean temperature of the rest of the material and high enough to cause the ionization of the surrounding molecules. It is thought that these plasmas can influence the yields of the different fractions (solid, liquid and gas) obtained in the pyrolysis as well as the composition of the gas produced [4]. These localised higher temperatures facilitate the extraction of volatiles from the matter. In addition, the plasmas enhance heterogeneous reactions (such as thermal cracking or the reforming of hydrocarbons) [2,11]; thus, modifying the composition of the evolved volatiles. Although the nature of these plasmas is unknown, there is some evidence to suggest that it is dependent on the gaseous molecules that are being ionized within the plasma. For example, during the microwave-assisted dry reforming of coke oven gas (55–60% H_2, 23–27% CH_4, 5–8% CO, 3–6% N_2, <2% CO_2 and hydrocarbons), microplasmas were formed reaching apparently much higher temperature compared to the microwave-assisted dry reforming of methane due to the presence of high proportions of H_2 in the coke oven gas [12]. For this reason, the carrier gas used in the pyrolysis can affect the microplasmas and influence the distribution of the product obtained in the process. Several works have been focused on the influence of the carrier gas on the pyrolysis in physical terms (i.e. contact time or dilution). However, there is a lack of studies on the influence of this parameter upon the microplasmas.

The objective of the present study is to fill this gap by undertaking an analysis of the yields and gas compositions obtained with N_2 and He as carrier gases and, in some cases, in the absence of a carrier gas in order to determine their influence on the process of microwave-induced pyrolysis.

2. Material and methods

2.1. Waste used in pyrolysis

The sample selected for this study was a dried and cleaned organic fraction from a municipal solid waste, supplied by BEFESA Gestión de Residuos Industriales S. L. (Seville, Spain). Details of the characterisation of this sample can be found elsewhere [13]. The

---

[☆] Selected Paper from Pyrolysis 2014, Birmingham, U.K. 19–23 May 2014.

* Corresponding author. Tel.: +34 985 118972; fax: +34 985 297672.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

http://dx.doi.org/10.1016/j.jaap.2014.12.005
0165-2370/

study of the influence of the carrier gas on pyrolysis was carried out using nitrogen, helium and no carrier gas.

2.2. Pyrolysis techniques and characterisation of the gases

Microwave-induced pyrolysis was performed at 400 and 800 °C using the system shown in Fig. 1b. This system consists of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample is placed (approximately 4 g of waste), coupled to a condenser and a gas collecting station (Fig. 1c). In the case of microwave-induced pyrolysis, the temperature measurement has been carried out in such a way that we measure the bulk temperature. Previously to the pyrolysis experiments, an optical infrared pyrometer was calibrated in the following manner: some char was introduced in the same reactor and then subjected to a constant microwave irradiation power. After stabilization of the temperature, the microwave power was switched off, and a thermocouple was introduced into the bulk. At the same time, the emissivity of the sample was adjusted so that both thermocouple and pyrometer measured temperatures were the same. This procedure was repeated several times until temperatures were equalised. The value of the adjusted emissivity was then utilised for the pyrolysis experiments in order to obtain the overall temperature. In this case, the temperature was measured with an error of about 3–5%. This procedure has demonstrated to be quite accurate in this experimental set-up, as has been reported in [14].

The gas collector is fitted with a pump by means of which the resulting pyrolysis gas is fed into a gas cylinder. A series of valves are so tuned as to prevent a vacuum from forming inside the reactor while the evolved gas is being compressed inside the station by means of a looping circuit. The valve-tuning procedure which is illustrated in Fig. 2 is as follows:

a) Cylinder purge: In order to ensure the removal of all previous pyrolysis gases from inside the cylinder, the pump is used to produce a vacuum inside the cylinder.
b) Cylinder inertisation: A carrier gas (N_2 or He) is fed into the cylinder so as to ensure a clean atmosphere inside.

Both steps are repeated three times. Once the cylinder has been cleaned and is in a state of vacuum, the pyrolysis process is initiated and the gas passes through the system until it reaches the cylinder where it is stored (step c in Fig. 2).

To study the influence of the carrier gas, the reactor was initially purged with N_2 or He for 30 min at a flow rate of 50 mL_{STP} min^{-1}. When no carrier gas was used, the purge was carried out with N_2. The flow rate was then reduced to 10 mL_{STP} min^{-1} (or switched

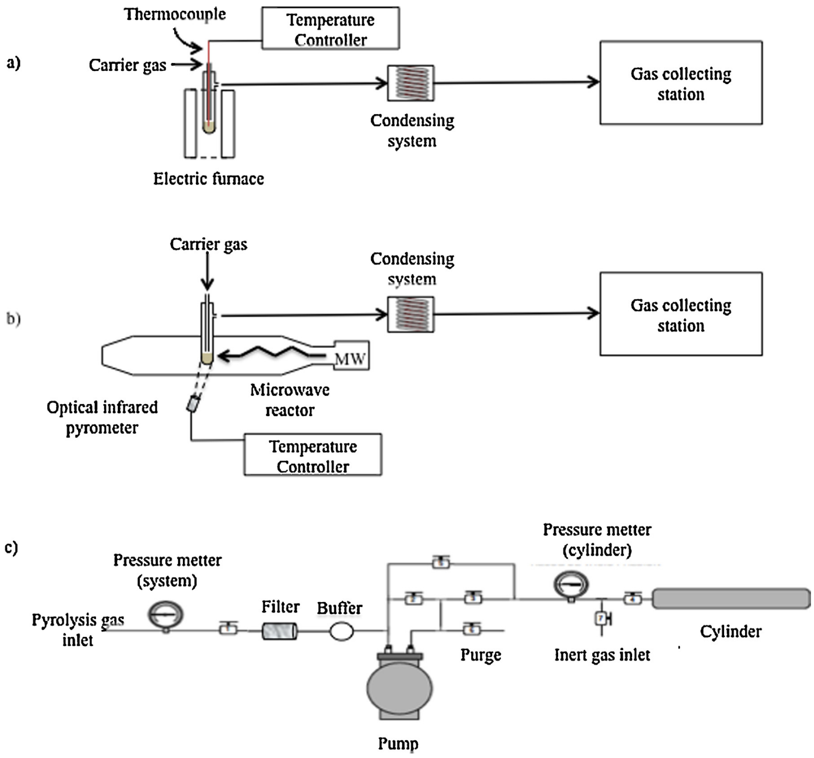


Fig. 1. Schematic of: (a) the experimental setup of conventional pyrolysis; (b) the experimental setup of microwave pyrolysis; (c) the gas collecting station.

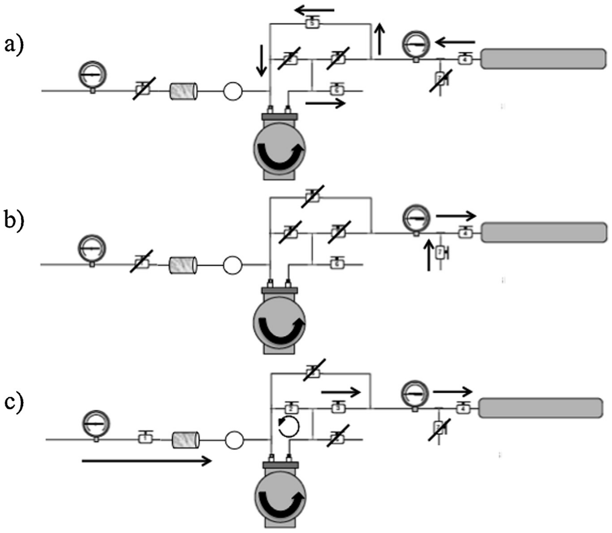


Fig. 2. Schematic of the gas collecting station during: (a) the cylinder purge; (b) the cylinder being filled with inert gas (N_2); (c) the cylinder being filled with the pyrolysis gas.

off in the event of no carrier gas being used), and the microwave irradiation was switched on during 1 h. The reflected power was regulated by means of tuning screws until it reached zero. However, owing to the poor capacity of organic wastes to absorb microwaves, it was necessary to use a microwave receptor to induce the pyrolysis. The char obtained from previous pyrolysis was used for this purpose, since it is a product of the process itself, does not contain any strange material that might influence the composition of the fractions and is known to facilitate rapid heating and to achieve the necessary pyrolysis temperature in a short time [4,6,13]. For this study, a receptor-to-residue mass ratio of 0.3:1 was selected. The volatiles evolved during the pyrolysis were forced to pass through a condensing system (cooled by a cryogenic solution of water and NaCl) where the condensable compounds were removed from the gaseous fraction. The gaseous fraction in the cylinder was then analysed by means of a Varian-CP3800 gas chromatograph equipped with a TCD detector and two columns connected in series. The first column was 80/100Hayesep Q (2 m × 1/8 inch × 2 mm) and the second column was a 80/100 Molesieve 13X (1.5 m × 1/8 inch × 2 mm). The second column was bypassed by a six-port valve for the analysis of the CO_2 and hydrocarbons. The carrier gas flow (He) was 30 mL min^{-1}. The initial oven temperature was set at 40 °C, which was maintained for 1.2 min. It was then programmed to rise from 40 to 65 °C at 50 °C min^{-1} with an isothermal step of 3.7 min. The temperature was then lowered from 65 to 55 °C at 20 °C min^{-1} and held for 3.1 min. The injector and detector temperatures were fixed at 150 °C. The TCD was calibrated using a standard gas mixture. The amounts of the solids and most of the liquids (ca. 90 wt%) were determined by direct weighing. The amount of rest of the oils stuck to the walls of the pipes after the pyrolysis experiments was determined by weighing the pipes before and after the experiment, adding the result to the liquid fraction. The gas fraction was determined balancing to 100 wt%. Each experiment was performed in duplicate to check the repeatability and the errors came to less than 6% both for the yields and the gas composition.

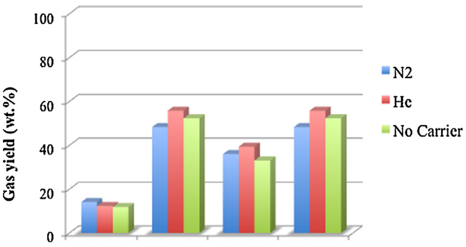


Fig. 3. Gas yields of the different experiments carried out at 400 and 800 °C employing different ovens, i.e. conventional pyrolysis (EF) or microwave pyrolysis (MW), and carrier gases.

For purposes of comparing the influence of different carrier gas in a different heating mode, conventional pyrolysis was performed in an electric furnace (EF) using the same quartz reactor (33.5 × 3.5 cm id), temperatures (400 and 800 °C), flowrate of carrier (10 mL$_{STP}$ min^{-1}) and oils collector as in MIP in order to determine whether the nature of the carrier gas affected the microplasmas generated during MIP, and in turn the fraction yields obtained from the pyrolysis. A schematic picture of the experimental setup is provided in Fig. 1a. In this case, the temperature during conventional pyrolysis was measured by means of a thermocouple of type K which measured with an error of 0.5%. The conventional pyrolysis was carried out without the addition of char to the residue, since this is not necessary to induce the pyrolysis. Although the char does not have significant porosity and superficial groups to act as a catalyst, the ashes contain certain metals (mainly Fe, Zn, Cu, Mn, Cr and Ni [6]) which could catalyse some reactions. This would take place in microwave-induced pyrolysis but also during conventional pyrolysis although not using char, since those metals remain in the solid fraction from the residue. In fact, the addition of char during conventional pyrolysis of organic waste has demonstrated to have little influence or, at best, no influence on the composition of the gas fraction. For instance, in the case of the conventional pyrolysis of microalgae, the addition of char did not show any significant difference in the gas composition [4].

3. Results and discussion

The effect of using different carrier gases during pyrolysis on the gas yield is illustrated in Fig. 3. As can be seen, there are almost no differences in the yields obtained with the different carrier gases (on a carrier gas free basis). The use of He enhances the gas yield slightly, although this enhancement cannot be strictly attributed to the microplasma phenomenon, since there is also a slight increase in the case of conventional pyrolysis at 800 °C, where no microplasmas are generated. Furthermore, MIP increases the gas yield more than conventional pyrolysis, regardless of whether N_2 or He is used, as has been reported previously [4,8].

The carrier gas also influences the gas composition (Table 1). In the case of MIP, N_2 and He produce nearly the same composition with a syngas ($H_2 + CO$) concentration at 400 °C of ca. 80 vol%. Nevertheless, if no carrier gas is used, the syngas proportion is less than that produced (ca. 69 vol%), the generation of CO_2 and CH_4 in this case being favoured. Consequently, it is thought that the use of a carrier gas during MIP may favour gasification and methane cracking reactions (Reactions (1) and (2)), by allowing a better contact between the solid and gas phases. At a higher temperature, 800 °C, MIP provides nearly the same composition regardless of whether a carrier gas is used or not.

$$C + CO_2 \leftrightarrow 2CO \tag{1}$$

$$CH_4 \leftrightarrow C + 2H_2 \tag{2}$$

In conventional heating, the absence of a carrier gas favours the generation of CO_2, aromatics and high hydrocarbons (>C_2). This gives rise to a low-quality gas fraction in terms of syngas production, especially at 400 °C, evidencing the superiority of MIP, since at 400 °C microwaves reduce the high hydrocarbon content from 52.36 vol% to virtually 0 vol%. For this reason, in the case of conventional pyrolysis, it is important to use a carrier gas at low temperatures. However, the differences with conventional pyrolysis at high temperature (800 °C) whether a carrier gas is used or not are not so great, the gas composition being nearly the same with N_2 and He, though without a carrier gas, the syngas concentration diminishes in favour of CO_2 and heavy hydrocarbons. This can be attributed to a smaller conversion of tar and gases to syngas, perhaps due to a poorer contact between the solid and gas phases.

Table 1
Compositions of the gas fractions obtained at 400 and 800 °C employing different ovens and carrier gases.

	400 °C					
	EF			MW		
	N_2	He	No carrier	N_2	He	No carrier
H_2	0.9	1.3	0.0	46.2	46.4	38.0
CO	13.4	2.5	11.7	33.3	33.9	31.0
CO_2	76.3	83.3	32.8	11.0	11.0	18.3
CH_4	1.9	3.0	1.8	5.1	5.3	8.3
C_2	1.3	2.1	1.3	4.4	3.4	4.4
Others	6.1	8.0	52.36	0.0	0.0	0.0
	800 °C					
	EF			MW		
	N_2	He	No carrier	N_2	He	No carrier
H_2	21.2	23.2	17.8	50.4	49.5	52.0
CO	25.3	26.4	17.1	36.2	37.6	33.9
CO_2	25.2	22.0	31.8	8.0	6.9	8.5
CH_4	12.6	13.6	11.0	3.3	3.7	4.3
C_2	8.4	8.7	8.5	1.3	2.4	1.4
Others	4.2	4.0	10.1	0.0	0.0	0.0

Table 2
Energy content of the gas fraction.

	400 °C					
	EF			MW		
	N_2	He	No carrier	N_2	He	No carrier
From the waste J/g of waste	0.9	0.8	3.2	8.7	9.7	8.0
In the gas J/g of gas	6.1	6.8	27.1	18.0	17.4	15.2
	800 °C					
	EF			MW		
	N_2	He	No Carrier	N_2	He	No Carrier
From the waste J/g of waste	6.9	6.8	6.9	8.6	10.2	9.3
In the gas J/g of gas	19.2	17.3	20.9	17.9	18.2	17.9

Besides the composition of the gas fraction, it is also necessary to consider the energy content in terms of the energy of the gas obtained both per gram of waste pyrolysed and per gram of gas, which depend on the pyrolysis yields and the composition of the gas fraction, as shown in Table 2. The largest differences correspond to conventional pyrolysis at low temperature. In this case the energy content per gram of gas is the maximum value obtained. This is due to the large proportion of heavy hydrocarbons, which are much more energetic than CH_4, H_2 or C_2 present in the gaseous fractions obtained under other experimental conditions. The large proportions of high hydrocarbons may be due to the longer residence time, as has been recently reported in the case of the pyrolysis of other wastes [15,16]. However, at higher temperatures, the differences are not as great. The energy extracted from the waste is almost the same and the energy contents of the gases are similar, the maximum value being reached in the experiment with no carrier gas.

When microwave heating is used more energy is extracted from the waste than under conventional heating. Both at low and high temperatures the energy extracted from the waste and the energy content of the gas are very similar regardless of the carrier gas used. When no carrier gas is used, the values are slightly lower than with N_2 or He.

4. Conclusions

The use of different carriers affects the yields of the fractions obtained during the pyrolysis of organic residues only slightly. In the case of conventional pyrolysis, the absence of a carrier gas promotes the generation of CO_2, aromatics and heavy hydrocarbons, yielding a gas fraction of low quality. Nevertheless, in microwave pyrolysis, and especially at high temperature, no significant differences in the gas composition were observed when using different carriers, though a small increase in the gas yield was obtained with helium as carrier gas. The results of this point the way to the implementation of microwave pyrolysis without the need for a carrier gas.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 311815 (SYNPOL project). D.B. also acknowledges the support received from PCTI and FICYT of the Government of the Principado de Asturias.

References

[1] F. Motasemi, M.T. Afzal, A review on the microwave-assisted pyrolysis technique, Renew. Sust. Energ. Rev. 28 (2013) 317–330.

[2] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Process. Technol. 91 (2010) 1–8.

[3] K.E. Haque, Microwave energy for mineral treatment processes – a brief review, Int. J. Miner. Process. 57 (1999) 1–24.

[4] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, Bioresour. Technol. 144 (2013) 240–246.

[5] X.H. Wang, H.P. Chen, X.J. Ding, H.P. Yang, S.H. Zhang, Y.Q. Shen, Properties of gas and char from microwave pyrolysis of pine sawdust, BioResources 4 (2009) 946–959.

[6] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Integrated microwave drying, pyrolysis and gasification for valorisation of organic wastes to syngas, Fuel 132 (2014) 20–26.

[7] http://www.synpol.org/

[8] Y. Fernández, J.A. Menéndez, Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes, J. Anal. Appl. Pyrolysis 91 (2011) 316–322.

[9] Z. Hu, X. Ma, C. Chen, A study on experimental characteristic of microwave-assisted pyrolysis of microalgae, Bioresour. Technol. 107 (2012) 487–493.

[10] J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, J.M. Bermúdez, A. Arenillas, Ball lightning plasma and plasma arc formation during the microwave heating of carbons, Carbon 49 (2011) 346–349.

[11] X. Zhang, D.O. Hayward, D.M.P. Mingos, Effects of microwave dielectric heating on heterogeneous catalysis, Catal. Lett. 88 (2003) 33–38.

[12] J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Microwave-assisted CO_2 reforming of coke oven gas: an exception to the general rule? Afinidad 69 (2012) 185–190.

[13] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste, J. Anal. Appl. Pyrolysis 105 (2014) 234–240.

[14] J.A. Menéndez, E.M. Menéndez, A. García, J.B. Parra, J.J. Pis, Thermal treatment of active carbons: a comparison between microwave and electrical heating, J. Microwave Power Electromagn. Energy 34 (1999) 137–143.

[15] D.Y.C. Leung, X.L. Yin, Z.L. Zhao, B.Y. Xu, Y. Chen, Pyrolysis of tire powder: influence of operation variables on the composition and yields of gaseous product, Fuel Process. Technol. 79 (2002) 141–155.

[16] F.J. Mastral, E. Esperanza, P. Garcíía, M. Juste, Pyrolysis of high-density polyethylene in a fluidised bed reactor. Influence of the temperature and residence time, J. Anal. Appl. Pyrolysis 63 (2002) 1–15.

Publicación VII

DIELECTRIC CHARACTERIZATION OF BIODEGRADABLE WASTES DURING PYROLYSIS

Fuel; doi: 10.1016/j.fuel.2016.01.016

Año 2015

Dielectric characterization of biodegradable wastes during pyrolysis

D. Beneroso[1], A. Albero-Ortiz[2], J. Monzó-Cabrera[2], A. Díaz-Morcillo[2], A. Arenillas[1], J.A. Menéndez[1]*
[1]*Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*
[2]*Department of Communication and Information Technologies, Technical University of Cartagena, Cartagena, Spain*
Corresponding author: Tel.: +34 985 119090
E-mail address: angelmd@incar.csic.es

Abstract

The lack of dielectric properties data has often been named as one of the reasons that has hampered the simulation of microwave processing of biomass feedstock and process design. In this work, the dielectric behavior of an organic fraction from municipal solid wastes during pyrolysis has been monitored as a function of temperature. Furthermore, the effect of the addition of a microwave absorbent material (carbonaceous char) to the raw biowaste upon the dielectric properties has been investigated for the first time.

The efficiency of the conversion of microwave energy to heat, measured by means of the tan δ parameter, is shown in this study to be nearly 20 times higher when the absorbent char is added to the reaction bulk at room temperature and this gap is even greater in the 600 – 800 ºC range. Nevertheless, the results suggest that the addition of increasing amounts of microwave absorbent (up to ca. 40%) impairs microwave penetration, which gives rise to a less homogeneous heating of the bulk. There is therefore an optimum proportion that balances heat conversion and penetration depth.

The results of this study lend support to the use of char as a means to induce thermochemical treatments by microwaves and reduce energy consumption in the process.

Keywords: Dielectric properties, Microwave pyrolysis, Biomass pyrolysis, Microwave heating modeling, Microwave absorbent

1. Introduction

On average, every one of the more than 500 million people living in the European Union (EU) throws away around half a ton of household rubbish a year. This is on top of the huge amount of waste generated from activities such as manufacturing (360 million tons) and construction (900 million tons), while the supply of water and the production of useful energy generate another 95 million tons. Altogether, the EU produces up to 3 billion tons of waste every year [1]. A significant proportion of waste going to landfill is organic material, (i.e. derived from both biomass and petroleum sources). Thermochemical conversion processes, involving pyrolysis and gasification, can convert this waste at source into potentially useful chemical feedstocks and fuels after the removal of the more readily recyclable materials, such as metals, glass, etc.

A number of processes are now under development or are at the demonstration stage, whose aim is to provide more cost-effective, environmentally and socially acceptable alternatives to incineration plants. One of these new technologies is microwave pyrolysis based on dielectric heating. This process benefits from the main advantages of using microwaves, such as rapid, volumetric and selective heating, and avoids the need to shred the feedstock and to pre-dry the samples, resulting in a substantial reduction in the costs associated with these steps [2-5]. In spite of these advantages, this technology has not yet reached industrial scale owing to the lack of economic analyses on a large scale and the absence of sufficient data to quantify the dielectric properties of the input feedstocks.

The property that determines the dielectric response of material under the influence of an electric field is the relative complex permittivity, ε^*, which is expressed as a function of a real component known as the dielectric constant (which represents the ability of dielectrics to store electrical energy) and an imaginary component known as the dielectric loss factor (which represents the ability of a material to absorb the electric energy):

$$\varepsilon^* = \varepsilon' - j\varepsilon''(1)$$

where $j = \sqrt{-1}$ and ε' and ε'' are the dielectric constant and the dielectric loss factor relative to the corresponding dielectric properties of free space.

An estimation of these properties is essential for the effective design and scaling up of microwave heating processes to ensure an accurate prediction of the absorbed power density; i.e. the rate at which the electromagnetic energy is converted to heat in the material. Dielectric properties may vary with composition, frequency, temperature and even material density [6] and, therefore, it is essential to characterize their variation in relation to those parameters.

Several studies have attempted to characterize the dielectric properties of coal [7] and some kinds of biomass [8, 9] since it is known that the dielectric loss of these materials at low temperatures is negligible, making them transparent to microwaves. However, when the substrates are subjected to higher temperatures (i.e. temperatures higher than 600 °C), the structures become essentially char, which is known to be a high microwave absorbing material due to the Maxwell-

Wagner effect which causes a very high displacement of π-electrons on carbonized structures [10]. It is for this reason that different microwave receptor materials are added to biomass during microwave pyrolysis, so that a high enough temperature is reached to induce pyrolysis [11, 12]. However, most published studies are focused solely on the dependence of dielectric properties upon frequency radiation at room temperature [13-16] and ignore the need for a comprehensive study of the whole microwave pyrolysis process. In other words, an in-depth and extensive study of the dependence of dielectric properties on temperature is needed to obtain a better understanding of the dielectric response of organic substrates during microwave pyrolysis and of mixed organic substrates when used with microwave susceptors.

This paper investigates the microwave absorption capability of a biodegradable waste and its mixture with microwave absorbent char on the basis of their dielectric properties, from room temperature up to 800 ºC at the commonly used frequency of 2.45 GHz.

2. Materials and Methods

2.1 Biowaste preparation and characterization

The biodegradable waste used for this study was an organic fraction from a municipal solid waste, obtained from a landfill in Seville (Spain). The waste was dried, partially cleaned of inerts such as glass or metals and size-reduced to 1-3 mm. This fraction has been labelled as MSWd. The pre-treatment of this organic residue allows a good homogeneity of this fraction. Actually, this fraction has been used in other studies to produce synthesis gas by means of microwave-induced pyrolysis and the composition of the gas was quite homogeneous when repeating the tests [17].

