

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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



Improving the stability and selectivity of furfural-to-aromatic catalytic process by co-feeding light alcohols



Juan Gancedo, Sergio Cañete, Laura Faba, Salvador Ordoñez

Catalysis, Reactors and Control Research Group (CRC), Dept. of Chemical and Environmental Engineering, University of Oviedo, Oviedo 33006, Spain

ARTICLE INFO ABSTRACT Keywords: This work demonstrates that green aromatics can be obtained with high selectivity by the gas-phase upgrading of Bicyclic aromatics furfural using ZSM-5. Furfural suffers a fast decarbonylation and cracking, yielding monoaromatics (benzene, LOHCs toluene, xylene, BTX) and naphthalenes. The low stability of this system is significantly enhanced by co-feeding MFI light alcohols (biomass derived platforms), also increasing the selectivity of aromatics. Ethanol increases the BTX Zeolites production (up to 36.4 % at 550°C), whereas maximum naphthalene selectivity is 14.9 % at 450°C. Using Furfural upgrading methanol strongly promotes the naphthalenes production (40.7 % at 450°C), without affecting the BTX one, yielding global selectivities up to 70 %. The stability of the catalytic process increases with the temperature, whereas the alkylation grade must be modulated to prevent both, undesired condensations of non-alkylated derivatives, and diffuse restrictions of polyalkylated derivatives (promoted when using methanol). The optimum equilibrium between these two opposite effects is reached with furfural-ethanol, achieving a stability 3.7 times higher than the one obtained when feeding only furfural. These results represent a significant improvement over the existing literature, both from the activity/selectivity and the stability points of view, describing a promising sustainable route for obtaining aromatics.

1. Introduction

The increasing pressure on fossil resources presents a challenge to the industrial production of aromatics for the near future. Aromatics constitute an important family of chemicals crucial for various industrial sectors including polymers, solvents, pharmaceuticals, agrochemicals, and fragrances. In fact, it is estimated that about 40 % (by mass) of bulk petrochemicals contain aromatic functionalities [1]. Currently, these compounds are primarily industrially produced by the catalytic reforming of naphtha or steam cracking of hydrocarbons. Nevertheless, the general trend of reducing our CO_2 footprint has opened opportunities to produce these chemicals from biomass.

The sustainable production of benzene, toluene, and xylene (BTX), three of the most used aromatics, has been studied by different routes, highlighting the catalytic fast pyrolysis (CFP), a single step process where the biomass decomposes into oxygenated pyrolysis vapors that are converted into a plethora of compounds, including aromatics and light olefins, inside the zeolite pores. This approach has deserved attention from numerous researchers, and very comprehensive studies about the aromatic formation mechanism (based on a Diels-Alder condensation) and the catalyst influence on conversion, selectivity and stability have been published in the last years [2–4]. In most of these studies, furan or furan derivatives are considered as the model dienes, whereas ethylene is the most typical dienophile used [5,6].

This background is a promising starting point for more specific routes, based on biomass-derived furans obtained in processes more selective than the pyrolytic one. Thus, previous works evaluate the BTX production from 2-methylfuran (MF), 2,5-dimethylfuran (DMF) or 5-hydroxymtheylfurfural (HMF) [7–11]. Although good yields are obtained, the high cost to produce these furans from lignocellulosic biomass hampers a possible scale-up of most of these alternatives.

In this context, using furfural as a diene precursor is an interesting alternative since this aldehyde can be selectively produced by the acid hydrolysis of nonedible lignocellulosic biomass [12]. Its current production at large scale (>200 kT/year), high reactivity and low cost (1–1.2 \notin /kg) make it an attractive platform molecule [13]. Its valorization has been deeply studied in the literature, encompassing reductions, oxidations, and condensations, as analysed in different reviews [14–17].

The great potential of producing aromatics from furfural contrasts

https://doi.org/10.1016/j.jece.2024.113571

Received 13 May 2024; Received in revised form 2 July 2024; Accepted 11 July 2024 Available online 13 July 2024

^{*} Corresponding author. E-mail address: sordonez@uniovi.es (S. Ordoñez).

^{2213-3437/© 2024} The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

with the early stage of research studies [18–20]. First studies highlight two main drawbacks, both directly related to its high oxygen content: the low aromatic yield (<30 wt%) and the fast deactivation by coke production. Furfural must undergo decarbonylation to obtain furan, the actual Diels-Alder diene. During this transformation, CO or CO₂ is released, fact that reduces the theoretical maximum yield to less than 60 wt% [21]. On the other hand, oxygen is a well-known coke precursor, and furfural conversion is significantly limited by undesired oligomerizations that reduce catalyst stability.

CFP studies demonstrate that the aromatics and olefins yield is a function of the hydrogen to carbon effective ratio of the feedstocks [22]. This concept was applied to furfural-to-aromatics studies proposing co-feeding of olefin (ethylene and propylene) [5,19,22], acrolein [23, 24] or methane [21] to improve the aromatic yields and reduce coke formation. Although good results are obtained, these carbon sources are expensive and not readily available, or have a petrochemical main origin, questioning the sustainability of this process.

In a previous work, we have suggested co-feeding furfural and ethanol to produce aromatics [25]. At reaction conditions (500°C, ZSM-5), furfural easily undergoes decarbonylation whereas ethanol dehydrates to ethylene. In this preliminary work, we have demonstrated that the Diels-Alder reactants can be in situ produced from these two renewable sources. In a first cycloaddition step, monoaromatics compounds are obtained (BTX), reaching 32 % yields. In a lesser extension, a second cycloaddition produces naphthalenes (9 %). Both the yields and the catalytic stability are conditioned by secondary reactions, including decarbonylation and hydrolysis of furan into olefins, olefins oligomerization, indenes production (graphitic coke precursors), and the production of oxygenated coke via benzofuran, an unstable intermediate produced by furan self-condensation [26].

