From Biomass to Green Aromatics: Direct Upgrading of Furfural–Ethanol Mixtures

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ABSTRACT: This work demonstrates that the production of aromatics by gas-phase Diels−Alder condensation of biomass platform molecules (furfural and ethanol) is feasible in the same terms as using chemicals from a petrochemical origin or more complex preparation procedures (as ethylene or furan). Thus, a double benefit for the environment is obtained since a waste biomass is proposed as the raw material to produce industrial high-value products by a renewable route. Experimental results with acid zeolites (ZSM-5) at 500 °C reveal total conversion and aromatic selectivities >42% (mono and bicyclic ones), with a similar catalytic stability to the most widely studied furan−ethylene system, a clear consequence that the furfural oligomerization is prevented by the prevalence of a Diels−Alder mechanism.

KEYWORDS: *Diels−Alder, Heterogeneous catalysis, Zeolites, MFI, BTX*
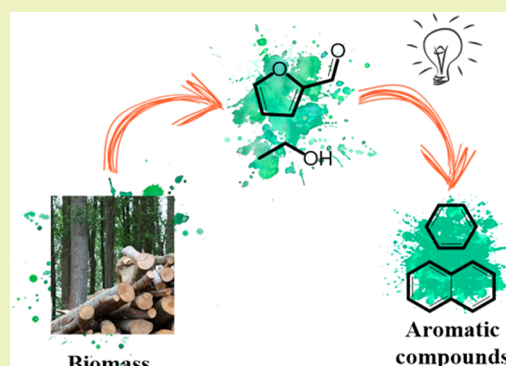
INTRODUCTION

The compulsory disruption of the use of petroleum as the reference raw material in the manufacture of chemicals has triggered interest in biobased production routes.[1−5] Among these chemicals, aromatics (monoaromatics such as benzene, toluene, and xylene-BTX- and naphthalenes) play a key role because of their intensive use as solvents and intermediates in industrial processes. They are precursors of polymers (polystyrene, rubber, and polyester), pesticides, and active pharmaceutical ingredients, among others. Hitherto, these aromatics are produced by different petrochemical routes, highlighting the catalytic reforming of naphtha or the steam cracking of hydrocarbons. Both processes have relevant drawbacks in terms of sustainability, the production of these aromatics constituting one of the biggest markets that must be assumed by the future biorefineries.

Considering this context, the sustainable production of aromatics has received great interest, proposing several biobased routes.[6] The Diels−Alder condensation is one of the most promising ones, a reaction involving a conjugated diene and a dienophile that fulfills the principle of atom economy (100% of carbons in reactants being included in products). Different aromatics could be obtained,[7−9] BTX being the main compound yielded when using furans and light alkenes.

This approach has been studied by different research groups in the last years. Initially, it was proposed with the aim to tune the products' distribution during the catalytic fast-pyrolysis of the biomass, once furans and alkenes were identified as common intermediates, obtained despite the biomass being treated. The production of BTX was observed when introducing MFI zeolite during the biomass cracking, taking advantage of the strong conditions of the thermal process.[10,11] Further studies delved into the optimization of reaction conditions[12−15] and catalytic properties to increase the selectivity of the reaction, including metal-modified zeolites,[16−22] observing in all the cases a high relevance of coke formation because of the severe conditions used.[23]

These results are the starting point for the aromatic production from biomass via Diels−Alder condensation, but they were strongly conditioned by the low selectivity of the thermal pretreatment. Trying to increase the control on the reaction, the next studies considered the possibility of using platform molecules obtained by specific and more selective production processes as reactants. With this perspective, furans could be obtained from furfural (aldehyde obtained from pentoses of hemicellulose) by decarbonylation.[24] As to the alkenes, nowadays produced by steam cracking and several other methods in the petrochemical industry,[25] they could also be obtained by alcohol catalytic dehydration, ensuring the sustainability of the process.[26]
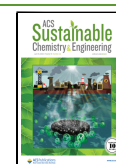
In the liquid phase, Chang and co-workers indicate promising results in the dimethylfuran and ethylene condensation catalyzed by a BEA zeolite, yielding more than 90% of p-xylene,[27] whereas Williams et al., obtained 75% using the Y-zeolite.[28] Teixeira and co-workers maximize the ethylbenzene yield using furan and working at high pressure and temperatures in the range of 200–300 °C.[29] Despite the lower graphitic coke produced, a relevant formation of benzofuran was observed, an undesired product directly related to catalytic deactivation.[30]