In order to assess the effect of adding char as microwave absorber to the biowaste upon the dielectric response, a carbonaceous solid char was prepared by subjecting the biowaste sample to a temperature of 800 ºC in an electric furnace for 1 h in an oxygen-free atmosphere. This has been labelled Char-MSWd. The mixtures of char:biowaste were prepared in weight ratios of 0.3:1 and 0.6:1. These two mixture ratios were considered on the basis of keeping the amount of char as low as possible to induce the microwave pyrolysis. In previous studies [17], we used 0.3:1 ratio; thus, we have used this same ratio in this work. Furthermore, a larger amount (0.6:1 ratio) was considered to study the effect of adding char to feedstock as microwave absorbent.

The moisture, ash content and volatile matter data of the residues were obtained on a LECO TGA-601 device. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The micro-analyzer provided data on the carbon, hydrogen, nitrogen, and sulfur percentage composition. The oxygen content was determined using the LECO-TF-900 furnace. The results of proximate and ultimate analyses of the MSWd and char-derived samples are presented in Table 1.

Table 1. Proximate and ultimate analyses of the MSWd and Char-MSWd fractions (*Dry basis)

Residue		**Municipal solid waste**	**Char from municipal solid waste**
Label		MSWd	Char-MSWd
Proximate analysis (wt.%)	Moisture	2.8	3.3
	Ash*	27.7	66.6
	Volatile matter*	61.1	1.7

Ultimate analysis (wt.%)	C	45.1	30.7
	H	5.4	0.1
	N	2.1	1.0
	S	0.4	0.7
	O	19.3	0.9

2.2 Measurement of dielectric properties

An inverse methodology to obtain the permittivity of the different biowastes was used (Fig. 1) [18]. This technique is one of the most appropriate; other techniques such as standard coaxial probes may lead to lower precision since air bubbles below the coaxial probe can result in lower values of permittivity; resonant-cavity technique is typically used for low-loss materials (which is not our case) and identifying the resonant frequency and quality factor (intrinsic parameters of this technique) would have been difficult due to the high absorption of the materials. First, each sample (see Sample R in Fig. 1) was introduced and uniformly compacted into a quartz tube (i.d. 5 mm, height 43 mm; MSWd bulk density: 166 kg/m^3; char bulk density: 353 kg/m^3) and heated up to a specific temperature in an oxygen-free atmosphere by a GALLUR convection oven. The samples were subjected to 25, 50, 100, 200, 300, 400, 500, 600, 700, 800 and 1000 ºC before being very quickly placed (maximum 3 s) in the middle of a WR-340 waveguide where the scattering parameters (i.e., S_{11}, S_{12}, S_{21} and S_{22}) were measured by means of a RHODE & SCHWARZ, model ZVA67 vector network analyzer set to a frequency of 2.45 GHz. S-parameters describe the response of an N-port network to voltage signals at each port. The first number in the subscript refers to the responding port, while the second number refers to the incident port. Thus S_{21} means the response at port 2 due to a signal at port 1. Afterwards, the measurement system was modeled (Sample S in Fig. 1) by using CST Microwave Studio (CST MWS) commercial software and, by inverse techniques, the value of the complex permittivity of each sample at the corresponding temperature was obtained. That is to say, an optimization method (a genetic algorithm combined with a gradient descent optimization method) [18] was applied to the model to obtain a simulated material that would induce the same scattering parameters as those previously measured. As initial values for the corresponding optimization method, the permittivity of the materials was measured in a portable DIMAS dielectrometer, model DIELKITV/DIELKITC at room temperature. The errors during measurements are included in the Supplementary Material. Furthermore, to minimize the uncertainty of the sample cooling on the permittivity measurements during the sample transfer from the oven to the waveguide, the cooling curve was previously estimated and can be found in the Supplementary Material. This curve allows establishing the operating temperature of the oven in order to reach the nominal temperature into the waveguide.

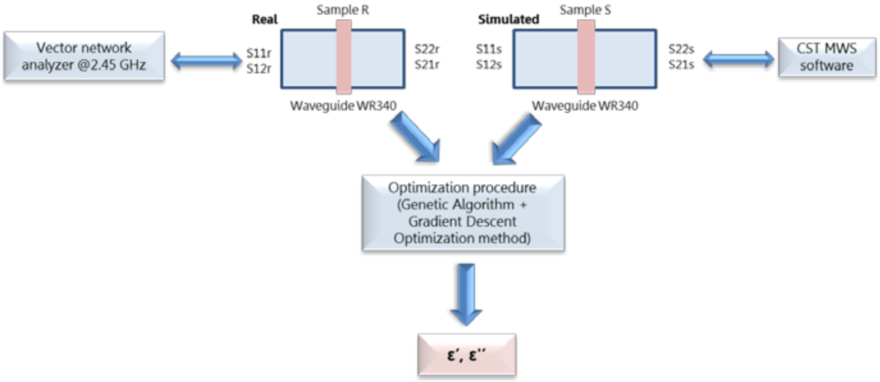


Figure 1. Inverse methodology for determining the dielectric properties based on the procedure described in [17]

2.3 *Loss tangent calculation*

The loss tangent is an important dielectric property which is directly related to the ability of a specific material to convert electromagnetic energy into heat at a given temperature and frequency. This property is defined as:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

Furthermore, the relationship between the dielectric properties of biowaste and char was investigated for the two material mixtures over the selected temperature range. The dielectric properties of a mixture of two different materials can be modeled by using different equations such as the Landau, Lifshitz and Looyenga equation (Equation 3), as reported in [19]:

$$\varepsilon^{*1/3} = \upsilon_{\mathrm{MSWd}}\left[\varepsilon^{*1/3}_{\mathrm{MSWd}} - \varepsilon^{*1/3}_{\mathrm{char-MSWd}}\right] + \varepsilon^{*1/3}_{\mathrm{char-MSWd}} \quad (3)$$

where υ_{MSWd} is the volumetric fraction of the material MSWd, which was calculated from its density, and $\varepsilon^{*}_{\mathrm{MSWd}}$ and $\varepsilon^{*}_{\mathrm{char-MSWd}}$ are the permittivity of the biomass and char fractions, respectively. The accuracy of this model was tested using the experimental data obtained over the temperature range selected.

2.4 *Skin depth calculation*

The skin depth, also known as penetration depth (D_s), is defined as the distance from the surface into the materials at which the travelling electromagnetic wave power drops to e^{-1} from its value at the surface. The skin depth can be calculated using Equation 4 [20]:

$$D_s = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi\varepsilon''} \ (4)$$

where λ_0 is the microwave wavelength in free space. The skin depth is an important parameter since the use of microwaves as a heating medium usually involves scaling-up limitations due to the difficulty of properly dispersing the microwaves as the material increases in volume [21].

3. Results and Discussion

The measured dielectric properties of the MSWd and Char-MSWd fractions are shown in Fig. 2 (a) and (b), respectively, versus the increase in temperature. As can be seen, the dielectric properties depend greatly on the temperature during pyrolysis, particularly at high temperatures.

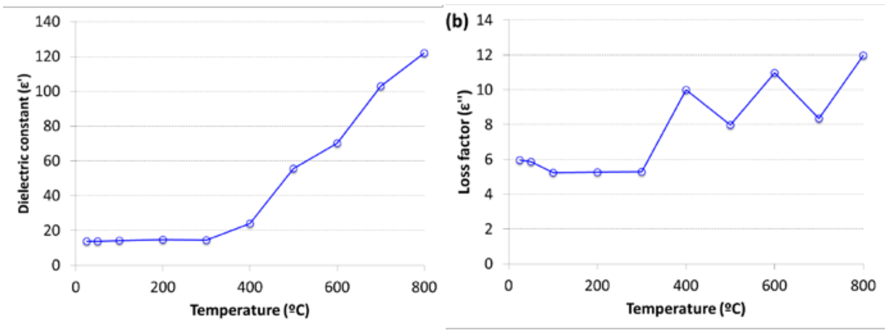


Figure 2. Dielectric properties of the (a) MSWd fraction (b) Char-MSWd fraction during pyrolysis.

The dielectric constant and loss factor for MSWd show a nearly constant value from room temperature up to 500 °C, corresponding to the pyrolysis step. A sharp increase in the dielectric constant is observed beyond 600 °C corresponding to development of char formation that shows a maximum value at 800 °C. In the case of the loss factor, there is a gradual increase up to 800 °C as a consequence of the higher conductivity of the sample because of the occurrence of π-electron conduction when aromatized structures are formed during pyrolysis [7, 10]. Although not graphed in this paper, a further temperature increase up to 1000 °C exponentially increased the loss factor up to $\varepsilon'' \approx 13$.

The Char-MSWd fraction follows the same dielectric constant pattern as the MSWd fraction, although it reaches much higher values. Of particular interest is the very high value even at room temperature, due to the greater capability of the carbon to store electrical energy from microwaves. However, the evolution of the loss factor with increasing temperature is quite different from that of MSWd. As can be seen in Fig. 2(b), the loss factor is $\varepsilon''=12$ at 800 °C; this value is similar to that of the MSWd fraction at 1000 °C, as reported above, which suggests that the higher the char concentration is, the lower the temperature required to reach large loss factors. Thus, it seems that the initial characteristics of the starting material have a significant influence on dielectric behavior during pyrolysis despite the fact that the solid material produced must be the same at the end of pyrolysis (char).

In addition, the loss factor peaks indicate a typical relaxation polarization behavior [7]. During the measurement of the dielectric properties of the Char-MSWd fraction, different local power absorption rates along the sample volume in the form of thermal runaway effect could have taken place and, therefore, increased the measurement uncertainty and loss factor fluctuation. This is not the case of the MSWd fraction, whose loss factor does not show any fluctuation.

Fig. 3 shows the variation of the *tan δ* parameter for the MSWd and Char-MSWd fractions.

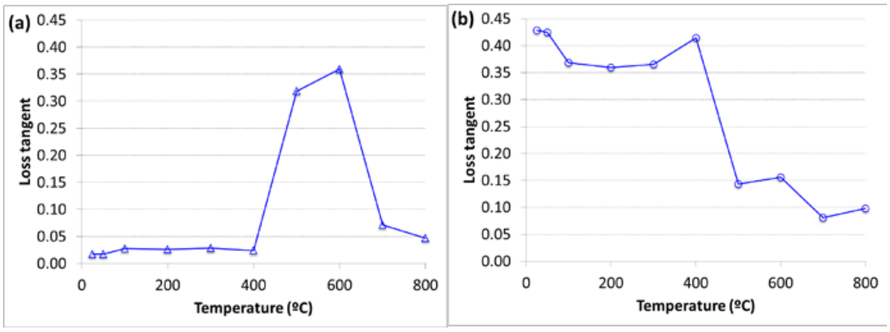


Figure 3. Evolution of *tan δ* during pyrolysis for the (a) MSWd and (b) Char-MSWd fractions.

At lower temperatures (<500 ºC), the thermochemical decomposition of organic matter takes place, and the polar compounds that might have contributed to the heating of the material are quickly released. Thus poor *tan δ* values (≈0.02) are attained in the case of the MSWd fraction. In the 500 - 600 ºC range, *tan δ* increases up to 0.35, but it decreases again after 600 ºC. From an energetic point of view, the 500 – 600 ºC range seems to be the most suitable for minimizing the consumption of energy during pyrolysis. However, a radical increase in *tan δ* (≈7.5) was observed at 1000 ºC (not shown in Fig. 3). In the case of the Char-MSWd fraction, *tan δ* is higher at low temperatures (≈0.40), which means that under these conditions char is a microwave absorbent material and so it can be used to induce the pyrolysis of biowastes and other biomass feedstock. This value is similar to those previously reported for similar materials, such as carbon black (0.35-0.85) and charcoal (0.11-0.29) at room temperature and 2.45 GHz [10]. However, it can be seen that at temperatures higher than 600 ºC, the microwave absorption capability decreases and *tan* δ approaches that of water (*tan* δ = 0.118 at 2.45 GHz and 25 ºC). A similar behavior was observed in the case of the char from oil palm shell [22]. This tendency has not yet been explained, but it is probably related to the fact that the dielectric constant increases monotonically with temperature, while the loss factor remains essentially within the same narrow range (ε''≈5-12).

The dielectric behavior of mixed biowaste and char was also investigated, for which an intermediate response somewhere between that obtained for the MSWd and char fraction was initially expected. The dielectric properties for the 0.3:1 and 0.6:1 mixtures obtained using the Landau, Lifshitz and Looyenga model are shown in Fig. 4 and Fig. 5 respectively, along with the experimental measurements. The values for temperatures lower than 500 ºC are also included at a higher scale to make them clearer. The model predicts the tendency of the measured dielectric constant values slightly well. Nevertheless, the loss factor is not modeled accurately, especially in the 600 – 800 ºC range, as it underestimates the experimental values. This suggests the occurrence of a thermal runaway effect when the organic feedstock is mixed with a microwave absorbent material, leading to the boosting of heat loss at lower temperatures compared to pure biowaste pyrolysis. This phenomenon occurs because the microwave energy is concentrated in the microwave absorbent (usually metallic oxides and carbonaceous materials), whose rate of absorption (referred to as thermal absorptivity) increases with temperature, leading to an exponential increase in the heating rate [23]. Consequently, microwave power needs to be properly controlled, especially beyond 600 ºC, to avoid a dramatic increase in temperature.

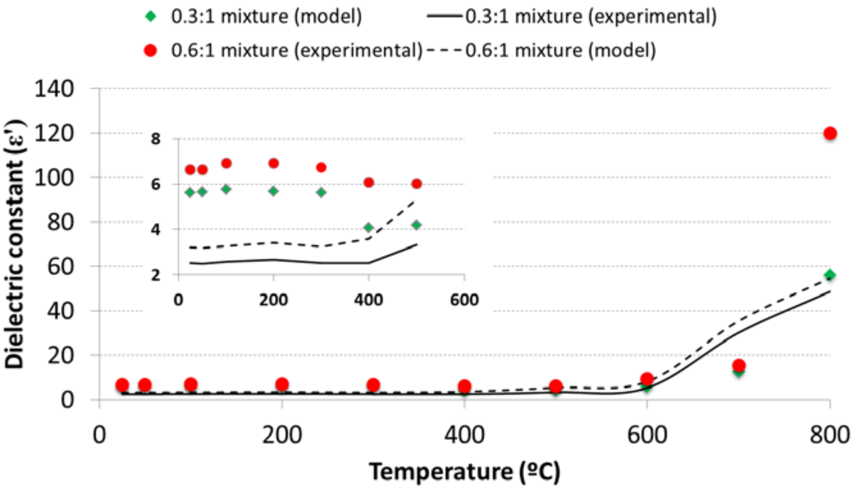


Figure 4. Dielectric constant of the mixtures.

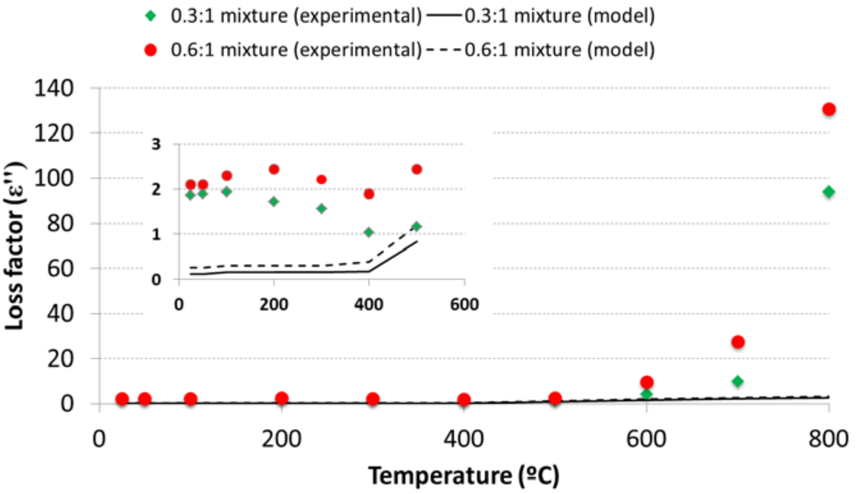


Figure 5. Loss factor of the mixtures.

In addition, the effect of the concentration of the microwave absorbent on *tan δ* is shown in Fig. 6. At lower temperatures, *tan δ* seems to remain approximately the same regardless of the char concentration. However, in the 200 - 700 ºC range, the higher char concentration (0.6:1 mixture) provides a better conversion of microwaves into heat, especially in the 500 – 700 °C range. As shown in Fig. 5, thermal runaway starts at a lower temperature in the case of a higher char concentration. Nevertheless, it is the lower char concentration that provides a more efficient heating at 800 °C. Again, this suggests that it is the initial characteristics of the starting material (in this case, the different char concentration) that determine dielectric behavior despite the fact that the final product is char.

From the observations made so far it follows that dependence of the dielectric properties on temperature must be taken into account when designing a microwave applicator to ensure an energy efficient operation and so obtain the desired products. For instance, the production of syngas (H_2+CO) from biowaste is highly favoured at 600 – 800 °C during microwave-induced pyrolysis, which matches with the highest energy conversion to heat [17]. As a means of comparison, the evolution of the loss tangent in the case of MSWd has been included in Fig. 6.

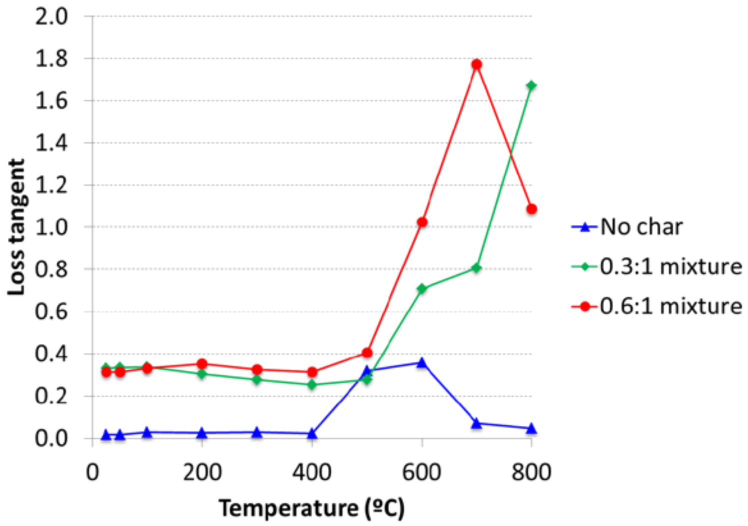


Figure 6. Evolution of *tan δ* during pyrolysis for the different char/biowaste mixtures. *tan δ* from MSWd fraction is also depicted as a means of comparison.

It can be seen that the addition of the microwave absorbent char improves the conversion of electromagnetic energy into heat, the loss tangent being ca. 17 times higher at room temperature (0.33 vs 0.02). This is an encouraging result for the scaling-up of microwave-induced pyrolysis, because the addition of char to the feedstock to be pyrolysed will contribute greatly to a reduction in energy requirements and costs. In a recent report, a reduction of 30% in energy expenditure was reported by properly mixing the organic feedstock with 10 wt.% char [24]. Consequently, the most appropriate way to carry out microwave-induced pyrolysis at high temperature is to use char as microwave absorbent mixed with the organic feedstock.

Besides, as reported in the Introduction, microwave processing avoids the need for pre-drying the feedstock. However, a pre-treated sample has been used in this work. As a means of comparison, the effect of the moisture content on the dielectric properties of the residue was measured (at 25 ºC): tan δ parameter increased up to 0.6 compared to 0.3; moisture can then slightly improve the microwave absorption of the residue at low temperature.

The skin depth of these mixtures during pyrolysis is illustrated in Fig. 7. A peak corresponding to the highest microwave skin depth was observed at 400 °C, as also reported by [25]. This is assigned to the onset of the pyrolysis, when volatiles begin to be released. However, a remarkable decrease in the skin depth is observed beyond 400 °C, which indicates strong microwave absorption by the char because of the high density of π-electrons. Throughout the pyrolysis process, the 0.6:1 mixture exhibits lower skin depths due to the higher concentration of microwave absorbent char, which is not surprising given its dielectric properties and hence higher microwave absorption capability.

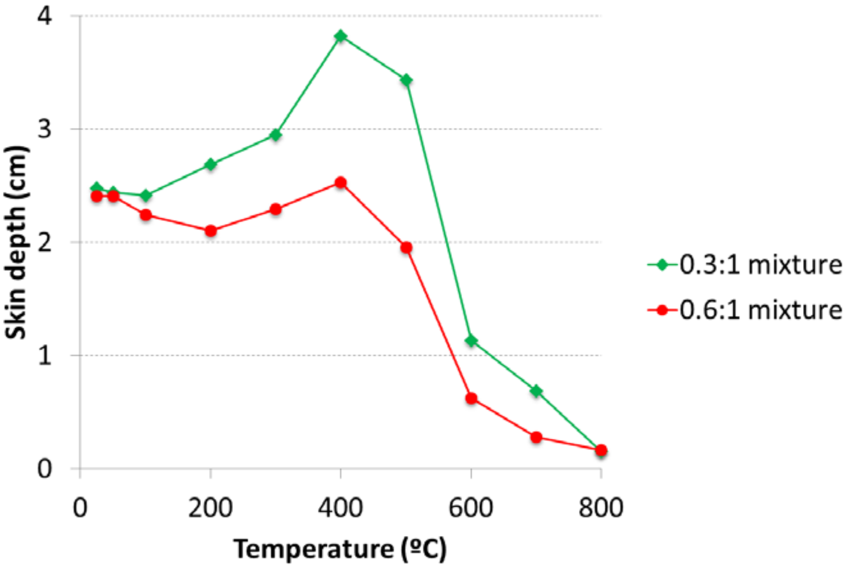


Figure 7. Microwave skin depth for the mixtures of MSWd with Char-MSWd during pyrolysis.

Two opposing effects then can be inferred from the microwave-absorbent concentration used to maximize both the skin depth and microwave absorption, as shown in Fig. 8. On the one hand, for homogeneously blended mixtures, the skin depth is greater at low char concentrations (Fig. 7) because a larger amount of transparent material (biowaste) is present, which ensures a more homogeneous heating, although it is possible that more energy will be consumed (Fig. 6). On the other hand, microwave absorption is greater at high char concentrations where the penetration depth is smaller since char is produced preferentially on the outer surfaces, leading to a more heterogeneous heating. These effects may have a direct influence on the process performance. For instance, the effect of char concentration on the microwave-induced pyrolysis of the biowaste used in our study to produce syngas was found to be determinant [12]. In their study, Beneroso *et al.* found that a low char concentration led to a higher syngas concentration in the gas from the pyrolysis, probably due to the greater penetration depth of microwaves into the bulk which led to a more homogenous heating.

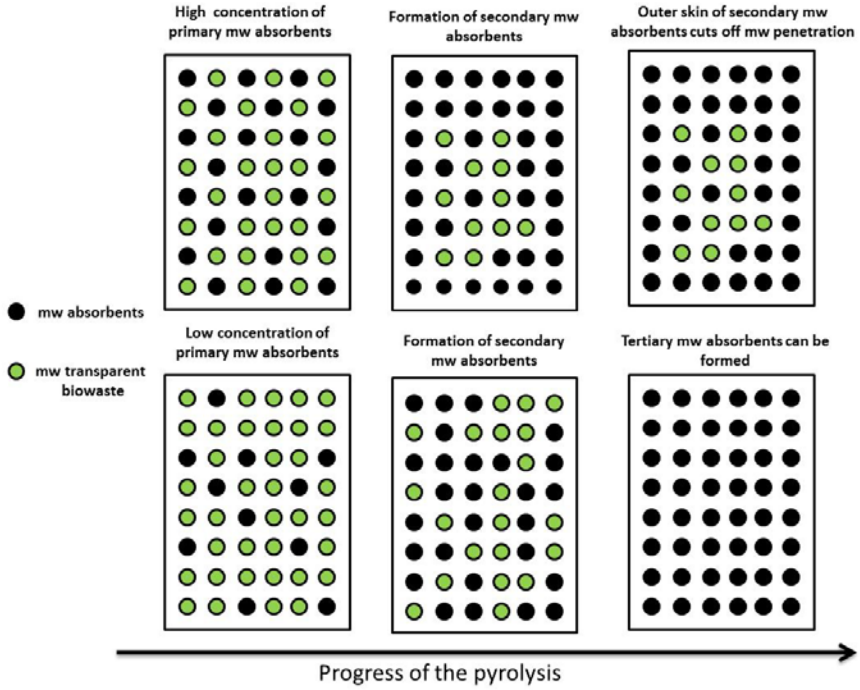


Figure 8. Effect of the microwave absorbent (mw absorbent) concentration on the microwave heating efficiency. In the initial phase, only the added microwave receptor is able to absorb microwaves and produce heat, which allows the nearby particles of the mw transparent biowaste to be heated by convection, conduction and radiation. Later, the removal of volatiles produces char, which will act as a mw absorbent, enabling the pyrolysis process to be sustained. Depending on the concentration of the initial mw absorbent, first, secondary, tertiary, etc. generations of mw absorbents may be obtained. Unlike the case of high char concentration, better penetration depths are attained at low char concentrations, making it possible to develop larger generations of mw absorbents during pyrolysis, and thereby facilitating more homogeneous heating.

4. Conclusion

The dielectric properties of an organic fraction from a municipal solid waste were determined at 2.45 GHz from room temperature to 800 ºC.