In this work, we deepen in the reaction conditions to optimize these preliminary results, analyzing the influence of the temperature on the selectivity towards BTX and on the catalytic stability. ZSM-5 (Si/Al=23) zeolite is chosen for this study, considering the shape selectivity of aromatization and the good correspondence between the kinetic diameter of target compounds and the internal porosity of this zeolite, as well as the optimum acidity of this material [27].

The substitution of ethanol by methanol is also evaluated in this work. In addition to the organic origin, large availability and low cost of this reactant, the use of methanol is expected to enhance the current yields because of two concomitant effects: (1) methanol is an alkylating agent and the positive correlation between the degree of BTX alkylation and catalyst stability has been previously confirmed (aromatics alkylation hinders further oligomerization reactions leading to graphitic coke) [7]; and (2) the methanol-to-olefin process catalyzed by ZSM-5 zeolite promotes the presence of light olefins in the reaction medium [28]. This transformation is needed to produce the Diels-Alder reaction, but the lower reactivity of methanol (in comparison to ethylene) could increase the control on the olefin distribution, with the subsequent

positive effect on the catalyst stability. Considering the reaction mechanism proposed in the literature, cofeeding methanol is expected to improve state-of-art without affecting the general pathway, as shown in Scheme 1.

Despite the expected improvements of using these light alcohols, there are no previous studies considering this approach for producing aromatics (combining furfural and light alcohols). Results obtained demonstrate that this methodology improves the preexisting results, both in terms of aromatics selectivity (mainly using methanol), and catalytic stability (more evident using ethanol).

2. Materials and methods

The NH₄-ZSM-5 (SAR: 11.5, Zeolyst, CBV2314) was thermally activated at 550°C for 12 hours to obtain the zeolite in its proton form, H-ZSM-5. The resulting catalyst was pelletized with 5 tons of pressure and sieved to a particle size range of $250 - 355 \mu$ m. This material has been characterized in a previous work (pore volume of $0.19 \text{ cm}^3/\text{g}$, and surface area of $353 \text{ m}^2/\text{g}$, total acidity 15.6 mmol NH₃/g, LAS/BAS = 0.23) [27].

Condensations were performed in a 0.7 wide U-shaped fixed-bed reactor covered by an electric furnace with temperature control, placing 180 mg of the catalyst, and feeding different compounds and mixtures with syringe pumps. With this configuration, heat transfer effects are expected to be negligible.

All the reactants were used as received: furfural (Sigma-Aldrich, 99 %), ethanol (VWR, 99.97 %), and methanol (VWR, 100 %). Helium (Air Liquide, >99.999 %) was used as the carrier gas, resulting in a total gas flow of 20 Nml/min. The tests using individual reactants were performed with 5 % v/v of organics, whereas reactions with the mixtures have a total organics concentration of 10 % v/v. To ensure reactants vaporization and prevent the products condensation, all the fittings and transfer lines were heated to 250°C. The process pressure was maintained at 2–2.5 bars, whereas different temperatures (from 350 to 600°C) were studied, being reached using an electric oven coupled to a PID controller.

Products' identification was performed by gas chromatography-mass spectrometry on a GC-MS Shimadzu QP 2010 instrument (capillary column: TRB 5MS, 30 m, 0.25 mm) analyzing the effluent previously condensed in acetone at 0°C. Structural isomers are considered together.

Reactions were analyzed online by gas chromatography, using a flame ionization detector (GC FID HP 6890Plus) with the same column as utilized in the GC-MS, and using commercial samples for calibration (when available) or applying response factors. Fig. S1 shows a typical chromatogram obtained for the reactor outlet.

All the reactions were performed twice, results discussed in the manuscript being the average value of both tests (error <3 %). Experimental results are analyzed as a function of the conversion and selectivity in carbon basis, considering the following equations:



Scheme 1. Reaction pathway of furfural and light alcohols aromatization (ethanol and methanol) over acid zeolites.

Conversion:
$$x_a$$
 (%) = $\left(1 - \frac{C_{a,exit}}{C_{a,entry}}\right) \cdot 100$ (1)

Selectivity:
$$\varphi_i \quad (\%) = \frac{n_i \cdot C_i}{\sum (n_a \cdot C_{a,entry})} \cdot 100$$
 (2)

Where "C" is the concentration and "n" is the number of carbon atoms in the molecule of "i" product or "a" reactant. Considering the carbon balance, the lack of total correspondence between mass and products is attributed to CO, CO₂, carbonaceous, and condensed compounds whose selectivity is named "Coke & COx".

Considering the microporosity of the ZSM-5 zeolite (pore sizes of 6.1 Å after applying the Norman radii correction to evaluate the thermal effect), the reaction is expected to be controlled by the internal mass-transfer (aspect theoretically corroborated in our previous work, [25]). However, all the reactions are performed at the same conditions, suggesting that transport limitations influence mainly to products and not to reactants, being the same for all the reactions. Thus, experimental results can be directly compared.

Spent catalysts were recovered after 5 h of reaction at 500°C to analyze the coke formation by temperature programmed oxidation (TPO) using a Micromeritics Autochem II 2920. The signals of CO_2 were monitored by mass spectrometry (Omnistar GSD301) whereas the temperature increases from 30 to 700°C with a lapse rate of 5°C/min, under 20 ml/min flowrate of 0.5 % O_2 in He.

3. Results and discusion

3.1. Reactants reactivity in the absence of any catalyst

The reactivity of furfural in the absence of a catalyst was initially studied to quantify the relevance of possible decomposition reactions that could interfere in the correct analysis of the catalytic activity. Its thermal stability was analyzed in the range of 350–600°C, as shown in Fig. 1, observing significant reactivity at temperatures above 400°C.

An exponential increase of furfural conversion is observed, from 4.8 % at 450°C to 80 % at 600°C. The product distribution suggests two simultaneous decomposition routes of this aldehyde: the decarbonylation yielding furan (maximum selectivity of 5.7 % at 500°C), and thermal cracking to small molecules, such as ethylene and CO_2 , molecules collectively referred to as "cracking products". This second route is the most relevant one, reaching up to 74 % of total selectivity at 600°C.

Ethanol is significantly more stable than furfural, see Fig. 1.b but its conversion also follows an exponential behavior, reaching up to 20 % of maximum value (600°C). The ethanol dehydration yields ethylene. This route is mainly favored at 600°C, temperature at which its selectivity reaches 10 %. At 500°C and 550°C, butene is observed with almost the same selectivity as ethylene. However, at 600°C, ethylene selectivity is twice that of butene (10 % vs. 5.3 %). This result is in good agreement with the high temperature dependence observed by other authors for the ethanol dehydration [29], and suggests that, at these conditions, unimolecular dehydration is energetically favored over oligomerization. The lack of methanol signals discards undesired dehydration mechanisms identified in the literature at high temperatures [29], supporting the appropriateness of using ethanol as a selective source of the required alkenes.

The corresponding studies in the absence of any catalyst feeding methanol demonstrate that this compound is completely non-reactive at the considered conditions (negligible conversion in all the cases). These results are in good agreement with the molecular stability of this compound, requiring medium Bronsted acids to activate it. Based on this, the behavior of mixtures involving methanol are expected to be not conditioned by any undesired thermal effect.

Considering these results, catalytic reactions conducted at temperatures below 500°C seem to be minimally influenced by the thermal stability of the molecule, irrespective of the reactants employed.



Fig. 1. Thermal stability of (a) furfural and (b) ethanol. Data summarized in terms of conversion (\diamond) and selectivity distribution: furans (yellow), ethylene (light green), butene (dark green), and cracking products (grey). Both reactions were performed with 5 %v/v of organics with a total flowrate of 20 ml/min using 180 mg of ZSM-5.

However, at temperatures exceeding this threshold, it becomes imperative to weigh the interplay between catalytic and thermal effects.

3.2. Furfural catalytic upgrading

The furfural gas-phase upgrading using H-ZSM-5 zeolite was analyzed in the range of 350–600°C, considering not only the activity and selectivity but also the stability of the reaction. Initial activities, evaluated in terms of product distribution, are shown in Fig. 2. The detailed distribution of all the compounds detected is included in the Supplementary Information (Table S1).

Almost total furfural conversion is reached for all the temperature tested (>97 %). At 350°C, aromatic compounds were detected only in traces, with less than 3 % of monoaromatics (including benzene, toluene, and xylenes, BTXs) and 2 % of naphthalenes. At these conditions, almost 95 % of the furfural converted is not transformed in any detected compound (grey bar in Fig. 2). According to the literature [25], the production of aromatics from furfural occurs via a Diels-Alder mechanism requiring two concomitant previous transformations. Furfural must suffer decarbonylation to obtain furan, i.e. the conjugated diene. In addition, furan cracking is also needed to obtain the alkenes required for the aromatization (reaction between furan and alkenes). Considering that neither furan nor ethylene were observed, the Diels-Alder reaction is considered as instantaneous when the surface catalyst is clean, being the decarbonylation the rate-limiting step. This result is congruent with the absence of furan during the thermal stability analysis and with previous literature that indicates that this reaction is strongly enhanced at temperatures over 500°C if no transition or noble



Fig. 2. Selectivity of different compounds detected in the furfural conversion over ZSM-5 zeolite as a function of the temperature feeding 5 %v/v of organic in a total flowrate of 20 ml/min, 180 mg of ZSM-5. Data corresponding to: BTX (white), alkenes (green), naphthalenes (pink), indenes (violet), CO_2 & coke (grey), and unconverted furfural (black lines).

metals are used to promote it [30].

The time-on-stream (TOS) analyses at these conditions (350° C), Fig. 3, reveal a very fast deactivation. Thus, 44 % of unconverted furfural appears after less than 0.5 h TOS, time at which 26 % of furan selectivity is observed, with negligible amounts of BTX or any other aromatics. The furan selectivity decreases continuously and disappears in less than 3 h. At longer TOS, furfural conversion remains constant at 12–14 %, with a total correspondence with the carbon balance



Fig. 3. Time-on-stream evolution of the product distribution in the furfural (5 %v/v, 20 ml/min, 180 mg of ZSM-5) upgrading at (a) 350 °C and (b) 500°C. Data corresponding to: BTX (white), alkenes (green), furan (yellow), naphthalenes (pink), indenes (violet), CO_2 & coke (grey), and unconverted furfural (black lines).

discrepancies.