The dielectric properties of the biowaste remained constant during pyrolysis up to 400 ºC; then there was a sharp increase in both the dielectric constant and loss factor, owing to the release of volatiles and honeycomb-like carbon structures with a high delocalised electron density. Furthermore, the addition of char as microwave absorbent to the feedstock proved to be an effective way to reduce the energy consumption of the pyrolysis process, because it provided the bulk with a high tan δ at room temperature, although it reduced the penetration depth, which resulted in a more heterogeneous heating when a high concentration of char was used.

The dielectric characterization addressed in this paper could serve as a starting point for the design of suitable equipment to perform the microwave-induced pyrolysis at industrial scale with the appropriate simulation software.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement n° 311815 (SYNPOL project). D. B. also acknowledges the financial support received from PCTI and FICYT of the Government of the Principado de Asturias.

References

[1] European Commission, Being wise with waste: the EU's approach to waste management, in, 2010.

[2] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Integrated microwave drying, pyrolysis and gasification for valorisation of organic wastes to syngas, Fuel, 132 (2014) 20-26.

[3] V.L. Budarin, P.S. Shuttleworth, J.R. Dodson, A.J. Hunt, B. Lanigan, R. Marriott, K.J. Milkowski, A.J. Wilson, S.W. Breeden, J. Fan, E.H.K. Sin, J.H. Clark, Use of green chemical technologies in an integrated biorefinery, Energy & Environmental Science, 4 (2011) 471-479.

[4] F. Motasemi, M.T. Afzal, A review on the microwave-assisted pyrolysis technique, Renewable and Sustainable Energy Reviews, 28 (2013) 317-330.

[5] D. Beneroso, J. Bermúdez, A. Arenillas, J. Menéndez, Microwave Pyrolysis of Organic Wastes for Syngas-Derived Biopolymers Production, in: Production of Biofuels and Chemicals with Microwave, Springer, 2015, pp. 99-127.

[6] J.B. Salsman, Technique for Measuring the Dielectric Properties of Minerals as a Function of Temperature and Density at Microwave Heating Frequencies, MRS Online Proceedings Library, 189 (1990) null-null.

[7] Z. Peng, J.-Y. Hwang, B.-G. Kim, J. Mouris, R. Hutcheon, Microwave Absorption Capability of High Volatile Bituminous Coal during Pyrolysis, Energy & Fuels, 26 (2012) 5146-5151.

[8] F. Motasemi, M.T. Afzal, A.A. Salema, Microwave dielectric characterization of hay during pyrolysis, Industrial Crops and Products, 61 (2014) 492-498.

[9] F. Motasemi, M.T. Afzal, A.A. Salema, J. Mouris, R.M. Hutcheon, Microwave dielectric characterization of switchgrass for bioenergy and biofuel, Fuel, 124 (2014) 151-157.

[10] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Processing Technology, 91 (2010) 1-8.

[11] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Microwave pyrolysis of microalgae for high syngas production, Bioresource Technology, 144 (2013) 240-246.

[12] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste, Journal of Analytical and Applied Pyrolysis, 105 (2014) 234-240.

[13] A.A. Salema, Y.K. Yeow, K. Ishaque, F.N. Ani, M.T. Afzal, A. Hassan, Dielectric properties and microwave heating of oil palm biomass and biochar, Industrial Crops and Products, 50 (2013) 366-374.

[14] R. Omar, A. Idris, R. Yunus, K. Khalid, M.I. Aida Isma, Characterization of empty fruit bunch for microwave-assisted pyrolysis, Fuel, 90 (2011) 1536-1544.

[15] S. Ramasamy, B. Moghtaderi, Dielectric properties of typical Australian wood-based biomass materials at microwave frequency, Energy & Fuels, 24 (2010) 4534-4548.

[16] A.A. Salema, M.T. Afzal, Numerical simulation of heating behaviour in biomass bed and pellets under multimode microwave system, International Journal of Thermal Sciences, 91 (2015) 12-24.

[17] M.E. Requena-Perez, A. Albero-Ortiz, J. Monzo-Cabrera, A. Diaz-Morcillo, Combined use of genetic algorithms and gradient descent optmization methods for accurate inverse permittivity measurement, Microwave Theory and Techniques, IEEE Transactions on, 54 (2006) 615-624.

[18] D.C. Dube, Study of Landau-Lifshitz-Looyenga's formula for dielectric correlation between powder and bulk, Journal of Physics D: Applied Physics, 3 (1970) 1648.

[19] J.P. Robinson, S.W. Kingman, E.H. Lester, C. Yi, Microwave remediation of hydrocarbon-contaminated soils – Scale-up using batch reactors, Separation and Purification Technology, 96 (2012) 12-19.

[20] J. Doucet, J.-P. Laviolette, S. Farag, J. Chaouki, Distributed Microwave Pyrolysis of Domestic Waste, Waste Biomass Valor, 5 (2014) 1-10.

[21] M. Tripathi, J.N. Sahu, P. Ganesan, T.K. Dey, Effect of temperature on dielectric properties and penetration depth of oil palm shell (OPS) and OPS char synthesized by microwave pyrolysis of OPS, Fuel, 153 (2015) 257-266.

[22] Y. Fernández, A. Arenillas, J.Á. Menéndez, Microwave Heating Applied to Pyrolysis, Advances in Induction and Microwave Heating of Mineral and Organic Materials, Stanisław Grundas (Ed.), ISBN: 978-953-307-522-8, InTech, InTech, 2011.

[23] D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics, Journal of Analytical and Applied Pyrolysis, 111 (2015) 55-63.

[24] J.P. Robinson, C.E. Snape, S.W. Kingman, Developing high power microwave processing as an effective technology for the thermo-chemical conversion of biodegradable municipal waste, in: Technology REsearch and Innovation Fund Project Report, University of Nottingham, 2010.

[25] H.H. Sait, A.A. Salema, Microwave dielectric characterization of Saudi Arabian date palm biomass during pyrolysis and at industrial frequencies, Fuel, 161 (2015) 239-247.

Capítulo 6

Resultados y Discusión: Bloque III

Síntesis de bioplásticos

En este bloque se incluye la Publicación VIII, en la que se analiza la posibilidad de utilizar el syngas producido en la pirólisis de residuos como sustrato de fermentación. Para ello, se ha cultivado la bacteria *Rhodospirillum rubrum* y se ha estudiado su fisiología, así como la producción de un importante biopolímero, el PHB, también llamado poli(3-hidroxibutirato).

6.1 Producción de PHB mediante la fermentación de syngas

La bacteria *Rhodospirillum rubrum* es capaz de sintetizar y acumular biopolímeros (polihidroxialcanoatos) en medios ricos en syngas (DO 2007). En concreto, puede producir el polímero PHB mediante una ruta metabólica consistente en tres reacciones enzimáticas a partir del intermediario de reacción acetil-CoA (Figura 6.1).

Una posibilidad para sintetizar las moléculas del intermediario acetil-CoA es a partir de los componentes del syngas a través de la conocida ruta metabólica *Wood-Ljungdhal*, tal como se expuso en la Introducción (OELGESCHLÄGER 2008).

El mecanismo propuesto para la síntesis de PHB en *Rhodospirillum rubrum* se describe a continuación. La primera etapa para la síntesis de PHB consiste en la condensación de dos moléculas del intermediario acetil-CoA catalizada por 3-ketotiolasa para producir acetoacetil-CoA. A continuación, tiene lugar la reducción de acetoacetil-CoA a 3-hidroxibutiril-CoA, reacción que es catalizada por la acetoacetil-CoA reductasa. Por último, la enzima PHB-sintasa provoca la polimerización de los monómeros de 3-hidroxibutiril-CoA para producir PHB.

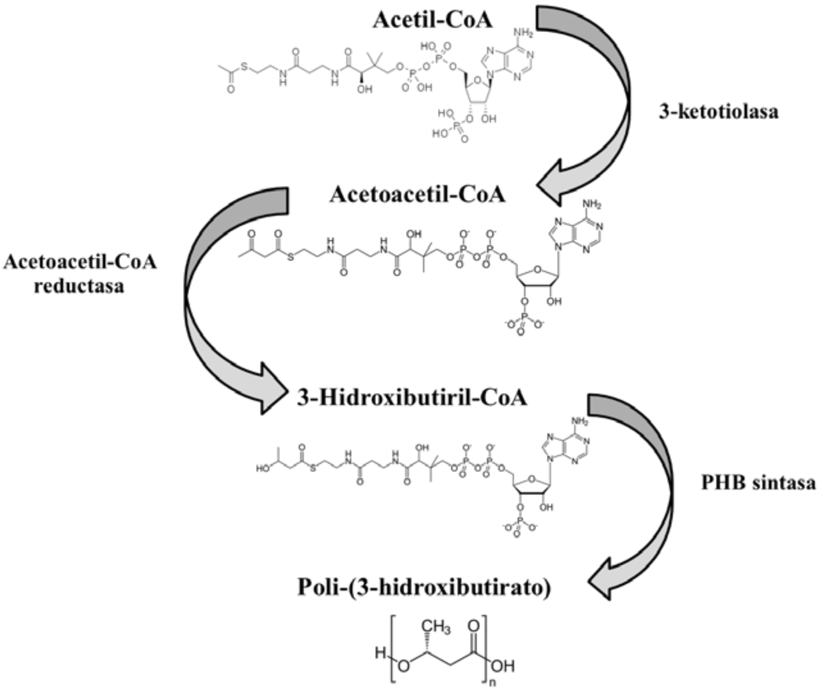


Figura 6.1 Ruta metabólica en *R. rubrum* para la producción de PHB a partir de acetil-CoA

En la **Publicación VIII**, se estudia la fermentación de syngas procedente de la pirólisis convencional y de la pirólisis inducida por microondas de la fracción orgánica de RSU a 800 °C y en ausencia de luz. Para ello, se ha determinado la velocidad de crecimiento de la bacteria en el medio, el consumo de la fuente de carbono, el rendimiento en biomasa y la producción de PHB. Los resultados revelan que la bacteria *R. rubrum* es capaz de llevar a cabo la fermentación de syngas bajo las dos condiciones estudiadas, habiéndose encontrado que la relación **CO/H_2** en el syngas **no es un parámetro determinante en la producción del biopolímero**, lo que supone una ventaja notable sobre los procesos catalíticos convencionales al no tener que ajustar la composición del syngas antes de la etapa catalítica.

Además, a efectos de comparación, se utilizó un syngas artificial con una composición 40% CO, 40% H_2, 10% CO_2 y 10% N_2. A pesar de las diferencias en concentraciones de gases, la **conversión** del **CO** fue prácticamente la misma en los diferentes syngas ensayados, aproximadamente un **40%**, así como la velocidad de crecimiento de las bacterias, aproximadamente 0.07 h^{-1}. Por otra parte, la producción de PHB también es similar en los diferentes casos, aunque algo superior al utilizar el syngas artificial, ya que se obtiene un rendimiento de un 15% en masa de biomasa seca frente a un 10% al usar los dos syngas derivados de la pirólisis del residuo.

Los resultados de esta Publicación VIII a escala de laboratorio sirven de referencia para el estudio de la fermentación de syngas a escala de planta piloto, el cual está siendo llevado a cabo por el grupo de investigación *Bioprocesses and Biomaterials* de *Haute Ecole Spécialisée de Suisse Occidentale* en colaboración con la empresa INFORS, también dentro del marco del proyecto SYNPOL.

Por otra parte, se analizó la posibilidad de eliminar el extracto de levadura del medio de cultivo y se comparó el crecimiento de *R. rubrum* en syngas con luz o en ausencia de la misma. En este caso, se observó que la bacteria solo crece al utilizar syngas obtenido a partir de pirólisis inducida con microondas, pero no en el syngas derivado de la pirólisis convencional (Tabla 6.1). Este hecho demuestra la ventaja de utilizar microondas como método de calentamiento, al menos en el crecimiento de las bacterias.

Tabla 6.1 Velocidad de crecimiento de *R. rubrum* en diferentes gases de síntesis sin añadir extracto de levadura

	Syngas a partir de pirólisis con microondas		**Syngas a partir de pirólisis convencional**	
Condiciones	LUZ	OSCURIDAD	LUZ	OSCURIDAD
μ (h^{-1})	0.031±0.005	0.022±0.005	ND*	ND*

* ND: Crecimiento no detectado

Referencias

Do, Y. S., J. Smeenk, K. M. Broer, C. J. Kisting, R. Brown, T. J. Heindel, T. A. Bobik and A. A. DiSpirito (2007). "Growth of Rhodospirillum rubrum on synthesis gas: Conversion of CO to H2 and poly-β-hydroxyalkanoate." *Biotechnology and Bioengineering* ***97****(2): 279-286.*

Oelgeschläger, E. and M. Rother (2008). "Carbon monoxide-dependent energy metabolism in anaerobic bacteria and archaea." *Archives of Microbiology* ***190****(3): 257-269.*

Publicación VIII

SYNGAS OBTAINED BY PYROLYSIS OF HOUSEHOLD WASTES AS FEEDSTOCK FOR POLYHYDROXYALKANOATE PRODUCTION

En preparación

Syngas obtained by pyrolysis of household wastes as feedstock for polyhydroxyalkanoate production

O. Revelles[1], D. Beneroso[2], J.A. Menéndez[2], A. Arenillas[2], J.L. García[1],
M.A. Prieto[1]

Abstract

Background: The massive production of urban and agricultural wastes arises a clear need for alternative processes of disposal and waste management. The current trends of bio-economy lies on waste revalorization strategies and are committed to the development and implementation of cost-efficient biotechnology processes for the conversion of wastes, into bulk bioproducts such as bioplastics. In this context, the utilization of organic household wastes to produce syngas (H_2+CO), is considered as potential feedstock for polyhydroxyalkanoates (PHA) by syngas fermentation, but the implementation of these strategies still requires many challenges to overcome (e.g. syngas productivity from wastes, mass transfer during the fermentation, presence of growth inhibitors in syngas, bioproduction yield, etc). *Rhodospirillum rubrum* is one of the microorganisms pointed as potential biocatalysts for this process, since it is able to growth in syngas and produces PHA. In this work, the use of *R. rubrum* as microbial cell factory for the production of PHA from household wastes is evaluated.

Results: The organic fraction of municipal solid wastes from a European city (Seville) has been subjected to two different high-temperature pyrolysis processes to produce syngas, i.e. standard pyrolysis and microwave pyrolysis. By determining growth rate, uptake rate, biomass yield and PHA production in *R. rubrum*, we performed a physiological analysis of the process, and the effectiveness of the different pyrolysis techniques was assessed. The results revealed strong syngas fermentation robustness where the ratio CO/H_2 is not a critical parameter for PHA production.

Conclusions: We demonstrate the potential of using biowastes as a primary source for the production of syngas to be applied in the production of biodegradable biopolymers by *R. rubrum*. Microwave induced pyrolysis appears as potential alternative to standard pyrolysis, allowing to reduce cost in terms of energy and time as well as increasing syngas production, while it gives the same syngas fermentation yield as the standard pyrolysis.

Keywords
Microwave pyrolysis, polyhydroxyalkanoates, syngas, waste management, syngas fermentation, *Rhodospirillum rubrum*

Background

The development of a bio-based industry requires the production of chemicals and biomaterials to be settled on the exploitation of non-fossil carbon resources. Municipal solid wastes and other waste resources, such as agricultural residues and sewage sludge contain significant reusable carbon fractions suitable for eco-efficient valorization processes. These resources take advantage over fossil sources as they are abundantly available, do not require additional production costs and are substrates that do not compete with human nutrition.

In this context, thermochemical conversion technologies, other than combustion, such as pyrolysis and gasification are becoming widely accepted as suitable valorization alternatives for non-fossil resources (ARENA, 2012, TANIGAKI, 2013); for instance, the gasification of organic wastes may produce syngas ($CO+H_2$), which as a platform chemical for the production of bulk chemicals such as ethanol, butanol, acetic acid or butyric acid. In this regard, the microbial bioconversion of wastes presents a highly attractive potential nowadays (KOUTINAS, 2014) (DRZYZGA, 2015). Of special interest is the development of the chemical industry devoted to produce biobased and biodegradable plastics, such as polyhydroxyalkanoates (PHA), with many short-life applications (REDDY, 2003, MADBOULY, 2014) and even medical uses (CHEN, 2005). These bioplastics represent an alternative to oil-derived plastics and are degraded by many microorganisms, having gained importance in the last years (KESHAVARZ, 2010, NIKODINOVIC-RUNIC, 2013).

The production of syngas from biomass and organic wastes is mainly accomplished by means of gasification processes, in which the organic substrate is partially oxidized with H_2O or O_2 at high temperature (800 – 1300 °C). However, there are new emerging thermal conversion technologies such as the microwave-induced pyrolysis, which avoids the use of gasifying agents. Compared to conventional pyrolysis processes, in which a free-oxygen atmosphere is used to thermally decompose the organic material at 400 – 800 °C producing large amounts of bio-oil instead of syngas, microwave pyrolysis has been reported as an effective way to increase the waste conversion to H_2 and CO at a lower energy consumption (BUDARIN, 2011, BENEROSO, 2013, BENEROSO, 2014).

Despite the toxicity of CO for most organisms, several microorganisms can use CO as source of carbon and/or energy for growth. In this regard, *Rhodospirillum rubrum*, which is the type strain for the *Rhodospirillaceae* family, is able to growth under a broad variety of conditions, including syngas (DO, 2007). This bacterium can utilize CO under anaerobic conditions as a sole carbon and energy source in the presence or absence of light (KERBY, 1995a). When exposed to CO, both a CODH and a CO-insensitive hydrogenase are induced. Part of the CO_2 produced is assimilated into cell material and the remaining CO_2, along with H_2, are released into the environment. Furthermore, *R. rubrum* is an attractive syngas utilizer for its ability to produce PHA as an energy storage molecule. Do *et al.* studied the growth of *R. rubrum* on seed corn-derived syngas observing the production of poly(3-hydroxybutyrate) (PHB) (DO, 2007). Heinrich *et al.* studied the heterologous overexpression of different genes encoding pyridine nucleotide transhydrogenases (pntAB, udhA) and acetoacetyl-CoA reductases (PhaB) in *R. rubrum* S1, which was also able to synthesize an industrially relevant copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) P(HB-HV) from syngas. This engineered bacterium was pointed out as a promising production strain for syngas derived second generation biopolymers (HEINRICH, 2015).

It is evident that fermentative production of chemicals and biopolymers via refining of waste and by-product streams is a highly important research area with significant prospects for industrial applications (MUNASINGHE, 2010, BENEROSO, 2015b). In this article we show the utilization of household waste-derived syngas for the production of PHB biopolymer. Of particular interest is the innovative use of microwaves to achieve this goal, as this technology provides a syngas able to induce an efficient growth of *R. rubrum* reducing cost in terms of energy and time at a much higher syngas productivity, compared to syngas from conventional pyrolysis technologies. The fermentative robustness of *R. rubrum* is further discussed.

Results and discussion

Effect of syngas derived from pyrolysis on R. rubrum physiology

R. rubrum catalyzes the bioconversion of syngas into PHA and biomass thanks to a CO-dehydrogenase and a CO_2 metabolic fixation system (REVELLES, 2015a, REVELLES, 2015b). The effect of the different syngas composition on the physiology of *R. rubrum* during syngas fermentation has been investigated. Both syngas samples obtained from the previous pyrolysis processes were used as substrate for the growing of *R. rubrum* in light on RRNCO medium (see Methods). The effect of microwave-induced pyrolysis and standard pyrolysis are showed in Table 1 comparatively when using commercial syngas (40% CO, 40% H_2, 10% CO_2 and 10% N_2).

Table 1 Kinetic Growth parameters of *R. rubrum* with syngas in darkness under different syngas composition

Syngas	Physiological Parameters				
	μ	**OD_{600}f**	**$Y_{x/s}$**	**q_s**	**PHB**
Synthetic	0.079 ±0.005	0.8±0.10	0.2±0.05	5.1±0.05	15±2
Microwave pyrolysis	0.071 ±0.005	0.45±0.05	0.31±0.05	3.3±0.40	10±1
Standard pyrolysis	0.074 ±0.010	0.5±0.05	0.42±0.07	5.9±1.00	10±2

μ (h^{-1}), specific growth rate; OD600f (-), optical density at 600 nm; $Y_{x/s}$ (gDW g^{-1}), biomass dry-weight production yield; q_s (mmol gDW^{-1} h^{-1}), carbon source uptake rate; PHB (% cell dry weight). Values represent the mean ± standard deviation of three independent biological replicates.

None difference in the growth rate μ (~0.07 h^{-1}) has been observed among the three syngas tested. However, the biomass productivity ($h^{-1} \cdot OD_{600}$) was significantly higher when synthetic syngas was used for the fermentation process (0.06 vs 0.03) due to the final OD_{600} reached with synthetic syngas (almost twice higher). The lower final OD_{600} observed in culture fed with syngas from microwave-induced pyrolysis and standard pyrolysis could be a consequence of different factors that will need further investigation. For example, the presence of CH_4 and heavier hydrocarbons could have an inhibitory effect in the final growth of the culture. By HPLC analysis the presence of extracellular products was measured and none intermediate was detected. Interestingly, when syngas from microwave-induced pyrolysis was used in the fermentation process slight differences were found for the acetate uptake rate (3.3 ± 0.4 mmol gDW^{-1} h^{-1}) compared to syngas obtained from standard induced pyrolysis and synthetic syngas. Further, the yield of biomass from acetate was approximately the same when either microwave-induced or standard pyrolysis was used during the fermentation processes (see Table 1). Another important factor that can affect the biomass yield of *R. rubrum* during the fermentation process is the lower concentration of the dissolved syngas components needed for the growth, especially CO (Table 2).

Table 2 Gas composition of the different syngas studied

Gases	Syngas composition (vol.%)		
	Synthetic	**Microwave**	**Standard**
CO	40	35	25
CO_2	10	10	25
H_2	40	50	20

The CO consumption along the growth curve for each different syngas fermentation process was monitored (see Methods). Samples at time zero and after 72 h of incubation were taken and the differences in the final CO values were measured using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The data are shown in Table 3. The CO conversion registered was of about 40% for all the cases analyzed, showing a clear CO consumption.

Table 3 CO consumption during syngas fermentation

Gas	% Conversion		
	Synthetic	**Microwave**	**Standard**
CO	39 ± 4	38 ± 10	38 ± 1.7

Biopolymers production from Syngas

Under CO-rich media, *R. rubrum* is known to accumulate PHB (DO, 2007). In the presence of acetate, *Rhodospirillum rubrum* catalyzes the bioconversion of syngas into PHB and biomass using the CO-dehydrogenase, which catalyzes the biological oxidation of CO into CO_2: CO_2 is then assimilated into cell material and PHB by the action of at least two carboxylases from the central carbon metabolism (REVELLES, 2015a). PHB is produced by a biosynthetic pathway consisting of three different enzymatic reactions from acetyl-CoA (Figure 1). The first step is the condensation of two acetyl-CoA molecules into acetoacetylCoA by 3-ketothiolase (PhaA). Then, acetoacetyl-CoA reductase (PhaB) allows the reduction of acetoacetyl-CoA by NADH to 3-hydroxybutyryl-CoA. Finally, the (*R*)-3-hydroxybutyryl-CoA monomers are polymerized into PHB by PHB synthase (PhaC). The depolymerase PhaZ is involved in the polyester hydrolysis for releasing the monomers to the central metabolism (Figure 1).

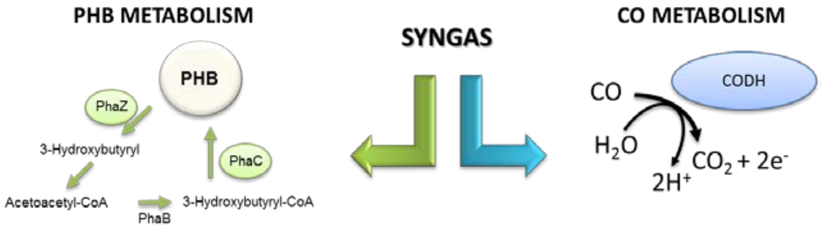


Figure 1 Polyhydroxybutyrate pathway of *R. rubrum*.

Previous studies by Revelles and coworkers (REVELLES, 2015a) have shown that approximately 40% of PHB total carbon backbone comes from the carbon fraction of syngas. However, the use of acetate during syngas fermentation is critical to accumulate PHB. In this study, the effect of syngas composition on PHB accumulation was also determined. The granules of PHB can be clearly observed in *R. rubrum* by transmission electronic microscopy (TEM) (Figure 2) during syngas fermentation when using microwave-induced pyrolysis (Figure 2.A) or standard pyrolysis (Figure 2.B). The % of PHB detected in the three tested conditions was similar being slightly higher for synthetic syngas (see Table 1).

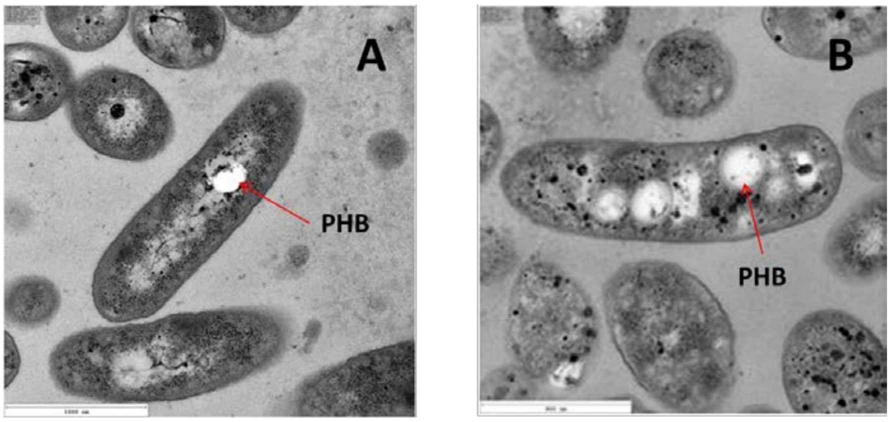


Figure 2 TEM micrography of *R. rubrum* growing in medium RRNCO fed with microwave (**A**) and standard (**B**) pyrolysis derived syngas, both containing PHB granules.

These results show the robustness of *R. rubrum* to accumulate PHB regardless the composition of syngas, as well as, the process used to produce such mixture.

Conclusion

Organic trash provides an excellent resource of biomass that can be utilized for generating commodity products such as biopolymers. Further, it is not exploited as other biomass feedstock such as lignocellulosics. In this work it is demonstrated the potential of these residues for producing syngas as chemical platform for the synthesis of biopolymers. The use of microwave-induced pyrolysis is an advantaged strategy versus standard pyrolysis since allows to reduce time and energy in the process of syngas synthesis, hence reducing cost, and permitting a much higher syngas volumetric productivity, without affecting syngas fermentation. Finally, using *R. rubrum* as biocatalyst expands the potential of this technology due to the higher robustness of this microorganism in the production of PHB during syngas fermentation.

Methods

Production of syngas

An organic fraction from a municipal solid waste provided by ABENGOA BIOENERGÍA from a landfill in Sevilla (Spain) was used in this study. This fraction was taken from an organic fraction from municipal solid waste and was subjected to removal of moisture and inert solids, such as glass or metals. After this pre-treatment, the fraction size was reduced to 1-3 mm. The characterization of the sample can be found in (BENEROSO, 2015a). To prepare the different syngas, the biowaste was subjected to pyrolysis at 800 °C by means of two different technologies: a standard pyrolysis in an electrical furnace and a microwave-induced pyrolysis in a microwave oven. The corresponding methodology has already been described in (BENEROSO, 2015a).

Culture Conditions

Starter cultures of *R. rubrum* (ATCC 11170) were grown under anaerobic conditions on RRNCO medium (KERBY) supplemented with 15 mM fructose at 30 ºC until stationary phase (OD_{600} 1.5). Briefly, RRNCO medium contains per liter of distilled water: 2 µg of biotin, 10 mL of a chelated iron-molybdenun solution (0.28 g of H_3BO_3, 2 g of Na_2EDTA, 0.4 g of ferric citrate, and 0.1 g of Na_2MoO_4 per liter of distilled water), 250 mg of $MgSO_4$ $7H_2O$, 132 mg of $CaCl_2$ $2H_2O$, 1 g of NH_4Cl, 20 µM $NiCl_2$, 1.0 g of yeast extract, 2.1 g of MOPS and 0.82 g of sodium acetate. Prior inoculation we added anoxic solutions of 1.91 M potassium phosphate (pH 7.0) (0.05 mL), of 1% Na_2S $9H_2O$ (0.1 mL) and of 0.5 M $NaHCO_3$ (pH 8.0) (0.25 mL). This culture was used as preinoculum for syngas fermentation. Syngas experiments were done in RRNCO supplemented with 10 mM acetate. Syngas fermentation was carried out in bottles of 100 mL containing 20 mL of RRNCO medium. Prior adding syngas the closed degasified serum vials were subjected to 1 min vacuum-purge and the atmosphere were further saturated with syngas to 1 atm of pressure. This procedure was repeated every day for syngas feeding (REVELLES, 2015b). When it was mentioned a commercial syngas provide by Air Liquide was used, this syngas is made out of 40% CO, 40% H_2, 10% CO_2 and 10% N_2 (Air Liquide, www.airliquide.com).

Growth characterization

The growth rate (µ) was determined from log-linear regression of time-dependent changes in optical density at 600 nm (OD_{600}), measured with a spectrophotometer (UV-VIS Spectophotometer Shimatzu UV mini 1240) with appropriate dilutions when needed. Acetate was quantified using an HPLC system (GILSON), equipped with an Aminex HPX-87H column. A mobile phase of 2.5 mM H_2SO_4 solution at a 0.6 mL/min flow rate was used and the column operated at 40 ºC. Rates of disappearance and/or appearance of substrates and products in the culture supernatants were determined (REVELLES, 2015b). To calculate specific biomass yields, correlation factors between cell dry weights and optical density (g_{CDW}/OD_{600}) were established for each condition.

PHB/PHA quantification by GC analysis

PHB/PHA was isolated and purified using cells harvested from different growing phases by centrifugation at 8,000 x *g* for 15 min at 4 °C (Eppendorf Centrifuge 5810R). Cells were then washed twice in distilled water and lyophilized in Cryodos-50 (Telstar, Terrasa, Spain) at -56 °C and 10^{-2} mbar. Further, PHB monomer composition and cellular PHB content were determined by gas chromatography (GC) of the methanolysed polyester. Methanolysis was carried out by suspending 5–10 mg of lyophilized cells in 0.5 mL of chloroform and 2 mL of methanol containing 15% sulfuric acid and 0.5 mg mL^{-1} of 3-methylbenzoic acid (internal standard), followed by an incubation at 80 °C for 7 h. After cooling, 1 mL of demineralized water and 1 mL of chloroform were added and the organic phase containing the methyl esters was analyzed by GC (DE EUGENIO, 2010). A standard curve from 0.5 to 2 mg of PHB (Sigma Cat: 36,350-2) was used to interpolate sample data.

CO analysis

The CO was analyzed by using a gas chromatograph (Agilent 7890A GC) equipped with a thermal conductivity detector (TCD) and two columns connected in series (80/100 Porapak Q and 70/80 Molesieve 13X) (REVELLES, 2015b). The initial oven temperature was 30 °C, which was maintained with an isothermic step of 5 min. It was then programmed with a rate of 25 °C min^{-1} until reached 180 °C. The injector and detector temperatures were 150 and 250 °C, respectively. Helium (Air Liquide, www.airliquide.com) was used as carrier gas. Samples were taken from the headspace of the culture a different times using a tight gas syringe and added to HS-vials, previously degasified with helium. Prior to the measurements the gas analyzer was calibrated by a standard gas and a calibration curve was established. The calculation for gas concentration was carried out using the GC data analysis software (ChemStation rev. B.04.03-SP1; Agilent Technologies, Inc.).

Author's contributions

DB designed the study, carried out syngas pyrolysis and wrote the manuscript. OR designed the syngas fermentation, physiological experiments and wrote the manuscript. AP, JLG, AA and JAM conceived the whole study and coordinated the work. All authors read and approved the final manuscript.

Author details

[1]Centro de Investigaciones Biológicas, CSIC, C/ Ramiro de Maeztu, 9, 28040 Madrid, Spain; [2]Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain.

Acknowledgments

This work has been funded by the EU project SYNPOL (grant agreement n° 311815) under the European Union's Seventh Framework Programme. D. B. also acknowledges the financial support received from PCTI and FICYT of the Government of the Principado de Asturias. The technical support of Inmaculada Calvillo and Ana Valencia is very much appreciated.

Competing interests

The authors declare they have no competing interests.

References

- Arena, U. (2012). "Process and technological aspects of municipal solid waste gasification. A review." Waste Management **32**(4): 625-639.
- Beneroso, D., J. M. Bermúdez, A. Arenillas and J. A. Menéndez "Influence of carrier gas on microwave-induced pyrolysis." Journal of Analytical and Applied Pyrolysis(0).
- Beneroso, D., J. M. Bermúdez, A. Arenillas and J. A. Menéndez (2013). "Microwave pyrolysis of microalgae for high syngas production." Bioresource Technology **144**: 240-246.
- Beneroso, D., J. M. Bermúdez, A. Arenillas and J. A. Menéndez (2014). "Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste." Journal of Analytical and Applied Pyrolysis **105**(0): 234-240.
- Beneroso, D., J. M. Bermúdez, A. Arenillas and J. A. Menéndez (2015a). "Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics." Journal of Analytical and Applied Pyrolysis **111**(0): 55-63.
- Beneroso, D., J. M. Bermúdez, A. Arenillas and J. A. Menéndez (2015b). Microwave Pyrolysis of Organic Wastes for Syngas-Derived Biopolymers Production. Production of Biofuels and Chemicals with Microwave. Z. Fang, J. R. L. Smith and X. Qi, Springer Netherlands. **3:** 99-127.
- Budarin, V. L., P. S. Shuttleworth, J. R. Dodson, A. J. Hunt, B. Lanigan, R. Marriott, K. J. Milkowski, A. J. Wilson, S. W. Breeden, J. Fan, E. H. K. Sin and J. H. Clark (2011). "Use of green chemical technologies in an integrated biorefinery." Energy & Environmental Science **4**(2): 471-479.

- Clark, D. E. and W. H. Sutton (1996). "Microwave Processing of Materials." Annual Review of Materials Science **26**(1): 299-331.
- Chen, G.-Q. and Q. Wu (2005). "The application of polyhydroxyalkanoates as tissue engineering materials." Biomaterials **26**(33): 6565-6578.
- de Eugenio, L. I., B. Galan, I. F. Escapa, B. Maestro, J. M. Sanz, J. L. Garcia and M. A. Prieto (2010). "The PhaD regulator controls the simultaneous expression of the pha genes involved in polyhydroxyalkanoate metabolism and turnover in Pseudomonas putida KT2442." Environ Microbiol **12**(6): 1591-1603.
- Do, Y. S., J. Smeenk, K. M. Broer, C. J. Kisting, R. Brown, T. J. Heindel, T. A. Bobik and A. A. DiSpirito (2007). "Growth of Rhodospirillum rubrum on synthesis gas: Conversion of CO to H2 and poly-β-hydroxyalkanoate." Biotechnology and Bioengineering **97**(2): 279-286.
- Drzyzga O., Revelles O., Durante-Rodríguez G., Díaz E., García J.L. and Prieto M.A. (2015). "New challenges for syngas fermentation: towards production of biopolymers." Journal of Chemical Technology and Biotechnology DOI: 10.1002/jctb.4721
- Fernández, Y. and J. A. Menéndez (2011). "Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes." Journal of Analytical and Applied Pyrolysis **91**(2): 316-322.
- Heinrich, D., M. Raberg and A. Steinbüchel (2015). Synthesis of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) from unrelated carbon sources in engineered Rhodospirillum rubrum.
- Kerby, R. L., P. W. Ludden and G. P. Roberts (1995a). "Carbon monoxide-dependent growth of Rhodospirillum rubrum." Journal of Bacteriology **177**(8): 2241-2244.
- Kerby, R. L., P. W. Ludden and G. P. Roberts (1995b). "Carbon monoxide-dependent growth of Rhodospirillum rubrum." J Bacteriol **177**(8): 2241-2244.
- Keshavarz, T. and I. Roy (2010). "Polyhydroxyalkanoates: bioplastics with a green agenda." Current Opinion in Microbiology **13**(3): 321-326.
- Koutinas, A. A., A. Vlysidis, D. Pleissner, N. Kopsahelis, I. Lopez Garcia, I. K. Kookos, S. Papanikolaou, T. H. Kwan and C. S. K. Lin (2014). "Valorization of industrial waste and by-product streams via fermentation for the production of chemicals and biopolymers." Chemical Society Reviews **43**(8): 2587-2627.
- Madbouly, S. A., J. A. Schrader, G. Srinivasan, K. Liu, K. G. McCabe, D. Grewell, W. R. Graves and M. R. Kessler (2014). "Biodegradation behavior of bacterial-based polyhydroxyalkanoate (PHA) and DDGS composites." Green Chemistry **16**(4): 1911-1920.
- Menéndez, J. A., A. Domínguez, Y. Fernández and J. J. Pis (2007). "Evidence of Self-Gasification during the Microwave-Induced Pyrolysis of Coffee Hulls." Energy & Fuels **21**(1): 373-378.
- Munasinghe, P. C. and S. K. Khanal (2010). "Biomass-derived syngas fermentation into biofuels: Opportunities and challenges." Bioresource Technology **101**(13): 5013-5022.

- Nikodinovic-Runic, J., M. Guzik, S. T. Kenny, R. Babu, A. Werker and K. E. O Connor (2013). Chapter Four - Carbon-Rich Wastes as Feedstocks for Biodegradable Polymer (Polyhydroxyalkanoate) Production Using Bacteria. Advances in Applied Microbiology. S. Sima and M. G. Geoffrey, Academic Press. **Volume 84:** 139-200.
- Reddy, C. S. K., R. Ghai, Rashmi and V. C. Kalia (2003). "Polyhydroxyalkanoates: an overview." Bioresource Technology **87**(2): 137-146.
- Revelles, O., P. Millard, J. P. Nougayrede, U. Dobrindt, E. Oswald, F. Letisse and J. C. Portais (2013). "The carbon storage regulator (Csr) system exerts a nutrient-specific control over central metabolism in Escherichia coli strain Nissle 1917." PLoS One **8**(6): e66386.
- Revelles O., Tarazona N., García J.L. and Prieto M.A. (2015a). "Carbon road map: From Syngas to PHA in Rhodospirillum rubrum." Enviromental Microbiology. In press.
- Revelles O., Calvillo I., Prieto A. and Prieto M.A. (2015b). "Syngas fermentation for polyhydroxyalkanoate production in Rhodospirillum rubrum." Hydrocarbon and Lipid Microbiology Protocols. Handbooks. In press.
- Tanigaki, N., Y. Fujinaga, H. Kajiyama and Y. Ishida (2013). "Operating and environmental performances of commercial-scale waste gasification and melting technology." Waste Management & Research **31**(11): 1118-1124.

Capítulo 7

Conclusiones

Esta memoria, y las publicaciones presentadas en ella, muestran los resultados derivados del estudio del proceso de pirólisis inducido por microondas de diferentes residuos orgánicos con el fin de producir un syngas adecuado para su posterior utilización en la síntesis de bioplásticos. A continuación se presentan las conclusiones más relevantes derivadas de dicho trabajo.

Producción de syngas a partir de sustratos sólidos orgánicos

- ✓ Se pueden utilizar determinados **residuos orgánicos** (fracción orgánica de RSU, residuos agrícolas y lodos de depuradora) para producir **syngas** mediante tecnologías de **pirólisis**.

- ✓ La pirólisis inducida por **microondas** de residuos orgánicos se puede utilizar para producir un **syngas de alta calidad**, es decir, con una concentración superior al 90 vol.% de H_2 + CO, incluso a temperatura relativamente baja (400 ºC).

- ✓ La producción de syngas se favorece a **mayores temperaturas** (800 ºC). Además, la velocidad de calentamiento en el caso de la pirólisis con microondas, al ser más alta que durante una pirólisis convencional, hace que se favorezca la **producción** de gas.

- ✓ Las **microalgas** también son un sustrato muy adecuado para producir syngas a partir de la pirólisis de las mismas con microondas.

- ✓ Al presentar una calidad excepcionalmente alta con una concentración prácticamente nula en hidrocarburos, el syngas procedente de la pirólisis con microondas puede utilizarse en producción de **bioplásticos** mediante la fermentación del mismo.

- ✓ La concentración de compuestos peligrosos, como los PAH, en los aceites procedentes de la pirólisis de residuos dependen tanto de la naturaleza de los mismos como del método de calentamiento. En general, los residuos muy heterogéneos, como los casos de la fracción orgánica de RSU o los lodos de depuradoras, producen menor concentración de PAH cuando se utiliza radiación microondas.

Parámetros influyentes en la pirólisis con microondas

- ✓ Para llevar a cabo la pirólisis con microondas de residuos orgánicos, que son transparentes a la radiación microondas, es necesario mezclar los residuos con un **material captador de microondas** para inducir la pirólisis.

- ✓ Cuanto mayor es la cantidad de captador añadida, éste se calienta más rápidamente y es el que absorbe prácticamente toda la radiación microondas y, por conducción, convección y radiación, transfiere el calor al residuo orgánico. De esta forma, las microondas no penetran hasta el centro del mismo. Sin embargo, si la cantidad de captador es menor, las microondas pueden penetrar en todo el volumen de residuo y, aunque en principio el calentamiento es más lento, también es más uniforme.

- ✓ La adición de un material captador permite reducir el consumo energético de la pirólisis, ya que la energía necesaria para inducir la pirólisis es menor.

- ✓ La **humedad** del residuo orgánico de partida influye en la producción de syngas mediante pirólisis inducida por microondas. Existe una humedad óptima a la cual la concentración de H_2+CO en la fracción gaseosa se maximiza.

En el caso del residuo estudiado, la fracción orgánica de RSU, esta humedad fue del 12%.

- ✓ El rendimiento en fracción gaseosa es mayor cuanto mayor es la humedad del residuo inicial debido a que dicho contenido en agua favorece las reacciones de gasificación del sólido carbonoso y de reformado de los aceites. Además, la producción de syngas se ve más favorecida en el caso del residuo húmedo a mayores concentraciones de captador, al contrario de lo que ocurre al usar el residuo seco.

- ✓ El **gas portador**, N_2 o He, utilizado durante la pirólisis con microondas de residuos no parece tener una influencia significativa en la producción de syngas. Es posible llevar a cabo la pirólisis con microondas de residuos sin utilizar un gas portador, sin que ello comprometa la calidad del syngas.

- ✓ Las **propiedades dieléctricas** de las mezclas de fracción orgánica de RSU con el captador carbonoso se mantienen aproximadamente constantes, con tendencia disminuir al acercarse a los 400 °C. A partir de 600 °C, dichas propiedades aumentan radicalmente hasta una permitividad de $\varepsilon^* = 56.1 - 93.8j$, en el caso de la mezcla 0.3:1, y de $\varepsilon^* = 119.9 - 130.7j$, en el caso de la mezcla 0.6:1, a 800 °C.

- ✓ Al añadir captador al residuo, se reduce la temperatura a la que aumentan exponencialmente las pérdidas de calor. Además, la conversión de energía microondas en calor es casi 20 veces superior a temperatura ambiente.

Síntesis de bioplásticos

- ✓ La bacteria *R. rubrum* es capaz de llevar a cabo la fermentación de syngas procedente tanto de pirólisis convencional como de pirólisis con microondas de la fracción orgánica de RSU a 800 °C. Por tanto, el *ratio* CO/H_2 en el syngas no es un parámetro determinante en la producción del biopolímero. Sin embargo, se demostró en el Bloque I de esta Tesis que la producción de syngas es bastante mayor en el caso de utilizar la pirólisis con microondas, lo que supone una ventaja competitiva respecto a la pirólisis convencional para ser integrada en la producción de bioplásticos.

- ✓ La **conversión** del CO fue prácticamente la misma en los diferentes syngas, aproximadamente un 40%, así como la velocidad de crecimiento de las bacterias 0.07 h^{-1}.

- ✓ La producción de **PHB** también es similar en los diferentes casos, aproximadamente un 10% en masa respecto a la biomasa seca producida.

- ✓ En ausencia de extracto de levadura en el medio de fermentación, el syngas procedente de pirólisis de microondas parece ser el único que posibilita el crecimiento de la bacteria *R. rubrum*.

Anexo

En este **Anexo** se adjunta como **Publicación IX** un capítulo del libro "*Production of Biofuels and Chemicals with Microwave*", titulado *Microwave Pyrolysis of Organic Wastes for Syngas-Derived Biopolymers Production*. En el mismo, se lleva a cabo un estudio del arte acerca del uso y de la versatilidad de la tecnología de microondas aplicada a la pirólisis para producir syngas.

Así mismo, se incluye el **Material Suplementario** de la Publicación I, Publicación II, Publicación III y Publicación VII.

MICROWAVE PYROLYSIS OF ORGANIC WASTES FOR SYNGAS-DERIVED BIOPOLYMERS PRODUCTION

Biofuels and Biorefineries

3 (99-127)

Año 2015

Chapter 6

Microwave Pyrolysis of Organic Wastes for Syngas-Derived Biopolymers Production

D. Beneroso, J.M. Bermúdez, A. Arenillas and J.A. Menéndez

Abstract Bioplastics production is a growing industry that offers an alternative to that of conventional fossil-derived plastics. Polyhydroxyalkanoates are biopolymers whose thermo-mechanical properties can be comparable to those of conventional plastics. Polyhydroxyalkanoates can be produced through the bacterial fermentation of carbon substrates, although to be commercially viable cheap renewable resources such as syngas ($CO + H_2 + CO_2$) from waste pyrolysis are required. Microwave pyrolysis has been demonstrated to have the potential of maximising both the gas production and syngas concentration. Hence it is an appropriate thermochemical route for further syngas fermentation. A combination of different factors, such as the type of waste, the moisture content, the pyrolysis temperature or the use of a microwave receptor makes microwave pyrolysis highly versatile, so that the syngas produced can be virtually tailored to the specific requirements of the bacteria.

Keywords Microwave heating · Pyrolysis · Syngas · Biopolymers · Polyhydroxyalkanoates · Waste valorisation

---

D. Beneroso · J.M. Bermúdez · A. Arenillas · J.A. Menéndez (✉)
Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain
e-mail: angelmd@incar.csic.es

D. Beneroso
e-mail: daniel.beneroso@incar.csic.es

J.M. Bermúdez
e-mail: jmbermudez@incar.csic.es

A. Arenillas
e-mail: aapuente@incar.csic.es

Z. Fang et al. (eds.), *Production of Biofuels and Chemicals with Microwave*,
Biofuels and Biorefineries 3, DOI 10.1007/978-94-017-9612-5_6

6.1 Introduction to Biopolymers: Classification, Uses and Production

The exploitation of fossil fuels for transportation purposes and for the production of commodity chemicals is deeply engrained in our society, but it is becoming increasingly evident that the continued use of these resources at current rates is unsustainable. The main drawbacks of fossil fuels are their limited reserves and their negative environmental impact as the combustion of these fuels releases not only CO_2 but other pollutants, such as sulphur and nitrogen oxides.

In 2012, the production of polymeric materials amounted to 288 Mt worldwide (mainly polyethylenes, polypropylenes, polyvinylchloride and polyurethane), more than 99 % of which originated from fossil resources [1]. The European Union alone produced ca. 20 % (i.e., 57 Mt) of these materials, of which more than 25 million tons were either landfilled or disposed of directly into the environment [2], causing serious environmental problems due to their high resistance to degradation. Therefore, there is a clear need for alternative processes of disposal via the development and application of industrial biotechnologies based on the conversion of renewable raw materials into sustainable, cost-efficient bulk bioproducts such as new biopolymers.

Biopolymers not only consist of bio-based polymers (i.e., polymers synthesised from biomass or renewable resources), but also of biodegradable materials even if synthesised from fossil resources. Figure 6.1 shows a common way of classifying biopolymers with examples of different types.

Polymers that are both bio-based and biodegradable are the most practical from the point of view of disposal since they can be degraded by microorganisms. Polyhydroxyalkanoates, such as PHB *poly(3-hydroxybutyrate)* or PHBV *poly(3-hydroxybutyrate-co-3-hydroxyvalerate)*, are well-known examples of biobased biodegradable polymers. They can be used in injection moulding, extrusion or paper coating, and in numerous other applications such as packaging, cutlery or office supplies [3]. They have also been successfully used in biomedical uses such as tissue repair and regeneration or drug delivery systems [4, 5]. Since polyhydroxyalkanoates are polyesters with a highly versatile structure, the possibilities of application are numerous. Their thermo-mechanical properties can even be tailored to make them comparable to conventional plastics [6, 7]. Table 6.1 shows a comparison between some polyhydroxyalkanoates and typical fossil-based polymers. Short chain-length polymers, such as PHB, are typically rigid and brittle, while medium chain-length polymers, such as PHBV, can be more elastic, but usually have less mechanical strength. As can be seen from Table 6.1, the melting point and tensile strength of polypropylene and PHB are very close, although the elongation to break differs a lot. However, the addition of 4-hydroxybutyrate to PHB allows a much higher elongation to break, close to that of polypropylene, although slightly reducing the tensile strength. In short, the thermo-mechanical properties can be tuned by blending different monomers in the appropriate proportion.