At 400°C, a significant increase in the initial production of BTX (8 %) and naphthalenes (11.4 %) is observed. As to stability, (see Supplementary Information, Fig. S2), same evolutions as at 350°C are obtained, but with softer trends. Total deactivation is observed in less than 1 h. These results suggest that the non-framework Lewis acidity required for furfural decarbonylation [20] are distributed at surface level (furan only disappears after the total deactivation of the catalyst), whereas there is a competition between two reactions taking place in the internal porosity (Bronsted sites on Si-O-Al groups), the furan cracking (required to produce the alkenes) and the furan oligomerization (oxygenated coke promoted at low temperatures) [26], the last being the predominant one. Once the pores are blocked, neither aromatics nor alkenes are detected, and the lack of carbon balance has a better correspondence with the CO released during the furfural decarbonylation. At initial times, this low carbon balance is the result of two contributions (coke and CO), whereas the coke growing is the only effect observed at longer TOS.

Increasing the temperature, the initial selectivity towards desired compounds significantly increases, with a total 44 % of aromatic production at 500°C (28.2 of BTX, 16.8 % or naphthalenes). Both mono and diaromatic selectivities decrease at higher temperatures, suggesting the subsequent oligomerizations resulting in graphitic coke. This is congruent with the appearance of indenes (coke precursors) at these conditions.

These results are substantially higher than those reported by Fanchiang & Lin, (15.7 % or aromatics using a ZSM-5 (Si/Al 80)) [26], and Karnajankom et al., reaching less than 10 % of aromatics using BEA zeolite [31], reinforcing the relevance of choosing an optimum catalyst in terms of pore size (DA is a shape-selective reaction) and acidity [27]. Moreover, conversion and product distribution obtained with furfural at 500°C is quite like the one obtained feeding furan [27], supporting the hypothesis of a fast furfural decarbonylation that does not affect the overall distribution. Thus, using furfural increases the green character of the process without reducing in the aromatics produced.

As to stability, (see Fig. 3b for results at 500°C, Fig. S3 for other conditions) TOS studies reinforce the previous premise about diffusion restrictions owing to coke formation, with a continuous decrease in BTX and naphthalene yields while furan remains the main product during the full induction-conversion-deactivation cycle. This effect is strongly marked when using furfural, with total disappearance of BTX after 1 h TOS, and trace remaining naphthalene selectivity after 3 h (<2 %). Furan selectivity remains almost constant with values higher than 45 % since the first hour, and total deactivation is not observed after 8 h. The deactivation step is faster as the temperature increases, and the lack of furfural net conversion is observed at 550°C (after 3.5 h) and at 600°C (after 3 h). To sum up, the poor stability obtained when using furfural is the main drawback of this configuration.

Considering that the production of graphitic coke is assumed to be the main cause of this deactivation, the possibility of cofeeding alkylation agents (the oligomerization trend has been demonstrated to be hindered for alkylated isomers [7]) is evaluated.

3.3. Catalytic upgrading of furfural mixtures

In this study, the activity of light alcohols (ethanol and methanol) as alkylation promoters is evaluated. Although the experiments with furfural clearly suggest an optimum reaction temperature (500°C), the study considering mixtures with ethanol (EtOH) and methanol (MeOH) has been extended to the range 400–600°C to identify if the presence of the co-reactant modifies this optimum point.

The fast ethanol dehydration proved in preliminary studies [25] suggests the possibility of using this alcohol as an in-situ alkene precursor, obtaining the desired alkylation effect cofeeding two primary bioplatform molecules. Thus, at 500°C, complete ethanol conversion is obtained, and the mixture is enriched in ethylene and other light alkenes (56.2 %), whereas 19.3 % of BTX and 23.6 % of coke & CO_2 are also detected [25]. An alternative configuration considers the use of methanol, taking advantage of its controlled reactivity in ZSM-5 under similar ranges of temperatures, producing the required alkenes with a lower polymerization trend [28]. This assumption, based on the methanol to olefins (MTO) process was experimentally tested to ensure that the required alkenes are obtained under reaction conditions, as well as to evaluate the polymerization trend of these alkenes. Results are summarized in Fig. 4.

Full methanol conversion is obtained at all the temperatures tested, with almost 80 % of alkenes production. Ethylene, propylene and butene are obtained as main products, with a clear increasing trend of ethylene (maximum selectivity at 600°C, >33 %) opposite to the decreasing one observed for butene (maximum selectivity at 400°C, 32 %). The presence of heavier alkenes is discarded, but a small fraction of BTX is congruent with the cyclization of these species. These results demonstrate the expected higher control on the reaction products when using methanol instead of ethanol. Considering these preliminary studies, the use of methanol as an alkene precursor at working conditions is demonstrated to be suitable and promising.

Regards the results using furfural-alcohol mixtures, the range 450°C-550°C is identified as the most interesting one for both BTX and naphthalenes production. Results obtained at these temperatures are compared in Fig. 5. Complementary results obtained at 400°C and 600°C are included in the supplementary information (Figs. S4-S5). The detailed distribution of all the products detected is included in Table S2 (furfural-ethanol) and Table S3 (furfural-methanol).

Full furfural conversion is obtained with all the configurations and for all the temperatures tested. However, relevant differences are observed in terms of selectivity. In presence of ethanol, results indicate a higher production of BTX than when the reaction is performed only with furfural, and a significant increase in the alkenes. These distributions enriched in alkenes significantly increase the carbon balance, with the expecting growth in stability (discussed below). Working with furfural and ethanol mixtures produces a maximum of >36 % of BTX at 550°C, a value almost 30 % higher than the optimum one obtained without the alcohol. The displacement of the optimum temperature from 500°C to 550°C is explained because of the need of activating both the furfural and ethanol molecules. Despite the zeolite, the higher temperature required to activate the ethanol was previously discussed in blank reactions. The mixture furfural + ethanol does not improve the maximum naphthalene selectivity obtained with furfural (16.8 % at 500°C).