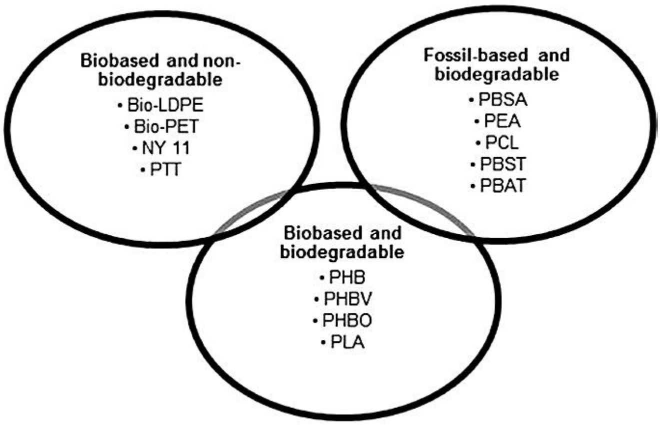


Fig. 6.1 Classification of biopolymers. *LDPE* low-density polyethylene; *PET* poly(ethylene-terephthalate); *NY 11* nylon 11; *PTT* polytrimethylene terephthalate; *PHB* poly(3-hydroxy-butyrate); *PHBV* poly(3-hydroxybutyrate-co-3-hydroxyvalerate); *PLA* polylactide; *PHBO* poly(hydroxybutyrate-co-hydroxyoctanoate); *PBSA* poly(butylene-succinate-co-adipate); *PEA* polyesteramide; *PCL* polycaprolactone; *PBST* poly(butylene-succinate-co-terephthalate); *PBAT* aromatic copolyesters

Table 6.1 Comparison of some thermo-mechanical properties of biopolymers from biopolymers and fossil-based polymers P(3HB-co-20 mol% 3HV): poly(3-hydroxybutyrate-co-3-hydroxy-valerate) containing 20 mol% of hydroxyvalerate; P(3HB-co-16 mol% 4HB): poly(3-hydroxybutyrate-co-4-hydroxybutyrate) containing 16 mol% of hydroxybutyrate

Polymer	Melting temperature (°C)	Glass transition temperature (°C)	Tensile strength (MPa)	Elongation to break (%)
PHB	180	4	40	5
P(3HB-co-20 mol% 3HV)	145	−1	20	50
P(3HB-co-16 mol% 4HB)	150	−7	26	444
Polypropylene	176	−10	38	400
Low-density polyethylene	130	−30	10	620

According to a *European Bioplastics* report [8], biopolymers are economically innovative and offer great potential for further economic growth along the value added chain, especially in Asia and South America. In 2009, biopolymers production amounted to 0.25 Mt worldwide, increasing in 2012 up to 1.40 Mt and with a projected production target of 6.19 Mt for 2017 and it has been predicted that the biopolymers industry will be worth $5 billion by 2018 [9]. Furthermore, the *European*

Bioplastics report estimates that bio-based polylactic acid and polyhydroxyalkanoates will spearhead the increased production capacity of biodegradable biopolymers.

Polyhydroxyalkanoates can be produced biologically, since some plant tissues are able to generate them through photosynthesis [10, 11], or through biosynthesis, though the former method still presents considerable challenges. Fermentation involves filling a bioreactor with a mineral medium and inoculating it with a seed that contains the microorganism. It is also necessary to provide a carbon source to allow cell growth and polyhydroxyalkanoate production. At present, high cost substrates such as sucrose, fructose, glucose, methanol or butyrate are used, and account for as much as 50 % of the total production cost of polyhydroxyalkanoates. For this reason, the use of cheaper renewable resources as substrates such as glycerol waste from biodiesel production or cellulose hydrolysates from paper industry wastewater is essential to ensure the commercial viability of the process [12].

Another interesting option consists of the use of syngas as will be discussed in the Sect. 6.2, since CO and CO_2 containing in the syngas could be used as carbon source to allow for the production of polyhydroxyalkanoates.

6.2 Biopolymers from Syngas Fermentation

Although biorefineries represent an alternative to fossil organic material-based petrochemical refineries, in some cases innovative processing methods are required for the more complex wastes. Organic waste is abundantly available (e.g. in municipal solid wastes, agricultural residues or sewage sludge), does not entail additional production costs and is a substrate that does not compete with human nutrition [13]. For these reasons, organic wastes are a potential feedstock for value-added products and are often insufficiently exploited. For example, their pyrolysis and gasification is able to yield syngas ($CO + H_2$), which is a valuable commodity. Despite the world market for syngas being dominated by the ammonia industry and the production of H_2 for use in refineries, the chemical conversion of syngas components can be expensive and highly susceptible to catalyst poisoning, with the consequent limitations on the chemical yields [14]. This has encouraged research into microorganisms that could be used to convert CO into different multicarbon compounds. Research related to the fermentative production of chemicals from syngas has greatly increased in recent years, especially in relation to the genetic manipulation of microorganisms to enhance the production of specifically targeted chemicals and to optimise reactors and fermentation media. Table 6.2 shows the production of valuable chemicals by different microorganisms which are able to ferment syngas. As can be seen, some microorganisms, such as *Clostridium ljungdahlii* or *Clostridium carboxidivorans*, are able to metabolise different syngas compositions and produce the same final products, thus making the fermentation step a very versatile one.

Table 6.2 Production of valuable chemicals using syngas fermentation

Microorganism	H_2 vol%	CO vol%	CO_2 vol%	H_2/CO	CO/CO_2	H_2/CO_2	Products	Reference
Acetogenium kivui	14	13	5	1.08	2.60	2.80	Acetate	[24]
Butyribacterium methylotrophicum	0	100	0	0.00	–	–	Acetate and butyrate	[25]
Butyribacterium methylotrophicum	0	100	0	0.00	–	–	Butyrate	[26]
Butyribacterium methylotrophicum	0	70	30	0.00	2.33	0.00	Acetic acid, ethanol and butyric acid	[27]
Clostridium aceticum	4	78	0	0.05	–	–	Acetate	[28]
Clostridium autoethanogenum	10	20	20	0.50	1.00	0.50	Acetate and ethanol	[29]
Clostridium carboxidivorans	0	25	15	0.00	1.67	0.00	Acetate, ethanol and butanol	[30]
Clostridium carboxidivorans	80	0	20	–	0.00	4.00	Acetate, ethanol, butyrate and butanol	[31]
Clostridium carboxidivorans	0	70	6	0	11.70	0	Acetate, ethanol, butyrate and butanol	[31]
Clostridium ljungdahlii	20	55	10	0.36	5.50	2.00	Acetate and ethanol	[32]
Clostridium ljungdahlii	18	55	11	0.33	5.21	1.71	Acetate and ethanol	[33]
Clostridium ljungdahlii	10	20	20	0.50	1.00	0.50	Acetate and ethanol	[29]
Clostridium ljungdahlii	20	55	10	0.36	5.50	2.00	Acetate and ethanol	[15]
Clostridium ljungdahlii	75	0	25	–	0.00	3.00	Acetate and ethanol	[34]
Clostridium ljungdahlii	0	80	20	0.00	4.00	0.00	Acetate and ethanol	[34]
Clostridium ljungdahlii	2	44	22	0.05	2.00	0.10	2,3-butanediol	[21]
Clostridium ljungdahlii ERI2	14	13	5	1.08	2.60	2.80	Acetate and ethanol	[24]
Clostridium ljungdahlii ERI2	17	14	4	1.21	3.50	4.25	Acetic acid	[24]

(continued)

Table 6.2 (continued)

Microorganism	H_2 vol%	CO vol%	CO_2 vol%	H_2/CO	CO/CO_2	H_2/CO_2	Products	Reference
Clostridium ljungdahlii isolate O-52	50	45	0	1.11	–	–	Acetic acid and ethanol	[24]
Clostridium ragsdalei	5	20	15	0.25	1.33	0.33	Acetate, ethanol, propanol and butanol	[35]
Clostridium ragsdalei	5	20	15	0.25	1.33	0.33	Acetate and ethanol	[36]
Eubacterium limosum	0	80	20	0.00	4.00	0.00	Acetate and butyrate	[17]
Eubacterium limosum	0	100	0	0.00	–	–	Acetate, ethanol and butyrate	[37]
Moorella sp.HUC22-1	80	0	20	–	0.00	4.00	Acetate	[38]
Rhodospirillum rubrum	9	17	16	0.51	1.06	0.54	Polyhydroxybutyrate and polyhydroxyvalerate	[18]

Gas concentrations are adjusted to standard temperature and pressure. H_2/CO, CO/CO_2 and H_2/CO_2 are molar ratios

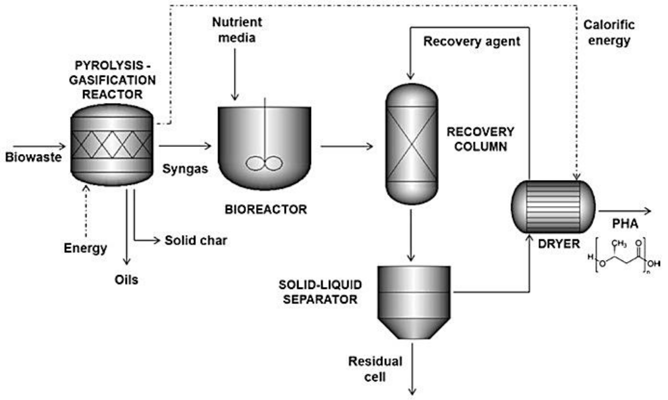


Fig. 6.2 Integrated pyrolysis and gasification of biowaste for the polyhydroxyalkanoates (*PHA*) production process through syngas fermentation

Although syngas fermentation has been proposed as an attractive conversion route to produce bulk chemicals such as ethanol, acetate or butyrate [15–17], and is exploited by companies such as *Coskata*, *INEOS Bio* or *LanzaTech*, no large-scale projects for producing biopolymers by this route have been undertaken. The use of syngas as substrate to produce polyhydroxyalkanoates is a truly novel research area, and this explains why so little information is available. Only the growth of *Rhodospirillum rubrum* on corn seed-derived syngas[1] (8.8 % H_2, 17.2 % CO and 16.3 % CO_2) has been studied, resulting in a mixture of 86 % poly(3-hydroxybutyrate) and 14 % poly(3-hydroxyvalerate) [18]. The polyhydroxyalkanoates content reached to 38 % of the cellular dry weight. The results of that research study were used to develop a techno-economic model to demonstrate the feasibility of polyhydroxyalkanoates production from biomass-derived syngas fermentation, concluding that the production of polyhydroxyalkanoates by syngas fermentation was \$2–\$4 cheaper to produce per kilogram than by sugar fermentation [19]. A US patent that involves the photoconversion of syngas to biodegradable plastics was granted to Weaver and Maness [20]; *Rhodobacter* sp. CBS were found to grow in mixtures of $H_2 + CO$ in an acetate medium with a limited amount of N_2, accounting for a very high PHB content of about 79 % of their dry weight.

---

[1] The gas fraction from pyrolysis and gasification can be mainly composed by syngas, being mixed with other gases such light hydrocarbons. Although syngas is strictly known as the mixture of H_2 and CO, the CO_2 resulting from pyrolysis of biowaste can also be fermented by some bacteria to produce biopolymers. Therefore, from now on, syngas will be referred to the mixture of H_2, CO and CO_2, being the gas fraction rich in syngas if the syngas concentration is greater than 80 vol%.

Another close alternative consists of the syngas fermentation to yield building blocks for further polyhydroxyalkanoates synthesis through their polycondensation. These blocks are mainly diacids and dialcohols such as succinic acid or 2,3-butanediol obtained from *Clostridium autoethanogenum, Clostridium ljungdahlii* or *Clostridium ragsdalei* [21].

Thus, organic waste pyrolysis and gasification followed by microbial fermentation processing has become a promising industrial procedure [13], and is schematically represented in Fig. 6.2. The downstream process, after the syngas fermentation bioreactor, consists in isolating the polyhydroxyalkanoates from the residual cell mass by means of a recovery agent. Although several agents have been proposed, such as 1,2-polypropylene carbonate or MTBE, extraction of the biopolymer with chloroform appears to be a commonly used approach as it has been reported to offer certain advantages over the other extraction methods, although on the downside it is not environmentally friendly [22]. Once the recovery agent has been mixed with the bioreactor output stream, the residual cell mass is separated in a solid-liquid separator and the stream containing polyhydroxyalkanoates can then be subjected to a drying process to yield the resulting product.

6.3 Syngas from the Microwave Pyrolysis of Organic Wastes

At present, the most widespread process for the production of syngas is the reforming of methane (natural gas) with steam, although this suffers from several drawbacks, such as the high-energy costs due to the endothermicity of the reforming reaction, the use of metallic catalysts or the need for an additional unit after the reformer to adjust the H_2/CO ratio depending on the intended use of the syngas produced. These disadvantages have encouraged efforts towards finding different ways of producing syngas such as the gasification of organic wastes. Moreover, although the current methods of syngas production from organic wastes are mainly based on steam gasification processes, novel operating conditions in the pyrolysis process could contribute to maximising the yield, and so, to a reduction in costs since no steam supply would be necessary.

Pyrolysis involves heating organic matter in an inert atmosphere (400–800 °C), to produce a volatiles fraction, containing gases (which, depending on the material being pyrolysed, may include syngas) and oil components, and a carbon-rich solid residue, which is usually referred to as *char*. To prevent combustion reactions, a previous inertisation of the reactor by means of N_2 is usually carried out both at lab-scale and industrially. However, once the pyrolysis has started it is a common practice in industry to recirculate the non-condensable gases from the outlet of the condensing system [23]. Two main stages can be distinguished in the pyrolysis process: primary pyrolysis, which involves the devolatilisation of the material (decarboxylation, dehydrogenation and dehydration); and secondary pyrolysis, which involves the thermal and catalytic cracking of the heavy compounds and char into light gases [39].

The yields of the pyrolysis products depend on the operating conditions (essentially temperature, heating rate and residence time of the volatiles in the hot zone), and on the hydrodynamics of the reactor employed. The operating temperature, which is related to the energy needed to break up the bonds in molecules also influences possible secondary reactions between the compounds generated and it therefore determines the final gas composition. In addition, the higher the heating rate is, the more quickly the decomposition reactions take place. Consequently, lower process temperatures and heating rates and longer volatiles residence times will favour the production of char; high temperatures and heating rates and longer residence times will increase the conversion to gas, while moderate temperatures and short volatiles residence times are required to produce oils [40]. Figure 6.3a shows a typical microwave pyrolysis unit at lab-scale, consisting of a magnetron that is controlled by means of a PID controller to adjust the power emitted to the sample. The volatiles evolved during pyrolysis pass through a condensing system and the incondensable gases are gathered in metallic cylinders using a gas pump. Meanwhile, Fig. 6.3b shows a pilot scale microwave pyrolyzer successfully used for biomass carbonisation purposes.

As mentioned above, although syngas production is mainly carried out through the steam reforming of natural gas, an alternative to this method is the thermochemical conversion of organic wastes, which has generally been studied either by applying high temperatures or by using a catalyst at a much lower temperature. The main drawback of these processes is that the syngas yield is usually lower than the oil yields. Nevertheless, in recent years microwave heating has been accepted as an alternative for the pyrolysis of biowaste [42, 43], since it has demonstrated its potential to maximise the gas yield and is therefore considered an appropriate heating method for obtaining syngas for fermentation purposes [44–47].

Fig. 6.3 **a** Microwave pyrolysis unit at lab-scale: *1* PID control panel; *2* cavity containing the magnetron; *3* tuning screws; *4* applicator-reactor; *5* waveguide; *6* thermocouple; *7* condensing system; *8* gas collecting system. **b** Continuous microwave biomass carbonization system. Reprinted with permission from [41], Copyright © 2014, Elsevier

Extensive research has been devoted to the valorisation of problematic wastes through microwave-induced pyrolysis. For instance, sewage sludge has been used for the production of bio-oil with negligible concentrations of hazardous polycyclic aromatic hydrocarbons under different operating conditions with the added advantage that the properties of this fuel are easily tuneable [48]. Sewage sludge has also been subjected to microwave radiation in order to obtain a syngas-rich gas fraction, resulting in yields of up to 62 vol% of $H_2 + CO$ compared to just 25 vol% obtained by conventional pyrolysis [49]. Another waste which poses a significant disposal problem is residual automotive engine oil. When subjected to microwave pyrolysis to obtain a gaseous fuel, a gas yield of 41 wt% containing up to 35 vol% of $H_2 + CO$, with a large amount of light hydrocarbons was achieved in one study [50]. Agricultural residues have also been widely used to produce a H_2-rich gas fraction by means of microwave-induced pyrolysis. In particular, rice straw has proved to be a good feedstock, yielding H_2 concentrations of ca. 51 vol% [51]. Experiments on a larger scale (ca. 30 kg) with corn stalk have yielded high amounts of H_2 from microwave pyrolysis [52]. Moreover, a key advantage with microwave heating pointed out in this study is that the pyrolysis of the centre of the stalk bale is completed after only 120 min, whereas just the evaporation of the moisture at the centre takes 300 min in conventional heating. This indicates that, for the same amount of power expenditure, microwave-induced pyrolysis is faster and, hence, more energy-efficient, apart from yielding more syngas than conventional pyrolysis.

In contrast to conventional heating, the microwave heating mechanism is a more volumetric process because the material itself generates the heat and can be very rapid and selective [53]. Therefore, if it is applied in pyrolysis processes, a different product distribution can be expected. However, not all materials absorb microwaves. For example, biomass contains water, so will absorb microwaves at room temperature. However, once the water is evolved, the biomass becomes more transparent to microwaves and therefore more difficult to be heated up to high temperatures (i.e., temperatures above 400 °C). In the case of high polymers, such as those present in biomass, the areas of these macromolecules that are polarisable by microwaves are further restricted by the rigidity of structures in the crystalline regions. As a result, only amorphous regions can align to the applied electric field, resulting in a smaller dielectric loss over a wide range of frequencies. For this reason, it is generally necessary to mix a highly microwave-absorbent material with the biomass to induce the pyrolysis. Then as the microwaves pass through the bulk, this material absorbs them and the temperature increases. The heat is then conducted throughout the bulk of the sample until a temperature high enough for pyrolysis to begin is reached. However, under certain circumstances the use of this microwave-absorbent material has seemed to be unnecessary [54].

As the pyrolysis proceeds, the organic waste is carbonised into char, as a result of which its structural order is modified allowing the conduction of free electrons (Fig. 6.4). This leads to a high dielectric constant and loss factors and, hence, a high microwave absorption capacity, so that from then on the remaining biowaste can be directly pyrolysed [55, 56]. Therefore, the most appropriate material for use

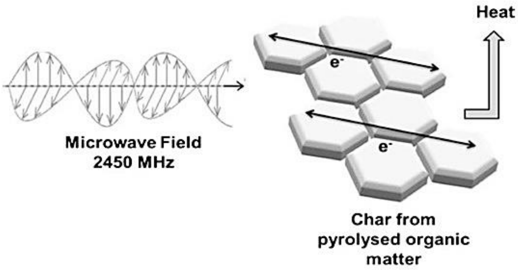


Fig. 6.4 The resulting char from organic feedstock pyrolysis is a microwave-absorbent material as a result of the delocalised π-electrons, which cannot couple to the changes of phase of the electric field, and so the accumulated energy dissipates in the form of heat

Table 6.3 Chemical reactions involving the production of the syngas components

Reaction number	Reaction	$\Delta H_{298\ K}$ (kJ mol^{-1})
1	$C + CO_2 \leftrightarrow 2\ CO$	173
2	$C + H_2O \leftrightarrow CO + H_2$	131
3	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	90
4	$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$	247
5	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	205
6	$C_nH_m + nH_2O \leftrightarrow nCO + (n + m/2)\ H_2$	
7	$C_nH_m + nCO_2 \leftrightarrow 2nCO + (n/2)\ H_2$	
8	$CH_4 \leftrightarrow C + 2H_2$	76
9	$C_nH_m \leftrightarrow nC + (m/2)\ H_2$	
10	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41

as microwave-absorbent might be the char obtained from each previous pyrolysis, since it is a direct product of the actual pyrolysis process itself and so does not contain any foreign material that might influence the composition of the fractions.

Owing to its volumetric nature, microwave heating greatly favours heterogeneous reactions between the volatiles released during pyrolysis and the char [57]. This makes it possible to increase the gas yield and concentration of valuable products for the production of biopolymers, such as CO, since the carbonaceous char can be gasified with the CO_2 and H_2O resulting from the volatiles evolved during pyrolysis, as can be seen in reactions 1–3 in Table 6.3. Table 6.3 shows the main chemical reactions that will result in the desired syngas components for the production of biopolymers (H_2, CO and CO_2). In addition, hydrocarbons (e.g., CH_4, C_2H_4 or C_2H_6) can be reformed by the action of CO_2 and H_2O (reactions 4–7) and cracked to yield coke and H_2 (reactions 8 and 9). As a result of all these reaction pathways, the conversion to syngas can be substantially enhanced.

Table 6.4 Syngas component yields (L_{STP} kg^{-1}) from conventional (CP) and microwave (MIP) pyrolysis of organic feedstock

Feedstock (temperature, °C)	H_2 production		CO production		CO_2 production		Reference
	CP	MIP	CP	MIP	CP	MIP	
Microalgae (400)	0.0	287.4	3.2	123.6	23.4	89.4	[47]
Coffee hulls (500)	35.7	220.3	79.3	159.5	217.6	175.7	[59]
Macroalgae industrial solid waste (750)	68.5	259.6	55.2	115.9	108.4	88.4	[60]
Glycerol (800)	280.4	370.0	472.6	488.2	13.6	19.1	[61]
Sewage sludge (1,000)	134.1	170.7	74.9	100.2	54.6	43.6	[62]

To demonstrate the potential of microwave heating to enhance the reactions presented above, Table 6.4 provides a comparison of syngas components production when different organic feedstocks are subjected to temperature-controlled pyrolysis by means of conventional and microwave heating. Regardless of the nature of the feedstock, it can be seen that Microwave-Induced Pyrolysis (MIP) is able to produce much larger amounts of syngas than conventionally-heated pyrolysis processes (CP). For instance, the MIP of the macroalgae industrial solid waste produces 463.9 L_{STP} of syngas per kg of waste, which is twice the amount produced by conventional pyrolysis (232.1 L_{STP} kg^{-1}). Microwave heating initiates a process that proceeds at temperatures higher than the operating temperature due to the presence of microplasmas, consisting of *hot spots* that last just a fraction of a second but in that time reach temperatures considerably higher than the mean temperature [58]. This induces the thermal cracking of the volatiles into lighter gaseous molecules, such as H_2 and CO.

Apart from the greater yield achieved by means of MIP, there is also an enhancement of the quality of the syngas, i.e. the concentration of the main gases. Table 6.5 contains an analysis of the gas fraction compositions from the two pyrolysis processes (CP and MIP). Regardless of the organic feedstock and

Table 6.5 Gas fraction composition (vol%) from conventional (CP) and microwave (MIP) pyrolysis of organic feedstock

Feedstock (temperature, °C)	H_2		CO		CO_2		Syngas		Hydrocarbons		Reference
	CP	MIP	CP	MIP	CP	MIP	CP	MIP	CP	MIP	
Microalgae (400)	0.0	47.9	9.2	20.6	66.8	14.9	76.0	83.4	24.0	16.6	[47]
Coffee hulls (500)	9.3	35.6	20.6	25.8	56.6	28.4	86.5	89.8	13.5	10.2	[59]
Macroalgae industrial solid waste (750)	22.8	51.8	18.4	23.1	36.1	17.6	77.3	92.5	22.7	7.5	[60]
Glycerol (800)	28.9	34.6	48.7	45.9	1.4	1.8	79.0	82.3	21.0	17.7	[61]
Sewage sludge (1,000)	35.5	48.8	19.9	28.7	14.5	12.5	69.9	90.0	30.1	10.0	[62]

temperature, it can be observed that there is an increase in H_2 and CO concentrations in MIP with respect to CP. However the CO_2 content is reduced by MIP with the exception of glycerol, which is nearly the same as in CP. Also remarkable is the decrease in hydrocarbon concentration. For instance, the MIP of the macroalgae industrial solid waste produces a reduction in the hydrocarbon content of around 67 vol% while the syngas concentration is increased by around 20 vol%.

The advantage of MIP over CP is not only the better quality of the gas produced, but also the reduced feedstock pre-treatment required and the energy saved by the significantly reduced process temperatures [45]. Microwave-induced pyrolysis offers an excellent opportunity for recovering commercially valuable products from wastes and for diverting organic wastes away from the traditional disposal methods, such as landfill and incineration.

6.4 Tuning the Syngas Composition by Microwave Heating

The most important factors in MIP for the resulting gas are the nature of the waste and its moisture content, the microwave power emitted (and therefore, the temperature), the presence of microwave-absorbent materials and the design of the reactor. Owing to the influence of so many parameters and the interrelationships between them, a small change in any one parameter could lead to a very different syngas. This makes MIP a very versatile process.

The yield and quality of the biopolymers produced via syngas fermentation can be affected by the operating parameters in the MIP. This implies that these factors can be tuned to obtain the most suitable gas fraction for the production of biopolymers, i.e. a gas fraction containing the maximum possible quantity of syngas ($H_2 + CO$ and/or CO_2) in relation to other by-products. So-called acetogenic bacteria can be used to ferment these syngas components via the biochemical mechanism referred to as *Wood-Ljungdahl* [63] and then it should be identified the better syngas composition for each bacteria.

6.4.1 Effect of the Type of Waste

Depending on the type of waste, i.e. its chemical structure, the production and quality of the syngas produced through MIP can be adjusted. Most of the studied substrates are lignocellulosic residues, such as coffee hulls [59], algae [47, 60], wheat straw [64], rice straw [51] and corn stalk [52]. Lignocellulosic substrate has the peculiarity that it produces a rich-syngas fraction, allowing the syngas concentration to exceed 90 vol% in all the cases studied, which is of special interest for syngas fermentation.

The use of sewage sludge and municipal solid wastes for syngas production by MIP has also attracted increasing interest in recent years [49, 65–67]. Table 6.6

Table 6.6 Proximate and ultimate analyses of some organic wastes

	Organic solid waste [68]	Plastic solid waste [68]	Sewage sludge [68]	Waste automotive engine oil [50]
Moisture content (wt%)	46.3	1.3	3.4	4.0
Percentage mass basis (dry)				
Volatile matter	68.0	88.9	74.5	97.9
Fixed carbon	9.4	2.2	10.1	1.1
Ash	22.6	8.9	15.4	1.0
C	36.0	70.9	43.8	81.0
H	5.8	9.7	6.1	15.0
O	33.8	9.1	24.9	2.1
N	1.6	1.2	9.7	0.1
S	0.2	0.5	0.1	0.8

shows the proximate and ultimate analyses of some selected organic wastes, which often cause environmental problems. It can be seen that the volatile matter content is typically high, which is useful for the production of gases in thermochemical processes. However, the ash contents are diverse, due to the presence of different metallic compounds including Fe, Zn or Cu. These ashes may have a certain catalytic effect on liquid and gas production, and alter the composition of the syngas [57]. Both the ashes and the fixed carbon contribute to increasing the solid yield during pyrolysis. However, it is not the lowest sum of ash and fixed carbon contents that results in the smallest solid yields in MIP. This is the case of the plastic solid waste shown in Table 6.6, which gives rise to the highest solid yield as depicted in Fig. 6.5. In fact, as the plastic fraction is mainly formed by

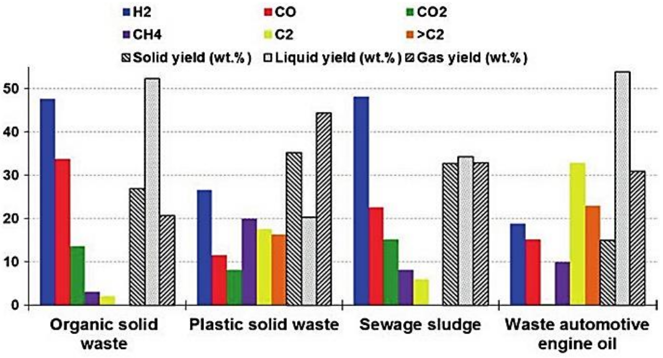


Fig. 6.5 Gas composition and fraction yields from MIP at 800 °C of different organic wastes. The values of gas concentrations are given in vol% units

hydrocarbon chains (C_nH_m), they can easily be decomposed by microwaves, to yield coke which increases the solid yield (Table 6.3, reaction 9).

Moreover, the moisture content is usually variable in organic wastes. For instance, as a result of the elevated moisture content of the organic solid waste in Table 6.6, a high liquid yield is obtained (see Fig. 6.5), being then this liquid fraction formed by a large aqueous portion. But moisture also affects the gas fraction composition and so it is an important tuneable parameter for obtaining an adequate syngas for biopolymers synthesis and will be discussed in Sect. 6.4.2.

Moreover, the carbon, hydrogen and oxygen contents of the wastes have an important influence on the syngas composition. For instance, the organic solid waste and the sewage sludge fractions from Table 6.6 have relatively a high oxygen content, which leads to a high proportion of carbon oxides (CO and CO_2), as shown in Fig. 6.4. However, the low oxygen content in the waste engine oil and the plastic waste leads to relatively low concentrations of carbon oxides. Of special interest is the low amount of CO, the production of which is known to be greatly promoted by MIP. Moreover, the typically high carbon content in plastics and engine oils, due to their hydrocarbon nature, allows the production of CH_4, paraffins and olefins, which are generally produced in small amounts from other residues.

As for sulphur-containing compounds, the gas fraction from pyrolysis may contain traces of H_2S, though it has been found that some microorganisms employed in syngas fermentation show a sulphide tolerance of ≥ 2 % H_2S or COS [69]. Indeed, the presence of small quantities of H_2S in the syngas could be useful for increasing the growth rates of microorganisms, as pointed out by Do et al. in their study of the production of biopolymers via syngas fermentation [18].

Nitrogen may be present in large amounts as in the case of sewage sludge, in various forms such inorganic nitrogen, proteins, pyrrole and pyridine. These compounds may generate gaseous NH_3 and HCN during pyrolysis. Tian et al. [70] studied the microwave pyrolysis of sewage sludge and pointed out that NH_3 and HCN production can be reduced using this method. In the least favourable case, which occurred at 500–800 °C, the contribution of the nitrogenous gas emission was just 24.9 wt% of the total nitrogen content of the sewage sludge, which represents only 1.2 wt% of the sewage sludge bulk (on a dry basis). Nevertheless, this tiny amount of nitrogenous compounds could prevent sewage sludge from being used to yield syngas for biopolymers, depending on the possible inhibiting effect on the metabolism of each bacterium.

Thus the nature of the wastes has an important impact on the quality of the syngas and not all organic wastes are suitable for producing an adequate syngas for biopolymer production. As previously mentioned, some wastes yield high quantities of hydrocarbons within the gas fraction (CH_4, olefins, paraffins and aromatics), mainly due to the depolymerisation of the large carbon chains and their low oxygen content compared to that of other organic wastes [50, 71]. These gases may severely inhibit the uptake of syngas by the microorganisms used to produce the biopolymers [72]. However, such gases can be almost totally removed if the proper residue is selected for pyrolysis by microwave irradiation. MIP is highly advantageous for the minimisation of these undesired compounds, since large quantities of hydrocarbons are usually generated in conventional pyrolysis processes [73].

In short, it would seem that the most suitable organic wastes for subsequent syngas fermentation are organic fractions from municipal solid wastes and agricultural residues; since they are capable of producing a reasonably pure syngas devoid of large hydrocarbons and sulphur and nitrogen-derived compounds toxic to bacteria.

6.4.2 Effect of the Moisture Content

It is well known that the drying of the feedstock before it is subjected to conventional pyro-gasification processes is desirable, since high moisture contents produce fuel gas with a lower effective heating value and also lead to higher transportation costs, even though a large amount of energy consumption is required to remove the moisture [74].

Microwave heating is known to be very tolerant of water compared with conventional heating due to its specific dielectric properties, which makes MIP a potential processing alternative for most biomass materials without the need for pre-drying [75–77]. The steam generated from the moisture during MIP can serve as a gasification agent for volatiles and carbonaceous solid char (Table 6.3, reactions 2, 3, 5 and 6).

The influence of the moisture content on the gas characteristics in pyrolysis and gasification processes has been evaluated in several studies, although most of these works were carried out using conventional heating. Xie et al. [78] reported that an increase in the moisture content in sewage sludge improved the contents of CO_2 and H_2 and reduced the tar yield under air gasification, resulting in higher gas yields. Xiong et al. [79] conducted conventional pyrolysis of different sewage sludge and found that a steam-rich environment favoured the steam reforming reactions of volatiles (Table 6.3, reactions 5–6), as well as the gasification of solid char (Table 6.3, reactions 2–3), improving the gas yield and the H_2 and CO_2 concentrations. Conventional heating methods and MIP both seem to generate steam that can increase the H_2 and CO_2 content, possibly due to the water-gas shift reaction (Table 6.3, reaction 10).

On the other hand, the influence of the moisture content on syngas characteristics when microwave heating is applied has been less studied. Wang et al. [65] conducted microwave pyrolysis of sewage sludge at 850 °C in a single mode reactor and observed an increase in the H_2 and CO concentrations at higher moisture contents while the CO_2 and CH_4 contents decreased. This may indicate that methane steam reforming (Table 6.3, reaction 5) would be favoured in these operating conditions.

The effect of the moisture content of an organic municipal solid waste subjected to microwave heating has also been studied in a previous work by Beneroso et al. [66].

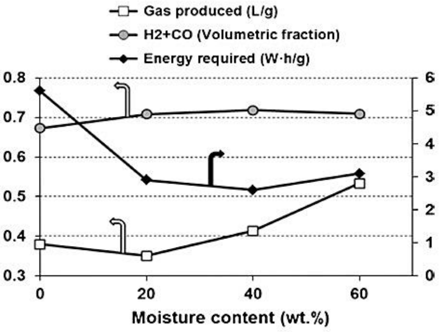


Fig. 6.6 Influence of the moisture content on the gas yield, syngas concentration and the energy consumption in the MIP of feces simulant. Data extracted from Ref. [76]

The wet samples (45 wt% of moisture) were observed to produce higher gas yields regardless of the microwave power and microwave receptor concentration with H_2 and CO_2 concentrations being most favoured, especially at low power.

A detailed study on the gas fraction obtained from MIP of feces simulants with different moisture contents has been conducted by Serio et al. [76]. In general, the gas composition did not appear to be significantly influenced by the water content of the sample. Interestingly, as can be seen in Fig. 6.6, the presence of moisture may enhance the gas volume produced on a dry basis. This can be attributed to gasification and steam reforming reactions as in the case of conventional pyrolysis. In the present study, the energy consumption of the process was also assessed. Although larger amounts of water should have led to a higher energy demand, it was the dry sample that unexpectedly required twice the amount of energy to complete the pyrolysis, compared to the wet samples, at least on the lab-scale. Figure 6.6 shows a decreasing trend in the energy requirement as the moisture content increases, although above 40 wt% the energy requirement starts to increase. This result is attributed to the fact that water is a good microwave receptor, resulting in a more efficient absorption of microwaves. This result is of great importance because the need for a previous waste pre-drying step in the pyrolysis reactor may not then be necessary. Moreover, the $H_2 + CO$ concentration is maximised with a minimum energy requirement. Hence, 40 wt% would seem to be an optimal moisture content. It has also recently been suggested that an optimal moisture content can be obtained by maximising the $H_2 + CO$ concentration in the MIP of an organic municipal waste [77]. The study in question proposes a new biorefinery integrated process called the *all-in-one* process, where the drying, pyrolysis and gasification are carried out in the same microwave reactor.

In the biopolymer production process, the increased moisture content in organic wastes may lead to a higher gas production in MIP, which may help to increase the production of biopolymers. Furthermore, the gas composition can be enriched with H_2, CO_2 or CO, by using the moisture content of the pyrolysed feedstock as the tuning parameter.

6.4.3 Effect of the Temperature

Temperature plays an important role in the conversion of reactants through a specific reaction pathway. Temperature has the same effect in microwave-assisted pyrolysis processes as in conventional pyrolysis processes: higher temperatures promote the release of volatiles from the feedstock. Moreover, high heating rates yield higher gas fraction yields. This may be the case of MIP, since the heating rate during microwave heating is known to be high enough to favour gas production [45].

To reach a certain temperature by means of microwave irradiation it is necessary to control the microwave power emitted to the reaction bulk. However, depending on the amount of power, the heating rate will vary, thus affecting the syngas yield and composition. Zhao et al. [64] studied the effect of the temperature on the yields of products from the microwave pyrolysis of wheat straw. They conducted the pyrolysis at 500 °C applying 400, 500 and 600 W until the desired temperature was reached; hence, the heating rate was increased each time. As a result, under a microwave power of 600 W, the gas yield was increased from 20 wt% (at 400 W) to 30 wt%. In addition, the concentration of $H_2 + CO$ produced rose from 56 vol% at 400 W to 69 vol% at 600 W. This was accompanied by a reduction in the CO_2 concentration from 33 to 23 vol%.

Temperature can be maintained at a constant value if the appropriate microwave power is selected. Domínguez et al. [59] investigated the quality of the gas fraction from the MIP of coffee hulls at 500, 800 and 1,000 °C by adjusting the appropriate power (130, 270 and 420 W respectively). As a result of the increase in temperature, the $H_2 + CO$ concentration rose from 61 to 73 vol%, while the CO_2 concentration decreased from 28 to 18 vol%. Similar findings were recorded for the MIP of a microalga, where the gas yield was enhanced by ca. 30 wt% when temperature was increased from 400 to 800 °C [47]. The $H_2 + CO$ concentration rose in this case from 69 to 88 vol%. This behaviour has also been observed in numerous other studies of the MIP of organic wastes [61, 66]. A greater amount of microwave power favours the production of syngas.

An increase in both microwave power (and hence, heating rate) and temperature in MIP has been demonstrated to produce higher H_2 and CO concentrations. However, most studies on MIP have been conducted on a small scale, so it is important to determine whether microwave heating will also be a good alternative for syngas production if a larger-sized feedstock were used. In this regard, Zhao et al. [52] obtained useful information from the operation of a large-scale MIP of corn stalk bale. In their study, microwave powers of 0.334 and 0.668 kW kg^{-1} were used, providing a final temperature in the range of 575–625 °C, depending on the position of the thermocouples, although when 0.668 kW kg^{-1} was used, the final temperature was achieved much more quickly. The $H_2 + CO$ concentration was higher than 50 vol%, while the gas yield was ca. 25–30 wt%, similar to lab-scale experiments [64]. The special heating characteristics of microwaves which maximises the production of H_2 and CO, as mentioned in Sect. 6.3, also seem to take place also at a larger scale, implying that microwave-induced pyrolysis would be a highly appropriate way to produce syngas from organic waste at industrial scale.

The integration of MIP into the production process of biopolymers does seem feasible, especially considering the high quality of the resulting gas. The pyrolysis temperature can then be exploited as a handy tuning parameter to adjust the $H_2 + CO$ and CO_2 contents necessary for the subsequent fermentation stage.

6.4.4 Effect of Microwave-Absorbent Addition

As mentioned in Sect. 6.3, bio-solids and most organic wastes are, in general, almost transparent to the microwave radiation (i.e., poor dielectric properties), and are unable to absorb enough energy to achieve the necessary pyrolysis temperature. The addition of a microwave-absorbent material (henceforth, it will be called *receptor*) to the reaction bulk will help to achieve the desired temperature. The receptor is one of the main factors in MIP, since, depending on the type of receptor (and hence its dielectric properties), different heating profiles can be obtained. A typical heating profile is as follows. First, the temperature rises from the ambient temperature to 100 °C, enabling the feedstock moisture to be evaporated. After this, the temperature usually reaches a *plateau* before arriving at the pyrolysis temperature; the temperature then rises quickly corresponding to the stage at which the release of the majority of the volatiles occurs. Once the corresponding volatiles have evolved, a thermal equilibrium is achieved [52].

Accordingly, the receptors that lead to both high heating rates and temperatures favour the production of gaseous compounds, causing changes to the yield and composition of the syngas. The heating mechanism by which the mixture of organic feedstock and receptor achieves a high temperature is qualitatively depicted in Fig. 6.7.

In the initial phase [Fig. 6.7(1)], only the added microwave receptor is able to absorb microwaves and produce heat (red circles), which allows the adjacent particles of the microwave-transparent materials, i.e. organic wastes (blue circles), to be heated by conventional heat transfer mechanisms (conduction, convection and radiation). This heat flux allows the removal of volatiles producing char, which will act as a microwave receptor contributing to the final pyrolysis temperature [Fig. 6.7(2, 3)]. Finally, a thermal equilibrium is reached [Fig. 6.7(4)]. In this way, the creation of the microwave-receptor bulk resembles what occurs in a chain reaction for which an initiator, often a free chemical radical, is required.

It has been stated that the temperature achieved by MIP is mainly due to the dielectric properties of the receptor. Zuo et al. [80] highlighted the importance of the receptor in the production of biofuel by the MIP of sewage sludge. They used activated carbon, pulverous silicon carbide, graphite and a pyrolytic carbonaceous residue from sewage sludge as receptors in the same concentrations. At a constant microwave power of 1,000 W, the silicon carbide allowed the temperature rise to 1,130 °C, whereas the use of graphite resulted in the lowest temperature of 780 °C. As a result, the highest gas yield was obtained by microwave pyrolysis with SiC as receptor, 28 wt% higher than the gas yield obtained from microwave pyrolysis using graphite (Fig. 6.8).

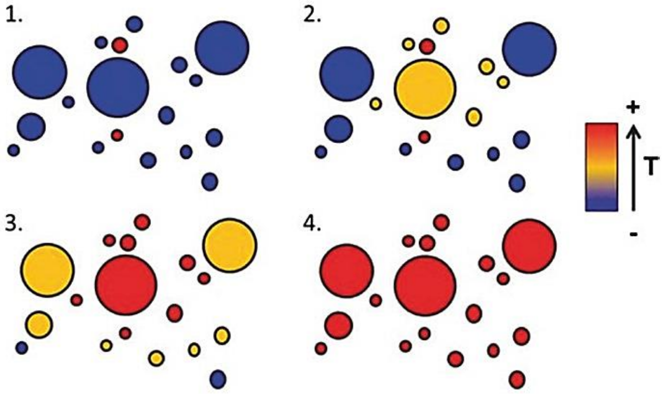


Fig. 6.7 Phases during the MIP of mixed microwave-transparent material particles (*blue circles*) and microwave receptors (*red circles*), where the formation of microwave receptors is shown along with temperature (*T*) increase

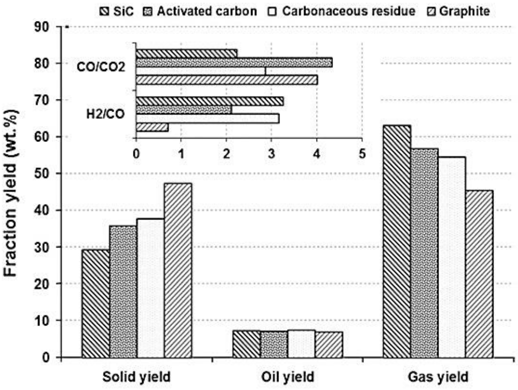


Fig. 6.8 Comparison of the fractions yields and syngas quality from the MIP of a sewage sludge using different receptors. Data extracted from Ref. [80]

Moreover, the heating rate is usually related to the chemical composition and physical structure of the receptor. In the same study Zuo et al. observed that high heating rates minimised condensation reactions from the oil to the solid fraction, as occurs when activated carbon is used as receptor. In addition to the differences found in the fraction yields, Fig. 6.8 also shows the syngas quality obtained. As can be seen, with the exception of graphite, all the receptors favoured the concentration of H_2 to the detriment of the concentration of CO. Thus, if the syngas obtained from this sewage sludge for use in biopolymers production needed to be adjusted to a high CO concentration, the use of graphite as receptor would be an interesting option. The CO_2 concentration was minimal when activated carbon or graphite were employed. Nevertheless, it is important to bear in mind that the results depend on the nature of the feedstock and the microwave power. For instance, the use of graphite dust as microwave-absorbent material in the MIP of the microalga *Scenedesmus almeriensis* led to the opposite behaviour: a higher H_2/CO ratio and a lower CO/CO_2 ratio were obtained compared to when the carbonaceous residue from the microalga was used [47].

Hu et al. [81] showed the enhancement of the microwave-induced pyrolysis reactions of the microalga *Chlorella vulgaris* by mixing it with activated carbon, CaO, SiC and the solid residue obtained from the pyrolysis of the microalga. Under 1,500 W, the gas yields increased by 75.7, 50.0, 24.5 and 25.8 % with respect to the pyrolysis of the pure microalga. These differences were attributed to both the thermal and catalytic cracking of bio-oil vapours into incondensable gases at high temperatures, the receptors possibly acting as catalysts for some reaction pathways. However, no gas analyses were performed to establish the quality of the syngas.

The MIP of municipal solid waste using different receptors has also been performed by Gedam and Regupathi [67]. Charcoal, graphite powder and iron powders were used as microwave-absorbent materials. At the same microwave power, the use of charcoal or graphite instead of iron powders always led to a greater volatilisation of the waste.

However, it is not only the type of the receptor that leads to different products, but also the quantity of receptor added. Salema and Ani [82–84] studied the MIP of oil palm biomass in a multimode reactor, and found that the product yields depend on the ratio of the receptor to the biomass. Under 450 W, the following different ratios were tested using char from oil palm as receptor: 0.25:1, 0.5:1 and 1:1. The addition of char resulted in an increase in the temperature and the gas yield was maximised in the case of the highest receptor addition (ratio 1:1), although the most remarkable differences correspond to the solid yield [82]. These authors repeated the same pyrolysis process in an overhead stirred reactor, with quite different results from the previous work: the temperature profiles were observed to decrease with the addition of the receptor [84]. They suggested that at high receptor-to-biomass ratios, the temperature might have dropped owing to the selective heating nature of microwave irradiation, since the receptor gets heated due to localised heating and the heat cannot be transferred efficiently to the biomass material, with the result that the heating period stage is delayed. In this way, with low receptor quantities, the volatile matter is released much earlier from the biomass materials and thus, a higher temperature can be achieved [83]. Hence, syngas production was lower for a high receptor-to-biomass ratios. Similar results were obtained by Beneroso et al. [66] who studied the influence of the receptor in the MIP of an organic municipal solid waste to produce syngas in a single-mode reactor. The use of lower receptor-to-waste ratios resulted in the most appropriate conditions for optimising the concentration and production of syngas.

There is, therefore, some controversy as to the most important factor, type or concentration of receptor, to ensure a rapid heating in MIP and the production of syngas, the last-mentioned being perhaps the most important. Some studies included estimations of the complex permittivity of mixtures of materials to describe thermal behaviour under microwave irradiation. In the case of the microwave pyrolysis of plastics, some of these equations have been used to predict the dielectric properties of mixtures consisting of polyethylene and a microwave-receptor material [85]. In these cases, when Landau and Lifshitz, Looyenga mixture equation is used, the concentration of the receptor seems to have more influence on the permittivity of the mixture. However, it is important to note that the hydrodynamic conditions of the reactor may alter this result.

Although the effect of the addition of receptor on the gas composition has not generally been the main topic of interest, since the majority of studies have focused on the production of oil, it seems clear that, depending on the configuration of the reactor, the addition of a suitable microwave-absorbent material to the pyrolysis medium may well help to enhance the generation of syngas for biopolymer production.

6.5 Equipment: The Challenge of Scaling-Up

The interest generated by microwave-induced pyrolysis for the generation of syngas that can be used in fermentation processes, has been mentioned in previous sections. However, there is a considerable obstacle to overcome prior to its industrial implementation and that is the scaling-up of the process.

For biopolymer production, the high gas yields and the possibility of tuning the composition of the gaseous fraction are two outstanding advantages of this technology. However, other important features of MIP must also be considered, including:

- Better control of the heating process compared to conventional heating due to minimisation of the inertia during heating and cooling [42, 86].
- Non-contact and selective heating [56].
- Reduced processing time, and an increase in the production rate [87].
- Enhancement and acceleration of the chemical reactions [88, 89].
- Avoidance of the need to shred the feedstock and to pre-dry the sample, leading to a reduction in the costs associated with this step [75, 77, 88].

In spite of all of these advantages, this technology has not yet reached industrial scale. Although success has accompanied the scaling-up of microwave heating in other processes such as food processing, drying applications or rubber vulcanisation [90, 91], certain factors have hampered the industrial development of microwave-induced pyrolysis. There are almost no studies that deal with the energy and economic costs of this technology on a large scale. Moreover, the absence of sufficient data to quantify the dielectric properties of input feedstocks or to dispel doubts about the heat transfer and chemical reactivity nature of microwave heating, are factors that have hindered the design of suitable equipment [50, 88, 91]. Design parameters such the operation mode (continuous or batch), the addition of a stirring system to the process, the frequency of the microwave radiation to be used or the mode of heating (single mode or multimode) must be carefully considered to obtain optimum designs that can prove economically competitive [91].

To overcome these problems, some scale-up attempts have been tried by several researchers and companies, such as the reactors designed by the Centre for Biorefining of the University of Minnesota, the Scandinavian Biofuel Company or the King Mongkut's Institute of Technology Ladkrabang. These efforts have produced encouraging results and have shown that MIP technology could become competitive with the right financial incentives. However, from the point of view of the use of this technology for syngas production, the results are not conclusive. In the case of the equipment designed by the University of Minnesota and the Scandinavian Biofuel Company, the aims of the projects were focused on the production of bio-oils. In the case of the reactor designed by the King Mongkut's Institute of Technology Ladkrabang, which is shown in Fig. 6.3b, the main objective of the project was to use the equipment for the carbonization of biomass [41]. The main goal of these projects was not the production of syngas and the designs were not optimised for this purpose. The design parameters such as temperature, reactor geometry and downstream reforming steps for maximising gas production differ from those used to maximise liquid and solid fractions [92]. A design similar to that of Serio et al. [93] would be more suitable for assessing the viability of MIP for syngas production. In this design, high temperatures were applied and a cracking zone was embedded in the reactor, increasing the gas yield and diminishing the production of oils and solids. However, the amount of sample used (ca. 100 g) was a long way off from large scale proportions.

Probably, the most important factor that can tip the scales in favour of or against the industrial implementation of microwave-induced pyrolysis is its energy efficiency. Although this is not the only factor to take into account when deciding whether to apply this technology for the generation of syngas for biopolymer production, reducing the energy consumption will clearly contribute to making these processes economically viable [50, 91]. Although the cost of the biopolymers will depend on many factors, the pyrolysis process is by far the most energy—intensive step in the production chain, and so improving microwave-induced pyrolysis technology is extremely important [86].