The influence of the light alcohol is significantly more evident when cofeeding methanol. All the samples are enriched in the target families



Fig. 4. Selectivity of different compounds detected in the methanol conversion (5 %v/v, 20 ml/min), over ZSM-5 zeolite (180 mg) as a function of the temperature. Data corresponding to: BTX (white), ethylene (light green), propylene (medium green), butene (dark green), and CO_2 & coke (grey).



Fig. 5. Product distribution obtained in the upgrading of different mixtures at (a) 450°C, (b) 500°C and (c) 550°C. In all the cases 180 mg of ZSM-5 were used as the catalyst. Experiment with only furfural has 5 %v/v of organics, whereas mixtures have a total concentration 10 %v/v (1:1) in a total flow of 20 ml/min. Data corresponding to: BTX (white), alkenes (green), furan (yellow), naphthalenes (pink), indenes (violet), CO_2 & coke (grey), and unconverted furfural (black lines).

(BTX and naphthalenes), and the increase in the reaction control is relevant, increasing the carbon balance to values lower than 20 % in all the cases (increase control as the temperature increases). For this combination, 450°C is the optimum temperature to promote the naphthalenes production, with a selectivity almost three times higher than the one obtained with only furfural (40.7 % vs. 14.1 %), a value also higher than when cofeeding ethanol (14.9 %). This unexpected naphthalene selectivity when using methanol could be due to the accumulation of these compounds when their production is enhanced but their high alkylation prevents its disappearance by hindering subsequent condensations (both aspects, alkylation and stability are discussed below). This effect is more evident at lower temperatures, when the competence with the formation of coke is less relevant. As for the BTX, the reaction mixture is enriched in this family when working at 550°C, obtaining a global selectivity of 37.5 %, a quite similar value than when using ethanol.

The relative weight of each isomer in the main fractions (BTX, alkenes, naphthalenes) is analyzed in Fig. 6. The selectivities of each compound considered in each family is detailed in the supplementary information (Table S1-S3). The average alkylation grades of both BTX and naphthalenes increase when cofeeding ethanol and, especially, methanol. The presence of more alkylated molecules, as well as the increase in the number of alkylations of a given molecule, hinders the further condensations because of steric limitations. Thus, when BTX are enriched in xylenes and other trimethylbenzenes, the second condensation to produce naphthalene is not favored, obtaining a final mixture enriched in BTX when the alkylation is promoted, i.e., at high



Fig. 6. Comparison of the relative weight of each grade of alkylation as a function of the reagent(s) used. Data corresponding furfural (blue), furfural + ethanol (orange), and furfural + methanol (green) obtained at (a) 450°C, (b) 500°C, and (c) 550°C. In all the cases 180 mg of ZSM-5 were used as the catalyst. Experiment with only furfural has 5 %v/v of organics, whereas mixtures have a total concentration 10 %v/v (1:1) in a total flow of 20 ml/min. Symbols: (B) benzene; (T) toluene, (X) xylene; (E) ethylene, (P) propylene, (But) butene; (N) naphthalene; (MN) methylnaphthalene; and (DMN) dimethylnaphthalene.

temperatures and using methanol.

As to alkenes, the lower oligomerization trend of methanol in comparison to ethanol is also observed, with a distribution in the alkene family enriched in ethylene and propylene, being depleted in butene. The alkylation capacity of these alkenes increases when the carbon chain decreases, because alkyl chains introduce steric limitations. This justifies the lower total selectivity to alkenes and the higher alkylation grade of aromatics obtained when using methanol.

The increment in the alkylation grade of the aromatics is expected to have a direct effect on the stability of the process (the main drawback of feeding only furfural). To study this aspect, the time-on-stream (TOS) evolution of all the products was analyzed, obtaining significant differences between them. As significant examples, the profiles obtained at 500°C with ethanol and methanol are compared in Fig. 7, whereas data corresponding to other temperature tested are included in the supplementary information (Figs. S6-S7).

Furfural conversion remains 100 % for an initial period (induction time directly conditioned by the temperature and the reactants) after which it decreases following an exponential behavior to reach an almost 10 % remaining conversion that is not related to the aromatics production but to the furan one. On the contrary, the alcohol conversion follows a significantly softer deactivation trend. As explained before, this behavior is congruent with the continuous blockage of internal porosity where the aromatization takes place and a remanent decarbonylating activity of surface acidity. Times shown in Fig. 8 correspond to the TOS at which the furfural conversion decreases up to 50 %.

As observed, cofeeding light alcohols has a relevant positive influence on the catalytic stability. This parameter increases with the



Fig. 7. Time-on-stream evolution of the product distribution in the (a) furfuralethanol and (b) furfural-methanol upgrading at 500°C. Data corresponding to: BTX (white), alkenes (green), furan (yellow), naphthalenes (pink), indenes (violet), CO_2 & coke (grey), unconverted furfural (black lines), unconverted alcohols (blue lines).



Fig. 8. : Analysis of the catalytic stability as a function of the temperature and the reactants used for the aromatic green production. Results expressed in terms of the time after which the initial total furfural conversion decreases to 50 %. Data correspond to feeding furfural (blue), furfural + ethanol (orange), and furfural + methanol (green).

temperature, following an exponential trend. The low stability observed at low temperature suggests a deactivation strongly conditioned by furfural or furan condensation, leading to oxygenated coke. The amorphous structure of these solids is congruent with the fast deactivation, with total pore blockage in short periods of time. Alcohols or their derivatives are not involved in this type of coke, explaining the similar deactivation times obtained despite the reactants used (deactivation directly related to furfural).