Several authors have claimed that the use of microwaves as heating source can lead to greater energy efficiency compared with conventional pyrolysis [50, 56, 88, 91]. However, energy efficiency has not been studied in depth, and the reports that can be found in the literature once again are focused on the production of oils rather than syngas [50]. Moreover, there are almost no works on the variation of

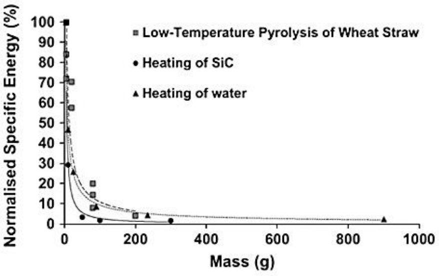


Fig. 6.9 Normalised trends of the energy required per gram of sample for different microwave-assisted processes with increasing sample weight. Adapted from [77]

energy consumption with scale. Some researchers subscribe to the idea that specific energy consumption declines as the scale increases, regardless of the type of microwave-heated process, since there is a critical mass at which the specific energy consumption needed to achieve a desired temperature falls exponentially as can be seen in Fig. 6.9. The first results in support of this were obtained by Budarin et al. [75]. In their work, it was found that energy consumption in the low-temperature microwave-assisted pyrolysis of wheat straw decreased from above 120 kJ/g (sample amount, 0.2 g) to 2.2 kJ/g (sample amount, 200 g). Moreover, a subsequent scale-up to a pilot plant able to process 30 kg/h revealed that the energy consumption decreased to less than 2 kJ/g. In the light of these results, the authors concluded that the energy efficiency of this microwave-assisted process was 1.5 times higher than the energy efficiency achieved by a conventional process.

To sum up, in spite of the wide research that has been conducted on microwave-induced pyrolysis, the industrial development of this technology is still faced with a big challenge. There are several obstacles that must be overcome before pyrolysis processes can be optimised and demonstrated to be commercially attractive.

6.6 Conclusions and Future Outlook

Syngas fermentation is attracting widespread interest for implementation in biorefineries and great efforts are being made to metabolically engineer microorganisms for the production of specifically targeted chemicals such as biopolymers. In this chapter, we have explained how microwave-induced pyrolysis has the potential to produce a high quality syngas from organic wastes by drastically reducing the hydrocarbons content. The integration of a microwave reactor into a biorefinery will allow the treatment and recycling of complex biological and chemical wastes and raw materials aided by the innovative biotechnological approach of biopolymer production from syngas, which will not only benefit the environmental management of terrestrial wastes, but also reduce the harmful environmental impact of petrochemical plastics.

Acknowledgments The research leading to this chapter has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 311815 (SYNPOL project). D. B. also acknowledges the support received from PCTI and FICYT of the Government of the Principado de Asturias.

References

1. European Bioplastics (2014) Frequently asked questions on bioplastics
2. Plastics Europe (2013) Plastics—the facts 2013
3. Gumel AM, Annuar MSM, Chisti Y (2013) Recent advances in the production, recovery and applications of Polyhydroxyalkanoates. J Polym Environ 21(2):580–605
4. Chen G-Q, Wu Q (2005) The application of polyhydroxyalkanoates as tissue engineering materials. Biomaterials 26(33):6565–6578
5. Philip S, Keshavarz T, Roy I (2007) Polyhydroxyalkanoates: biodegradable polymers with a range of applications. J Chem Technol Biotechnol 82(3):233–247
6. Sudesh K, Abe H, Doi Y (2000) Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters. Prog Polym Sci 25(10):1503–1555
7. Loo C-Y, Sudesh K (2007) Polyhydroxyalkanoates: bio-based microbial plastics and their properties. Malays Polym J 2(2):31–57
8. European Bioplastics (2014) Bioplastics facts and figures
9. The Freedonia Group (2009) World bioplastics
10. Snell KD, Peoples OP (2009) PHA bioplastic: a value-added coproduct for biomass biorefineries. Biofuels, Bioprod Biorefin 3(4):456–467
11. Suriyamongkol P, Weselake R, Narine S, Moloney M, Shah S (2007) Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plants—a review. Biotechnol Adv 25(2):148–175
12. Koller M, Atlić A, Dias M, Reiterer A, Braunegg G (2010) Microbial PHA production from waste raw materials. In: Chen GG-Q (ed) Plastics from bacteria, microbiology monographs, vol 14. Springer, Berlin, pp 85–119
13. Mohammadi M, Najafpour GD, Younesi H, Lahijani P, Uzir MH, Mohamed AR (2011) Bioconversion of synthesis gas to second generation biofuels: a review. Renew Sust Energ Rev 15(9):4255–4273
14. Tirado-Acevedo O, Chinn MS, Grunden AM (2010) Production of biofuels from synthesis gas using microbial catalysts (Chap. 2). In: Allen IL, Sima S, Geoffrey MG (eds) Advances in applied microbiology, vol 70. Academic Press, London, pp 57–92
15. Younesi H, Najafpour G, Mohamed AR (2005) Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, *Clostridium ljungdahlii*. Biochem Eng J 27(2):110–119
16. Griffin DW, Schultz MA (2012) Fuel and chemical products from biomass syngas: a comparison of gas fermentation to thermochemical conversion routes. Environ Prog Sustain Energy 31(2):219–224
17. Chang I-S, Kim B-H, Kim D-H, Lovitt RW, Sung H-C (1999) Formulation of defined media for carbon monoxide fermentation by *Eubacterium limosum* KIST612 and the growth characteristics of the bacterium. J Biosci Bioeng 88(6):682–685
18. Do YS, Smeenk J, Broer KM, Kisting CJ, Brown R, Heindel TJ, Bobik TA, DiSpirito AA (2007) Growth of Rhodospirillum rubrum on synthesis gas: conversion of CO to H_2 and poly-β-hydroxyalkanoate. Biotechnol Bioeng 97(2):279–286
19. Choi D, Chipman D, Bents S, Brown R (2010) A techno-economic Analysis of Polyhydroxyalkanoate and hydrogen production from syngas fermentation of gasified biomass. Appl Biochem Biotechnol 160(4):1032–1046
20. Weaver PF, Maness PC (1993) Photoconversion of gasified organic materials into biologically-degradable plastics. US Patent 5250427 A

21. Köpke M, Mihalcea C, Liew FM, Tizard JH, Ali MS, Conolly JJ, Al-Sinawi B, Simpson SD (2011) 2,3-Butanediol production by acetogenic bacteria, an alternative route to chemical synthesis, using industrial waste gas. Appl Environ Microbiol 77(15):5467–5475
22. Kunasundari B, Sudesh K (2011) Isolation and recovery of microbial polyhydroxyalkanoates. Express Polym Lett 5(7):620–634
23. Fernandez-Akarregi AR, Makibar J, Lopez G, Amutio M, Olazar M (2013) Design and operation of a conical spouted bed reactor pilot plant (25 kg/h) for biomass fast pyrolysis. Fuel Process Technol 112:48–56
24. Gaddy JL (2000) Biological production of ethanol from waste gases with *Clostridium ljungdahlii*. US Patent 6136577 A
25. Worden RM, Grethlein AJ, Zeikus JG, Datta R (1989) Butyrate production from carbon monoxide by *Butyribacterium methylotrophicum*. Appl Biochem Biotechnol 20–21(1):687–698
26. Grethlein AJ, Worden RM, Jain MK, Datta R (1990) Continuous production of mixed alcohols and acids from carbon monoxide. Appl Biochem Biotechnol 24–25(1):875–884
27. Heiskanen H, Virkajärvi I, Viikari L (2007) The effect of syngas composition on the growth and product formation of *Butyribacterium methylotrophicum*. Enzyme Microb Technol 41(3):362–367
28. Sim JH, Kamaruddin AH, Long WS, Najafpour G (2007) Clostridium aceticum—a potential organism in catalyzing carbon monoxide to acetic acid: application of response surface methodology. Enzyme Microb Technol 40(5):1234–1243
29. Cotter JL, Chinn MS, Grunden AM (2009) Influence of process parameters on growth of *Clostridium ljungdahlii* and *Clostridium autoethanogenum* on synthesis gas. Enzyme Microb Technol 44(5):281–288
30. Huhnke RL, Lewis RS, Tanner RS (2006) Indirect or direct fermentation of biomass to fuel alcohol. US Patent 20070275447 A1
31. Liou JS-C, Balkwill DL, Drake GR, Tanner RS (2005) *Clostridium carboxidivorans* sp. nov., a solvent-producing clostridium isolated from an agricultural settling lagoon, and reclassification of the acetogen *Clostridium scatologenes* strain SL1 as *Clostridium drakei* sp. nov. Int J Syst Evol Microbiol 55(5):2085–2091
32. Phillips JR, Klasson KT, Clausen EC, Gaddy JL (1993) Biological production of ethanol from coal synthesis gas. Appl Biochem Biotechnol 39–40(1):559–571
33. Clausen EC, Gaddy JL (1992) *Clostridium ljungdahlii*, an anaerobic ethanol and acetate producing microorganism. US Patent 5173429 A
34. Phillips J, Clausen E, Gaddy J (1994) Synthesis gas as substrate for the biological production of fuels and chemicals. Appl Biochem Biotechnol 45–46(1):145–157
35. Kundiyana DK, Huhnke RL, Wilkins MR (2010) Syngas fermentation in a 100-L pilot scale fermentor: design and process considerations. J Biosci Bioeng 109(5):492–498
36. Kundiyana DK, Wilkins MR, Maddipati P, Huhnke RL (2011) Effect of temperature, pH and buffer presence on ethanol production from synthesis gas by "*Clostridium ragsdalei*". Bioresour Technol 102(10):5794–5799
37. Chang I-S, Kim D-H, Kim B-H, Shin P-K, Sung H-C, Lovitt R-W (1998) CO fermentation of Eubacterium limosum KIST612. J Microbiol Biotechnol 8(2):134–140
38. Sakai S, Nakashimada Y, Inokuma K, Kita M, Okada H, Nishio N (2005) Acetate and ethanol production from H_2 and CO_2 by *Moorella* sp. using a repeated batch culture. J Biosci Bioeng 99(3):252–258
39. Solomon PR, Serio MA, Suuberg EM (1992) Coal pyrolysis: experiments, kinetic rates and mechanisms. Prog Energ Combust 18(2):133–220
40. Horne PA, Williams PT (1996) Influence of temperature on the products from the flash pyrolysis of biomass. Fuel 75(9):1051–1059
41. Payakkawan P, Areejit S, Sooraksa P (2014) Design, fabrication and operation of continuous microwave biomass carbonization system. Renew Energ 66:49–55
42. Appleton TJ, Colder RI, Kingman SW, Lowndes IS, Read AG (2005) Microwave technology for energy-efficient processing of waste. Appl Energ 81(1):85–113

43. Arenillas Y, Fernández A, Menéndez JÁ (2011) Microwave heating applied to pyrolysis. In: Advances in induction and microwave heating of mineral and organic materials, Stanislaw Grundas, Lublin
44. Domínguez A, Fernández Y, Fidalgo B, Pis JJ, Menéndez JA (2008) Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge. Chemosphere 70(3):397–403
45. Luque R, Menendez JA, Arenillas A, Cot J (2012) Microwave-assisted pyrolysis of biomass feedstocks: the way forward? Energy Environ Sci 5(2):5481–5488
46. Menéndez JA, Domínguez A, Inguanzo M, Pis JJ (2005) Microwave-induced drying, pyrolysis and gasification (MWDPG) of sewage sludge: vitrification of the solid residue. J Anal Appl Pyrol 74(1–2):406–412
47. Beneroso D, Bermúdez JM, Arenillas A, Menéndez JA (2013) Microwave pyrolysis of microalgae for high syngas production. Bioresour Technol 144:240–246
48. Tian Y, Zuo W, Ren Z, Chen D (2011) Estimation of a novel method to produce bio-oil from sewage sludge by microwave pyrolysis with the consideration of efficiency and safety. Bioresour Technol 102(2):2053–2061
49. Menéndez JA, Domínguez A, Inguanzo M, Pis JJ (2004) Microwave pyrolysis of sewage sludge: analysis of the gas fraction. J Anal Appl Pyrol 71(2):657–667
50. Lam SS, Russell AD, Lee CL, Lam SK, Chase HA (2012) Production of hydrogen and light hydrocarbons as a potential gaseous fuel from microwave-heated pyrolysis of waste automotive engine oil. Int J Hydrogen Energy 37(6):5011–5021
51. Huang YF, Kuan WH, Lo SL, Lin CF (2010) Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. Bioresour Technol 101(6):1968–1973
52. Zhao X, Song Z, Liu H, Li Z, Li L, Ma C (2010) Microwave pyrolysis of corn stalk bale: a promising method for direct utilization of large-sized biomass and syngas production. J Anal Appl Pyrol 89(1):87–94
53. Clark DE, Sutton WH (1996) Microwave processing of materials. Annu Rev Mater Sci 26(1):299–331
54. Robinson JP, Kingman SW, Barranco R, Snape CE, Al-Sayegh H (2009) Microwave pyrolysis of wood pellets. Ind Eng Chem Res 49(2):459–463
55. Motasemi F, Afzal MT, Salema AA, Mouris J, Hutcheon RM (2014) Microwave dielectric characterization of switchgrass for bioenergy and biofuel. Fuel 124:151–157
56. Menéndez JA, Arenillas A, Fidalgo B, Fernández Y, Zubizarreta L, Calvo EG, Bermúdez JM (2010) Microwave heating processes involving carbon materials. Fuel Process Technol 91(1):1–8
57. Menéndez JA, Domínguez A, Fernández Y, Pis JJ (2006) Evidence of self-gasification during the microwave-induced pyrolysis of coffee hulls. Energy Fuels 21(1):373–378
58. Menéndez JA, Juárez-Pérez EJ, Ruisánchez E, Bermúdez JM, Arenillas A (2011) Ball lightning plasma and plasma arc formation during the microwave heating of carbons. Carbon 49(1):346–349
59. Domínguez A, Menéndez JA, Fernández Y, Pis JJ, Nabais JMV, Carrott PJM, Carrott MMLR (2007) Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. J Anal Appl Pyrol 79(1–2):128–135
60. Ferrera-Lorenzo N, Fuente E, Bermúdez JM, Suárez-Ruiz I, Ruiz B (2014) Conventional and microwave pyrolysis of a macroalgae waste from the agar-agar industry. Prospects for biofuel production. Bioresour Technol 151:199–206
61. Fernández Y, Arenillas A, Díez MA, Pis JJ, Menéndez JA (2009) Pyrolysis of glycerol over activated carbons for syngas production. J Anal Appl Pyrol 84(2):145–150
62. Domínguez A, Menéndez JA, Inguanzo M, Pís JJ (2006) Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. Bioresour Technol 97(10):1185–1193
63. Bengelsdorf FR, Straub M, Dürre P (2013) Bacterial synthesis gas (syngas) fermentation. Environ Technol 34(13–14):1639–1651

64. Zhao X, Wang M, Liu H, Zhao C, Ma C, Song Z (2013) Effect of temperature and additives on the yields of products and microwave pyrolysis behaviors of wheat straw. J Anal Appl Pyrol 100:49–55
65. Wang X-L, Deng W-Y, Yu W-C, Su Y-X (2013) Hydrogen-rich gas formation characteristics during microwave-induced high temperature pyrolysis of sewage sludge. J Fuel Chem Technol 41(2):243–251
66. Beneroso D, Bermúdez JM, Arenillas A, Menéndez JA (2014) Influence of the microwave absorbent and moisture content on the microwave pyrolysis of an organic municipal solid waste. J Anal Appl Pyrol 105:234–240
67. Gedam V, Regupathi I (2012) Pyrolysis of municipal solid waste for syngas production by microwave irradiation. Nat Resour Res 21(1):75–82
68. Beneroso D, Bermúdez JM, Arenillas A, Menéndez JA (2014) Syngas from waste valorization for bioplastics production. Paper presented at the 20th international symposium on analytical and applied pyrolysis, Birmingham
69. Vega JL, Klasson KT, Kimmel DE, Clausen EC, Gaddy JL (1990) Sulfur gas tolerance and toxicity of co-utilizing and methanogenic bacteria. Appl Biochem Biotechnol 24–25(1):329–340
70. Tian Y, Zhang J, Zuo W, Chen L, Cui Y, Tan T (2013) Nitrogen conversion in relation to NH_3 and HCN during microwave pyrolysis of sewage sludge. Environ Sci Technol 47(7):3498–3505
71. Klepfer JS, Honeycutt TW, Sharivker V, Tairova G (2001) Process and reactor for microwave cracking of plastic materials. US Patent 6184427 B1
72. Nirmalakhandan N, Arulgnanendran V, Mohsin M, Sun B, Cadena F (1994) Toxicity of mixtures of organic chemicals to microorganisms. Water Res 28(3):543–551
73. He M, Xiao B, Liu S, Hu Z, Guo X, Luo S, Yang F (2010) Syngas production from pyrolysis of municipal solid waste (MSW) with dolomite as downstream catalysts. J Anal Appl Pyrol 87(2):181–187
74. Niu M, Huang Y, Jin B, Wang X (2013) Simulation of syngas production from municipal solid waste gasification in a bubbling fluidized bed using Aspen Plus. Ind Eng Chem Res 52(42):14768–14775
75. Budarin VL, Shuttleworth PS, Dodson JR, Hunt AJ, Lanigan B, Marriott R, Milkowski KJ, Wilson AJ, Breeden SW, Fan J, Sin EHK, Clark JH (2011) Use of green chemical technologies in an integrated biorefinery. Energy Environ Sci 4(2):471–479
76. Michael S, Joseph C, Marek W, Kanapathipillai W, John F (2012) Pyrolysis yields from microwave-assisted heating of solid wastes. In: 42nd international conference on environmental systems (ICES), American Institute of Aeronautics and Astronautics
77. Beneroso D, Bermúdez JM, Arenillas A, Menéndez JA (2014) Integrated microwave drying, pyrolysis and gasification for valorisation of organic wastes to syngas. Fuel 132:20–26
78. Xie LP, Li T, Gao JD, Fei XN Wu X, Jiang YG (2010) Effect of moisture content in sewage sludge on air gasification. J Fuel Chem Technol 38(5):615–620
79. Xiong S, Zhuo J, Zhang B, Yao Q (2013) Effect of moisture content on the characterization of products from the pyrolysis of sewage sludge. J Anal Appl Pyrol 104:632–639
80. Zuo W, Tian Y, Ren N (2011) The important role of microwave receptors in bio-fuel production by microwave-induced pyrolysis of sewage sludge. Waste Manage 31(6):1321–1326
81. Hu Z, Ma X, Chen C (2012) A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. Bioresour Technol 107:487–493
82. Salema AA, Ani FN (2011) Microwave induced pyrolysis of oil palm biomass. Bioresour Technol 102(3):3388–3395
83. Abubakar Z, Salema AA, Ani FN (2013) A new technique to pyrolyse biomass in a microwave system: effect of stirrer speed. Bioresour Technol 128:578–585
84. Salema AA, Ani FN (2012) Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer. J Anal Appl Pyrol 96:162–172
85. Khaghanikavkani E, Farid MM, Holdem J, Williamson A (2013) Microwave pyrolysis of plastic. J Chem Eng Process Tech 4(3):

86. Lam SS, Chase HA (2012) A review on waste to energy processes using microwave pyrolysis. Energies 5(10):4209–4232
87. Stein DF, Edgar RH, Iskander MF, Johnson DL, Johnson SM, Lob CG, Shaw JM, Sutton WH, Tien PK, Munns TE (1994) Microwave processing—an emerging industrial technology? In: MRS proceedings, p 347
88. Motasemi F, Afzal MT (2013) A review on the microwave-assisted pyrolysis technique. Renew Sust Energ Rev 28:317–330
89. Lidström P, Tierney J, Wathey B, Westman J (2001) Microwave assisted organic synthesis—a review. Tetrahedron 57(45):9225–9283
90. Metaxas AC, Meredith RJ (1983) Industrial microwave heating, vol 4. IET, London, UK
91. Moseley JD, Kappe CO (2011) A critical assessment of the greenness and energy efficiency of microwave-assisted organic synthesis. Green Chem 13(4):794–806
92. Puigjaner L (ed) (2011) Syngas from waste, green energy and technology. Springer, Berlin
93. Serio MA, Cosgrove JE, Wojtowicz MA, Wignarajah K, Fisher J (2013) A prototype microwave pyrolyzer for solid wastes. Paper presented at the 43rd international conference on environmental systems

Comparing the composition of the synthesis-gas obtained from the pyrolysis of different organic residues for a potential use in the synthesis of bioplastics

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*
Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain
* Corresponding author. Tel.: +34 985 118972; Fax: +34 985 297672
E-mail address: angelmd@incar.csic.es

Supplementary Data

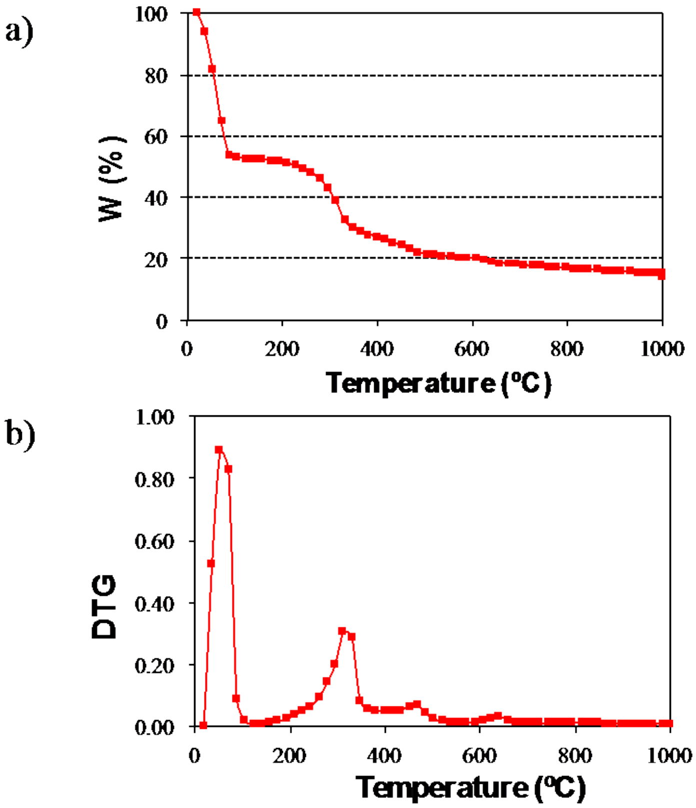


Fig. S1. (a) TGA and (b) DTGA profiles of the MSW

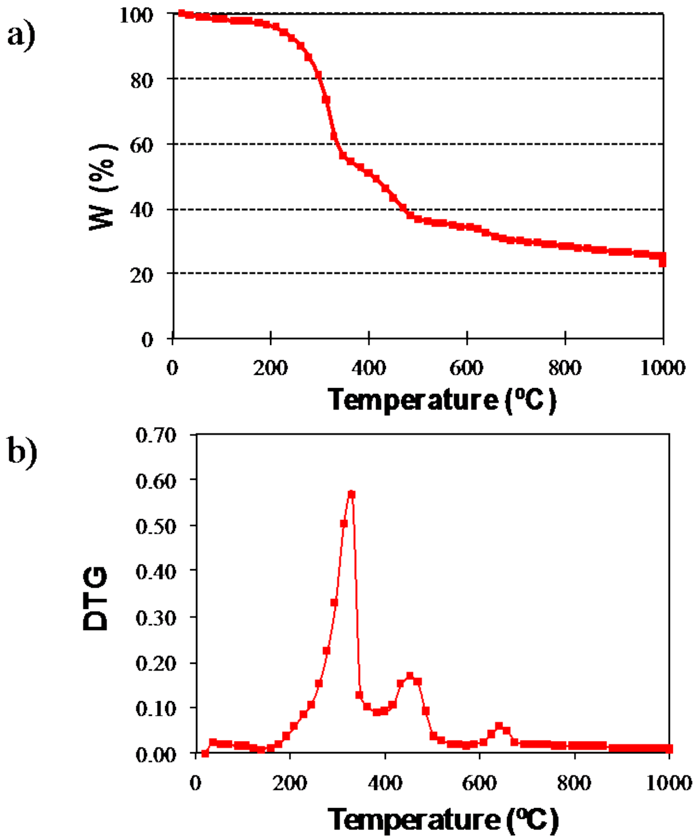


Fig. S2. (a) TGA and (b) DTGA profiles of the MSWd

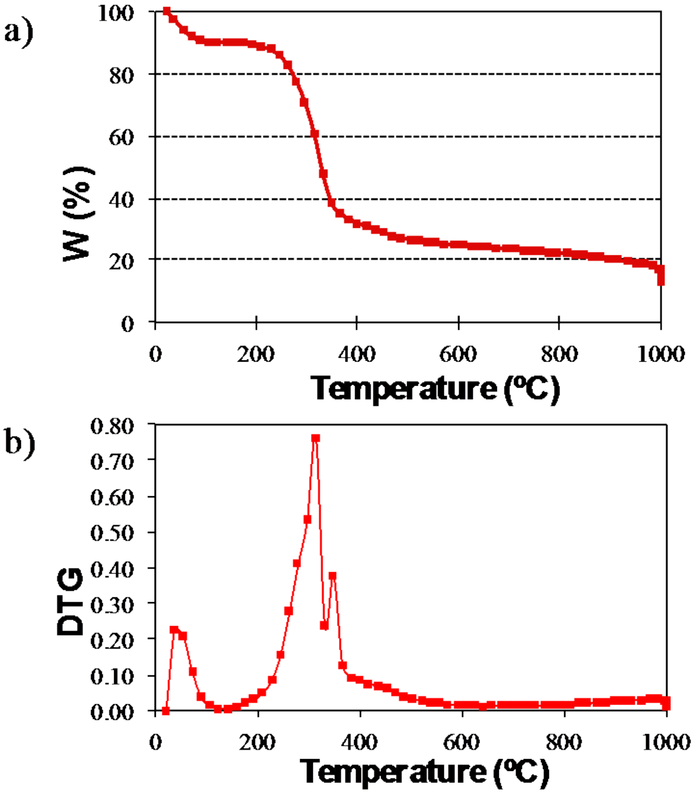


Fig. S3. (a) TGA and (b) DTGA profiles of the STR

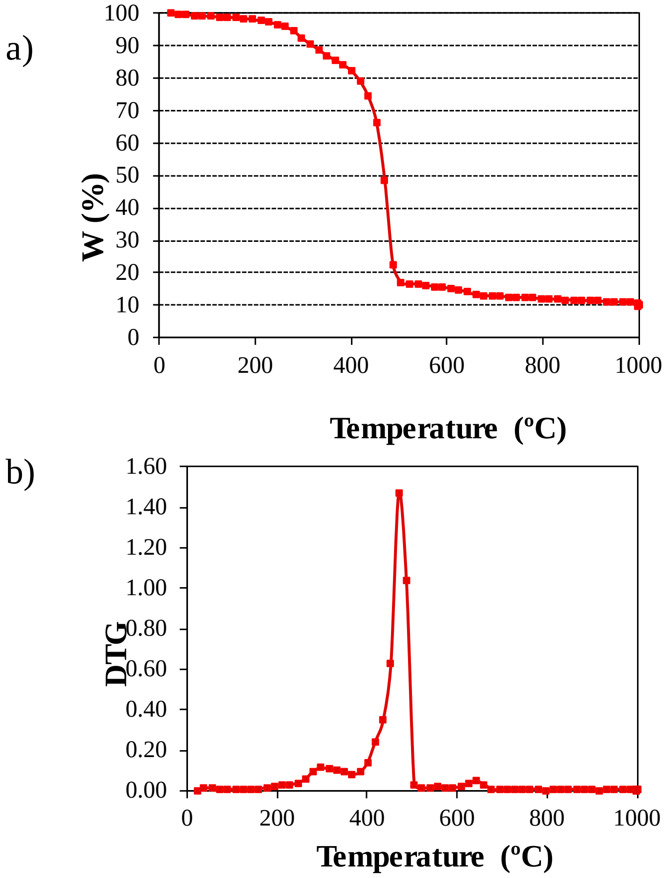


Fig. S4. (a) TGA and (b) DTGA profiles of the PLA

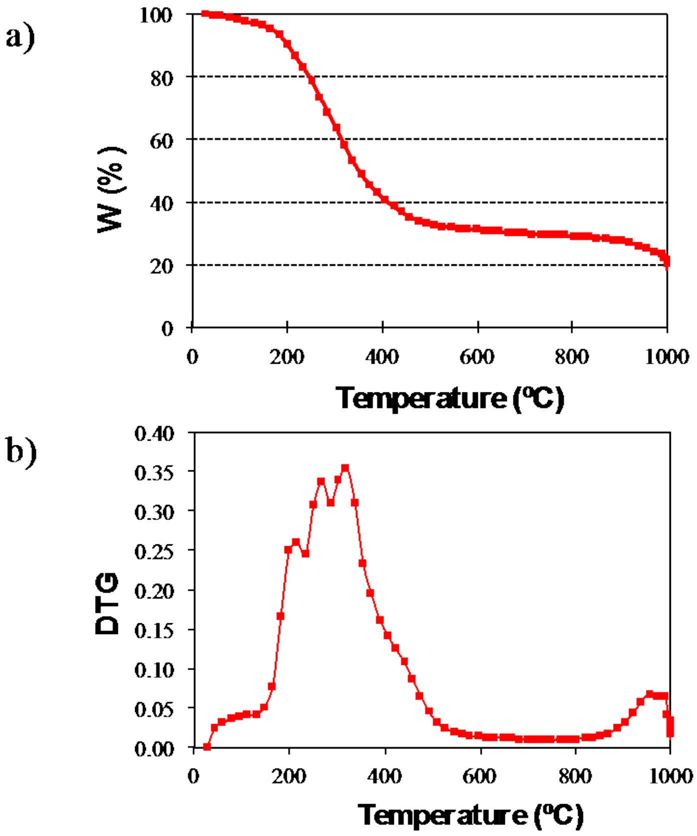


Fig. S5. (a) TGA and (b) DTGA profiles of the SSd

Oil fractions from the pyrolysis of diverse organic wastes: the different effects of conventional and microwave induced pyrolysis

D. Beneroso[a], J.M. Bermúdez[a], A. Arenillas[a], F. de la Peña[b], J.L. García[b], M.A. Prieto[b], J.A. Menéndez[a]*
[a] Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain
[b] Centro de Investigaciones Biológicas, CSIC, C/ Ramiro de Maeztu, 9, 28040 Madrid, Spain
* Corresponding author. Tel.: +34 985 118972; Fax: +34 985 297672
E-mail address: angelmd@incar.csic.es

Supplementary material

Compounds detected in the chromatograms of MSWd-derived oils from CP and MIP following the first preparation method described (without methanolysis).

Retention Time (min)	**Compound**	**Conventional Pyrolysis**	**Microwave Pyrolysis**
4.171	Pyridine	-	0.59
4.661	Toluene	0.58%	-
5.814	2-Methylpyridine	-	0.44%
6.253	2-Cyclopenten-1-one	1.00%	0.93%
6.863	Furfuryl alcohol	0.69%	0.82%
6.992	Ethylbenzene	0.53%	0.44%
7.766	Styrene	4.18%	5.60%
8.162	2-Methyl-2-Cyclopenten-1-one	0.47%	0.50%
9.668	3-Methyl-2-Cyclopenten-1-one	0.62%	0.48%
10.158	Phenol	4.55%	1.79%
11.25	2-Hydroxi-3-Methyl-2-Cyclopenten-1one	0.97%	1.64%
11.551	2,3 Dimethyl-2-cyclopenten-1-one	0.38%	0.27%
11.698	Indene	1.33%	1.61%
11.956	o-Cresol	1.26%	0.85%
12.222	1-Phenyletanone	1.94%	0.48%
12.455	Cresol	2.67%	1.32%
12.79	2-Methoxyphenol	1.10%	0.96%
13.177	2,6-Xylenol	0.31%	-
13.435	3-Ethyl-2-Hydroxi-2-Cyclopenten-1-one	-	0.61%
13.926	Toluene diisocyanate	0.68%	-
14.158	2-Methyl indene	1.21%	0.36%
14.304	1-Methyl-2-Cyclopropen-Benzene	0.55%	-
14.51	Benzoic acid	-	0.52%
14.528	2-Ethyl-Phenol	0.39%	-
14.958	Naphthalene	4.11%	4.02%
15.044	1-Dodecene	0.65%	0.31%
15.448	Methacrylic acid	-	0.85%
16.394	Caprolactam	0.94%	0.52%

16.979	1,12-Tridecadiene	0.90%	-
17.134	1-Tridecene	1.03%	0.45%
17.306	1-Methyl-Naftalene	1.90%	0.79%
17.427	p-Xilene	0.59%	-
17.659	2-Methyl-Naftalene	1.22%	0.79%
18.381	Syringol	0.31%	-
18.983	Biphenyl	2.31%	1.53%
19.104	Tetradecene	1.54%	0.95%
19.25	Tetradecane	0.33%	0.27%
20.343	Acenaphthylene	1.30%	1.05%
20.816	1,12-Tridecadiene	0.38%	-
20.945	Pentadecene	1.63%	0.90%
22.57	1,13-Tetradecadieno	0.48%	-
22.7	Fluorene	1.88%	1.54%
22.803	Hexadecane	-	0.32%
24.231	1,9-Tetradecadiene	0.49%	0.40%
24.342	Heptadecene	1.01%	0.78%
24.454	Heptadecane	-	0.48%
24.773	Stilbene	0.56%	-
25.383	Pyrrolo[1,2-a]pyrazine	-	0.68%
25.96	Phenanthrene	3.79%	2.31%
26.106	Anthracene	0.84%	0.39%
27.121	1-Phenylnaphthalene	0.41%	0.28%
27.319	Eicosadiene	0.49%	0.32%
27.405	Heptadecene	0.94%	0.83%
27.766	1-Methylanthracene	0.47%	-
27.887	Hexadecanoic acid, methyl ester	0.31%	0.47%
28.42	Hexadecanoic acid	6.05%	4.28%
28.755	2-Phenylnaphthalene	1.43%	0.50%
28.833	Octadecene	0.84%	0.77%
28.91	Eicosane	-	2.83%
30.037	Fluoranthene	1.03%	0.57%
30.114	Hexadecenol	0.49%	0.40%
30.192	Nonadecene	0.76%	0.56%
30.312	Oleic acid, methyl ester	-	0.33%
30.837	Oleic acid	4.72%	7.17%
31.112	Stearic acid	2.28%	2.12%
31.439	Phenol, 4,4'-(1-methylethylidene)bis	-	0.38%
31.499	1-Docosene	1.10%	0.46%

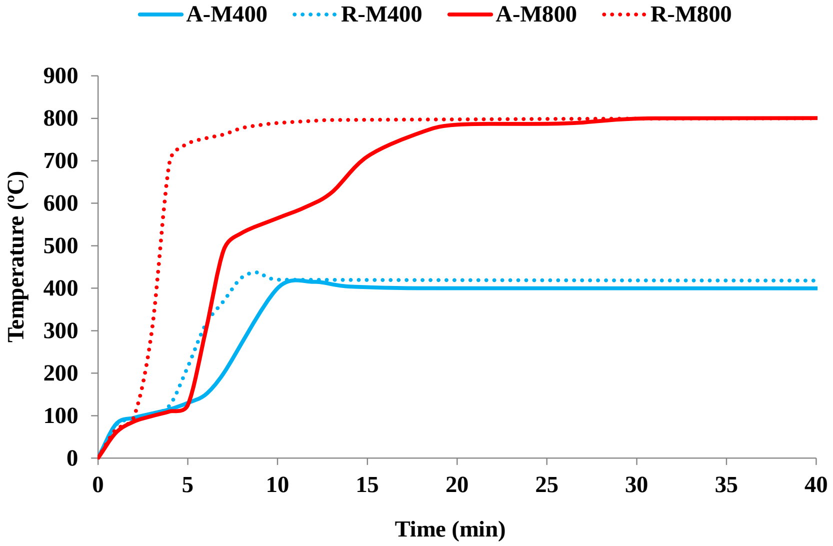
31.559	Docosane	-	0.27%
32.024	2-Methylfluoranthene	0.45%	-
32.239	Benzofluorene	0.42%	0.48%
32.669	Eicosadiene	-	0.27%
32.738	Nonadecene	0.83%	0.66%
34.932	Chrysene	0.66%	-
35.043	Triphenylene	0.38%	-
35.138	Nonadecane	-	0.38%
35.766	Phthalic acid	1.70%	3.63%
36.196	9-Tricosene	0.33%	
37.263	1-Nonadecene	0.67%	3.92%
38.295	Cyclooctacosane	1.49%	-
39.31	Benzoacephenantrilene	2.27%	2.32%
40.248	5-Nonadecene	1.06%	-
41.177	1-Docosene	1.30%	0.68%
42.071	Eicosene	1.13%	-
42.94	Dibenzochrysene	1.02%	-
42.948	Nonadecene	-	2.24%

Microwave pyrolysis of microalgae for high syngas production

D. Beneroso, J.M. Bermúdez, A. Arenillas, J.A. Menéndez*
Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain
* Corresponding author. Tel.: +34 985 118972; Fax: +34 985 297672
E-mail address: angelmd@incar.csic.es

Supplementary Data

Time-temperature profiles for the samples



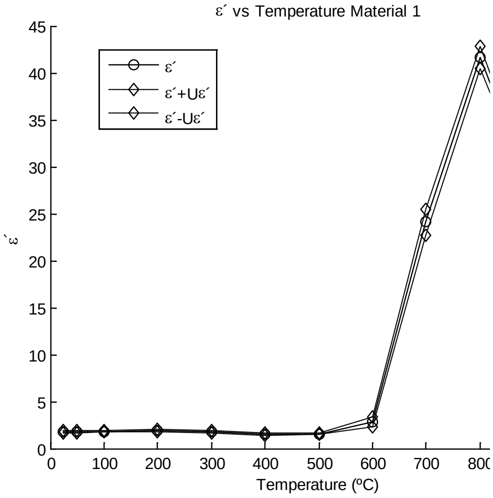
Dielectric characterization of biodegradable wastes during pyrolysis

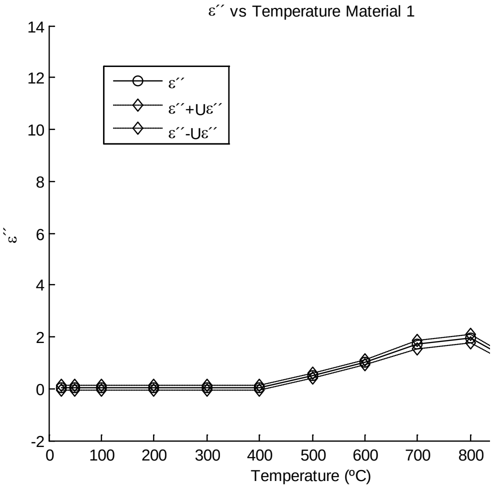
D. Beneroso[1], A. Albero-Ortiz[2], J. Monzó-Cabrera[2], A. Díaz-Morcillo[2], A. Arenillas[1], J.A. Menéndez[1]*
[1]*Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*
[2]*Department of Communication and Information Technologies, Technical University of Cartagena, Cartagena, Spain*
Corresponding author: Tel.: +34 985 119090
E-mail address: angelmd@incar.csic.es

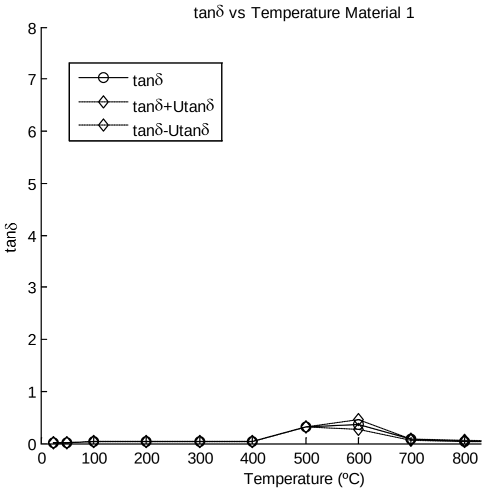
Supplementary Data

Error in measurements

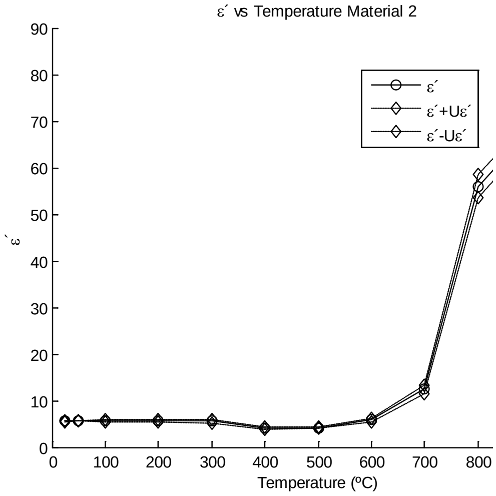
MSWd sample

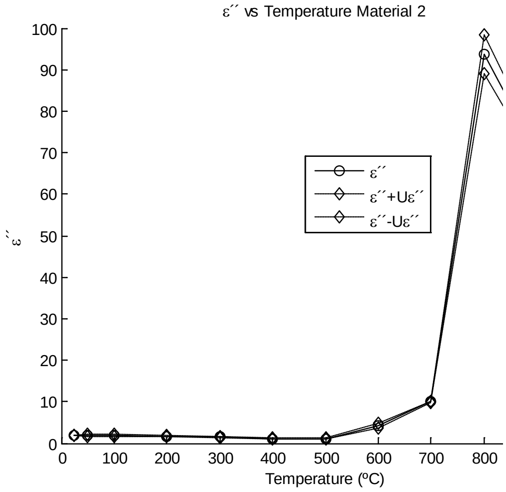


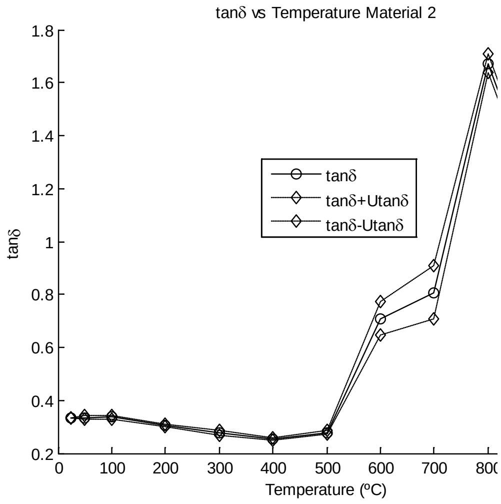



tanδ vs Temperature Material 1
tanδ
tanδ+Utanδ
tanδ-Utanδ
tanδ
Temperature (ºC)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
800

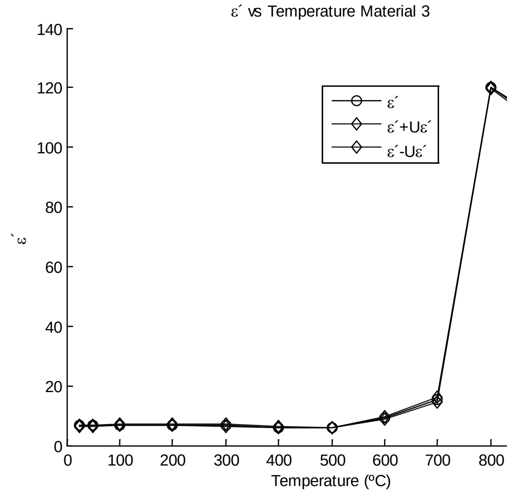
Mixture Char:MSWd (0.3:1)

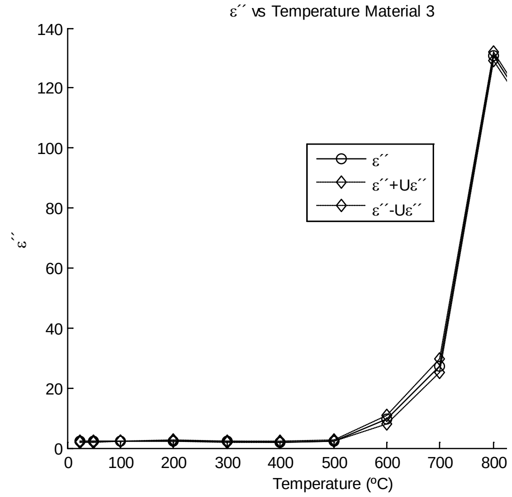


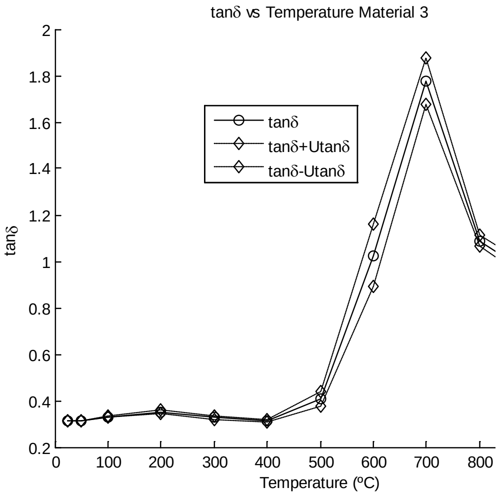



tanδ vs Temperature Material 2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
tanδ
0
100
200
300
400
500
600
700
80
Temperature (ºC)
tanδ
tanδ+Utanδ
tanδ-Utanδ

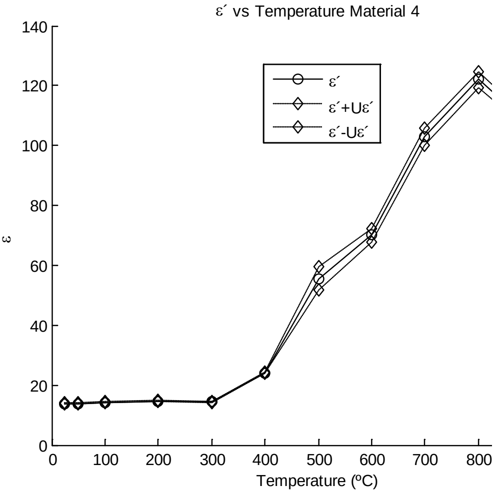
Mixture Char:MSWd (0.6:1)

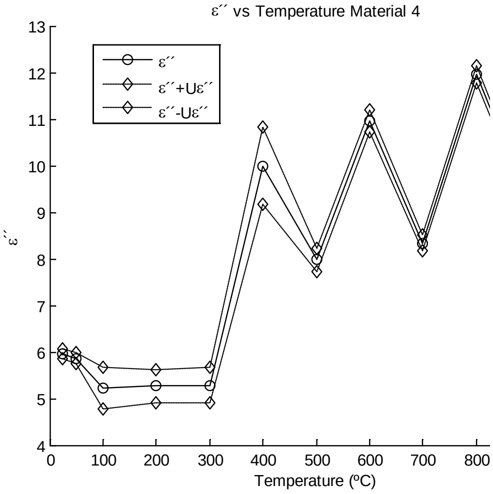


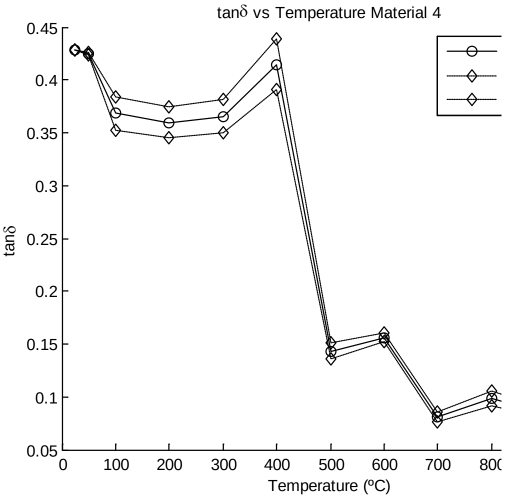



tanδ vs Temperature Material 3
tanδ
tanδ+Utanδ
tanδ-Utanδ
tanδ
Temperature (ºC)
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
100
200
300
400
500
600
700
800

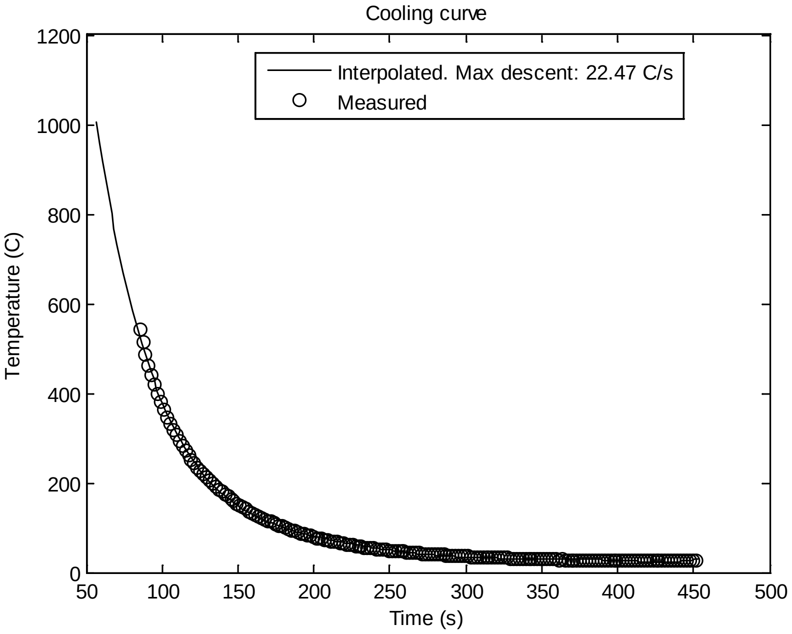
Char sample


ε´ vs Temperature Material 4
ε´
ε´+Uε´
ε´-Uε´
ε´
0
20
40
60
80
100
120
140
0
100
200
300
400
500
600
700
800
Temperature (ºC)


ε´´ vs Temperature Material 4
ε´´
ε´´+Uε´´
ε´´-Uε´´
ε´´
4
5
6
7
8
9
10
11
12
13
0
100
200
300
400
500
600
700
800
Temperature (ºC)


tanδ vs Temperature Material 4
tanδ
Temperature (ºC)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
100
200
300
400
500
600
700
80(

Cooling down curve



MCAT

Grupo de Microondas y Carbones para Aplicaciones Tecnológicas

CSIC
Consejo Superior de Investigaciones Científicas