Once the temperature increases enough to activate the alcohols reactivity and the Diels-Alder reaction, this effect is less relevant, the formation of graphitic coke promoted by uncontrolled condensations being more important. Thus, the increase in the alkylation grade obtained when introducing ethanol has a clear positive effect in the catalytic stability. The intermediate stability reached with methanol is explained by the shape selectivity effect, and the high size to polyalkylated derivatives. Thus, even when the further condensations are not promoted, this system produces streams enriched in these big isomers that also promote the deactivation. The influence of the reactant system used increases as the temperature does because benzene oligomerization and alkylations are promoted.

This discussion is confirmed by the TPO analyses of spent catalysts. Fig. 9 compares the evolution of the CO_2 signal obtained after 5 h at 500°C, using the three different feeding configurations compared in this work. The temperature for this analysis was chosen because of being representative of the most active conditions (500–550°C). The comparison at 550°C could be more affected by the different TOS, a parameter that clearly conditions the amount of coke obtained.



Fig. 9. CO_2 desorption profiles obtained for the TPO analyses of spent catalysts recovered after reactions at 500°C feeding furfural, furfural + methanol, and furfural + ethanol.

The fastest deactivation observed when feeding only furfural is congruent with the larger CO_2 obtained in the TPO. In fact, the total area (proportional to the amount of CO_2) is three times bigger than the area of the signal obtained with furfural+ethanol. In both cases, two different peaks are clearly observed (oxidation temperatures of 550–580 and 640–650°C), suggesting the presence of two different types of organic deposits. According to the literature, the lowest temperature corresponds to the desorption of oxygenated coke that is mainly obtained by furan and furfural oligomerization (disordered structure, less stable), whereas graphitic coke obtained by aromatics uncontrolled condensation requires more temperature to be oxidized (crystalline structure) [27]. The higher aromatics production obtained with furfural-ethanol is congruent with the relative prevalence of this type of coke over the oxygenated one.

An intermediate situation is observed in the TPO of the catalyst recovered after the reaction with furfural and methanol. In this case, the signal is almost two times bigger than the signal obtained with furfural and ethanol (1.86). However, the most relevant difference is the presence of only one signal that, with a slight displacement to high temperature, corresponds with disordered coke, in this case due to diffusional limitations of the most alkylated aromatics. The absence of crystalline coke is congruent with the main hypothesis to explain its activity results: increasing the alkylation grade of BTX decreases the condensation capacity of these aromatics.

All the catalysts recovered their initial white aspect, concluding that the thermal regeneration is a good option to reactivate the catalysts for further cycles of reaction.

To sum up, Table 1 summarizes the optimum results defined in this work in comparison to the best results of the literature.

Methanol is proposed as the best option to increase the aromatics production (mainly considering the naphthalenes) but ethanol is a good co-reactant to reach high BTX yields with an improved stability. Although deactivation is important for this reaction, deactivation times are significantly larger than other ones reported in the literature for catalytic processing of furanic compounds, even when cofeeding alkenes and modifying the ZSM-5 surface to introduce mesoporosity [32–34]. Our study and most of the reported studies uses fixed bed reactors with the aim to test catalysts and optimize operation conditions. However, scaling-up of these processes should require the use other reactor technologies, as fluidized bed. The main relevance of this study is, therefore, the promising selectivities obtained before this deactivation, being values significantly higher than those proposed in the literature for similar conditions [5,20].

4. Conclusions

This work demonstrates the possibility of obtaining aromatic compounds (mainly BTX and naphthalenes) with high selectivity and an improved stability from the co-feeding of different platform biomolecules directly obtained from biomass. The results obtained by exclusively feeding furfural demonstrate the potential to obtain these compounds through a Diels-Alder mechanism once furfural has undergone decarbonylation (yielding furan) and cracking (resulting in the necessary alkenes). These two processes occur instantaneously at the operating temperature; hence the obtained products directly correspond to the different aromatics. The mechanism is thus evidenced when the uncontrolled condensation of these aromatics (favored by the low degree of alkylation) allows the detection of furan as the major compound. The low stability of the process is, therefore, the main drawback of this configuration.

The stability of the process and the selectivity towards the desired products increase significantly when co-feeding light alcohols. Thus, ethanol is the alcohol that maximizes system stability, achieving an adequate degree of alkylation of the products and producing a maximum of 36.4 % BTX (550°C, total aromatic yield of 45.6 %). In contrast, methanol does not reach as much stability due to favoring the

Comparison of optimized results of this work with previous literature.

Reactants	Olefin/ Furan	T (°C)	Catalyst	SAR	WHSV (h^{-1})	Furan conv. (%)	BTX select. (%)	Napth. Select. (%)	Ref
FFL + EtOH FFL + MetOH FFL FFL + Propilene FFL + MetOH FFL + MetOH	1/1 1/1 - 2.3 2 5	550 450 500 600 550 500	ZSM-5 ZSM-5 1.5 %Zn/ZSM-5 ZSM-5 ZSM-5 ZSM-5	23 23 80 30 50 50	4.3 4.3 10.4 9.0 6.0 2.0	100 >98 100 100 100 100	37.5 29.3 25.4 41.1 15.9 32.8	9.2 40.7 0.9 1.6 <2.4 10.7	This work [20] [5] [35] [36]

production of more alkylated compounds (diffusional limitations in the zeolite), but it allows for highly selective streams to BTX (37.5 % at 550°C) and, notably, naphthalenes (40.7 % at 450°C). At optimum conditions, the total aromatic yield obtained with this system increases up to 70 %. These results significantly enhance the existing literature, representing a major advancement for the sustainable synthesis of aromatics.

CRediT authorship contribution statement

Sergio Cañete: Investigation, Methodology. Juan Gancedo: Writing – original draft, Investigation, Data curation. Salvador Ordonez: Writing – review & editing, Funding acquisition, Conceptualization. Laura Faba: Writing – review & editing, Supervision, Methodology, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This study has been financially supported by the Spanish Ministry of Science and Innovation (PID2020–112587RB-I00).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.113571.

References

- J. van Haveren, E.L. Scott, J. Sanders, Bulk chemicals from biomass, Biofuel Bioprod. Bior. 2 (2008) 41–57, https://doi.org/10.1002/bbb.43.
- [2] Y.K. Wu, J. Yang, G. Wu, W.R. Gao, E.E.S. Lora, Y.M. Isa, K.A. Subramanian, A. Kozlov, S. Zhang, Y. Huang, Benzene, toluene, and xylene (BTX) production from catalytic fast pyrolysis of biomass: a review, ACS Sust. Chem. Eng. 11 (2023) 11700–11718, https://doi.org/acssuschemeng.3c01202.
- [3] B. Valle, A. Remiro, N. García-Gómez, A.G. Gayubo, J. Bilbao, Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review, J. Chem. Technol. Biotechnol. 94 (2019) 670–689, https://doi.org/10.1002/jctb.5758.
- [4] J.M.J.M. Ravasco, R.F.A. Gomes, Recent advances on Diels-Alder driven preparation of bio-based aromatics, ChemSusChem 14 (2021) 3047–3053, https:// doi.org/10.1002/cssc.202100813.
- [5] Y.-T. Cheng, W. Huber, Production of target aromatics by Diels-Alder classes of reactions with furans and olefins over ZSM-5, Green. Chem. 4 (2012) 3114–3125, https://doi.org/10.1039/c2gc35767d.
- [6] S. Song, G.J. Wu, W.L. Dai, N.J. Guan, L.D. Li, Diels-Alder and dehydration reactions of furan derivatives with ethylene catalyzed by liquid Bronsted acid and Lewis acids, J. Molec. Catal. A 420 (2016) 134–141, https://doi.org/10.1016/j. molcata.2016.04.023.
- [7] J. Gancedo, L. Faba, S. Ordóñez, Role of reactant alkylation grade in the selectivity and stability of furan-alkene Diels-Alder reactions, ACS Sust. Chem. Eng. 10 (2022) 3057–3065, https://doi.org/10.1021/acssuschemeng.1c08544.

- [8] Y. Zhao, T. Pan, Y. Zuo, Q.X. Guo, Y. Fu, Production of aromatic hydrocarbons through catalytic pyrolysis of 5-hydroxymethylfurfural from biomass, Bioresour. Technol. 147 (2013) 37–42, https://doi.org/10.1016/j.biortech.2013.07.068.
- [9] A.E. Settle, L. Berstis, N.A. Rorrer, Y. Roman-Leshkóv, G.T. Beckham, R. M. Richards, D.R. Vardon, Heterogeneous Diels-Alder catalysis for biomass-derived aromatic compounds, Green. Chem. 19 (2017) 3468–3492, https://doi.org/ 10.1039/c7gc00992e.
- [10] R.C. Cioc, M. Crockatt, J.C. van der Waal, P.C.A. Bruijnincx, Targeting valuable chemical commodities: hydrazine-mediated Diels-Alder aromatization of biobased furfurals, ChemSusChem 15 (2022) e202201139, https://doi.org/10.1002/ cssc.202201139.
- [11] S. Dutta, N.S. Bhat, Catalytic synthesis of renewable p-xylene from biomass-derived 2,5-dimethylfuran: a mini review, Biomass-.-. Conver. Bior. 13 (2020) 541–554, https://doi.org/10.1007/s13399-020-01042-z.
- [12] E. Cousin, K. Namhaed, Y. Pérès, P. Cognet, M. Delmas, H. Hermansyah, M. Gozan, P.A. Alaba, M.K. Aroua, Towards efficient and greener processes for furfural production from biomass: a review of the recent trends, Sci. Total Environ. 847 (2022) 157599, https://doi.org/10.1016/j.scitotenv.2022.157599.
- [13] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López-Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, Energ. Environ. Sci. 9 (2016) 1144–1189, https://doi.org/10.1039/ c5ee02666k.
- [14] J. Husson, J. Dehaudt, L. Guyard, Furfuraldehyde: from plant harvest to light harvest? J. Environ. Chem. Eng. 3 (2015) 2292–2300, https://doi.org/10.1016/j. jece.2015.08.005.
- [15] X. Zhang, S.Q. Xu, Q.F. Li, G.L. Zhou, H.A. Xia, Recent advances in the conversion of furfural into bio-chemicals through chemo- and bio-catalysis, RSC Adv. 11 (2021) 27042–27058, https://doi.org/10.1039/d1ra04633k.
- [16] S. Dutta, Valorization of biomass-derived furfurals: reactivity patterns, synthetic strategies, and applications, Biomass-.- Conv. Bior. 13 (2021) 10361–10386, https://doi.org/10.1007/s13399-021-01924-w.
- [17] F. Deng, A.S. Amarasekara, Catalytic upgrading of biomass derived furans, Ind. Crop. Prod. 159 (2021) 113055, https://doi.org/10.1016/j.indcrop.2020.113055.
- [18] H. Zhang, Y. Wang, S. Shao, R. Xiao, An experimental and kinetic modelling study including coke formation for catalytic pyrolysis of furfural, Combust. Flame 173 (2016) 258–265, https://doi.org/10.1016/j.combustiflame.2016.08.019.
- [19] Y.-T. Cheng, G.W. Huber, Chemistry of furan conversion into aromatics and olefins over HZSM-5: a model biomass conversion reaction, ACS Catal. 1 (2011) 611–628, https://doi.org/10.1021/cs200103j.
- [20] W.-L. Fanchiang, Y.-C. Lin, Catalytic fast pyrolysis of furfural over H-ZSM-5 and Zn/H-ZSM-5 catalysts, Appl. Catal. A 419-420 (2012) 102–110, https://doi.org/ 10.1016/j.apcata.2012.01.017.
- [21] A. Wang, D. Austin, H. Qian, H. Zeng, H. Song, Catalytic valorization of furfural under methane environment, ACS Sust. Chem. Eng. 6 (2018) 8891–8903, https:// doi.org/10.1021/acssuschemeng.8b01257.
- [22] H.Y. Zhang, Y.T. Cheng, T.P. Vispute, R. Xiao, G.W. Huber, Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio, Energ. Environ. Sci. 4 (2011) 2297–2307, https://doi.org/ 10.1039/c1ee01230d.
- [23] T.S. Khan, S. Gupta, M. Ahmad, M.I. Alam, M.A. Haider, Effect of substituents and promoters on the Diels-Alder cycloaddition reaction in the biorenewable synthesis of trimellitic acid, RSC Adv. 10 (2020) 30656–30670, https://doi.org/10.1039/ d0ra04318d.
- [24] M. Shiramizu, F.D. Toste, On the Diels-Alder approach to solely biomass-derived polyethylene terephthalate (PET): conversion of 2,5-dimethylfuran and acrolein into p-xylene, Chemistry 17 (2011) 12452–12457, https://doi.org/10.1002/ chem.201101580.
- [25] J. Gancedo, L. Faba, S. Ordóñez, From biomass to green aromatics: direct upgrading of furfural-ethanol mixtures, ACS Sust. Chem. Eng. 10 (2022) 7752–7758, https://doi.org/10.1021/acssuschemeng.2c02285.
- [26] J. Gancedo, L. Faba, S. Ordóñez, Benzofuran as deactivation precursor molecule: improving the stability of acid zeolites in biomass pyrolysis by co-feeding propylene, Appl. Catal. A 611 (2021) 117980, https://doi.org/10.10169/j. apcata.2020.117980.
- [27] J. Gancedo, L. Faba, S. Ordóñez, Tuning the selectivity on the furan-propylene Diels-Alder condensation over acid catalysts: role of pore topology and surface acidity, Appl. Catal. A 641 (2022) 118683, https://doi.org/10.1016/j. apcata.2022.118683.
- [28] U. Olsbye, S. Svelle, M. Bjorgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity, Angew. Int. Ed. 51 (2012) 2–24, https://doi.org/ 10.1002/anie.201103657.

J. Gancedo et al.

- [29] J. Park, R. Zhu, M. Lin, Thermal decomposition of ethanol. I. Ab Initio molecular orbital/Rice-Ramsperger-Kassel-Marcus prediction of rate constant and product branching ratios, J. Chem. Phys. 117 (2002) 3224–3231, https://doi.org/10.1063/ 1.1490601.
- [30] O.O. James, S. Maity, L.A. Usman, K.O. Ajanaku, O.O. Ajani, T.O. Siyanbola, S. Sahu, R. Chaubey, Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxymethylfurfural, Energy Environ. Sci. 3 (2010) 1833–1850, https://doi.org/10.1039/b925869h.
- [31] S. Karnjanakom, A. Yoshida, A. Bayu, I. Kurnia, X. Hao, P. Maneecharkr, A. Abudula, G. Guan, Bifunctional Mg-Cu loaded β-zeolite: high selectivity for the conversion of furfural into monoaromatic compounds, ChemCatChem 10 (2018) 3564–3575, https://doi.org/10.1002/cctc.201800450.
- [32] X. Qi, W. Fan, Selective production of aromatics by catalytic fast pyrolysis of furan with in situ dehydrogenation of propane, ACS Catal. 9 (2019) 2626–2632, https:// doi.org/10.1021/acscatal.8b04859.
- [33] J.S. Gou, Z.P. Wang, C. Li, X.D. Qi, V. Vattipalli, Y.T. Cheng, G. Huber, W. C. Conner, D.J. Dauenhauer, The effects of ZSM-5 mesoporosity and morphology on the catalytic fast pyrolysis of furan, Green. Chem. 19 (2017) 3549–3557, https://doi.org/10.1039/c7gc01395g.
- [34] S.S. Shao, H.Y. Zhang, D.K. Shen, R. Xiao, Enhancement of hydrocarbon production and catalyst stability during catalytic conversion of biomass pyrolysis-derived compounds over hierarchical HZSM-5, RSC Adv. 6 (2016) 44313–44320, https:// doi.org/10.1039/c6ra05356d.
- [35] A. Zheng, Z. Zhao, S. Chang, Z. Huang, K. Zhao, H. Wu, X. Wang, F. He, H. Li, Maximum synergistic effect in the coupling conversion of bio-derived furans and methanol over ZSM-5 for enhancing aromatic production, Green. Chem. 16 (2014) 2580–2586, https://doi.org/10.1039/c3gc42251h.
- [36] C. Wang, Z. Si, X. Wu, W. Lv, K. Bi, X. Zhang, L. Chen, Y. Xu, Q. Zhang, L. Ma, Mechanism study of aromatics production from furans with methanol over zeolite catalysts, J. Anal. Appl. Pyrol. 139 (2019) 87–95, https://doi.org/10.1016/j. jaap.2019.01.013-.