The obvious next phase in the sustainability of the process is the reduction in the number of steps, suggesting the direct production of aromatics from the primary platform molecules, furfural and ethanol, involving the in situ transformation of these compounds into the furan and ethylene that undergo the Diels−Alder condensation. Considering the requirements of the first step, the reaction must be in the gas-phase, which requires strong control on the reaction conditions to produce the furfural decarbonylation and condensation, minimizing its oligomerization. The Diels−Alder reaction involving furfural has already been proposed in the literature using different dienophiles, such as ethylene,[31] acrylonitrile,[32] maleimides,[33] and methanol (in situ transformed into ethylene and propylene).[34−37] Despite the linking molecule used, in most of these works, 500 °C is defined as the optimum temperature to maximize the aromatic production minimizing coke formation. However, the use of ethanol as an alkene precursor for this reaction has not been explored yet, despite its renewable character and the ease of its transformation into ethylene.

This investigation pursues the direct use of two of the most relevant bioplatform molecules, furfural and ethanol, as reactants to obtain aromatics via Diels−Alder condensation. To the best of our knowledge, this is the first work considering this configuration, despite the inherent benefits of this approach. The performance of these mixtures will be compared to the behavior of the most widely proposed mixture, furan and ethylene. The complete understanding of the system requires the study of intermediate approaches, furfural−ethylene and furan−ethanol systems, as well as the analysis of the behavior of each compound independently. H-ZSM-5 is chosen as catalyst-based on the previous literature, highlighting its good activity based on its acidity as well as the correspondence between the kinetic diameter of the expected products and the pore size of this zeolite.[10,11,14−19] The performance of the different mixtures is discussed in terms of activity, selectivity, and catalytic stability.

EXPERIMENTAL SECTION

H-ZSM-5 was obtained from the commercial NH_3-ZSM-5 zeolite (Si/Al: 11.5, Zeolyst, CBV2314) by calcination at 550 °C. The catalyst was pelletized and sieved to 250−355 μm. Samples of 180 mg were placed in a U-shaped fixed-bed reactor inside an electric oven.

Furan (Sigma-Aldrich, 99%), furfural (Sigma-Aldrich, 99%), ethylene (Air Liquide, 99.5%), and ethanol (VWR, 99.97%) were used directly or mixed in a transfer line employing syringe pumps, using helium (Air Liquide, 99.999%) as the carrier gas, reaching a total gas flow of 20 N mL·min^{-1}. All the fittings and transfer lines were heated to 250 °C to facilitate reactant vaporization and prevent product condensation. The plant scheme is included in the Supporting Information (Figure S1). Reactions were carried out at 3 bar and 500 °C.

Reaction products were identified using a GC-MS Shimadzu QP 2010 equipped with a TRB 5MS capillary column, analyzing the effluent previously condensed in octane and acetone at 0 °C. The quantification was done by GC-FID (HP 6890Plus) using the same column. Structural isomers are considered together to facilitate the analysis.

Considering the microporosity of the ZSM-5 zeolite (crystallographic pore sizes of 5.4 and 6.1 Å after applying the Norman radii correction were used to evaluate the thermal effect), the Diels−Alder reaction is expected to be controlled by the internal mass-transfer resistance. This assumption has been theoretically corroborated, analyzing the bulk and Knudsen diffusivities of the four reactants studied. Despite the light discrepancies due to their different physical properties (see Table S2), all the values are in the same order of magnitude (effective diffusivities from 1.7×10^{-9} to 3.2×10^{-9} cm^2·s^{-1}), suggesting a similar relative weight of transport limitations independent of the reactants used. Thus, the experimental results can be directly compared.

The conversion of each reactant was evaluated considering eq 1, whereas the mass balance and selectivity are calculated in carbon units according to the equations expressed below:

$$\text{conversion:} \quad x(\%) = \left(1 - \frac{C_a}{C_{a,0}}\right) \cdot 100 \tag{1}$$

$$\text{carbon balance:} \quad \text{CB}(\%) = \frac{\sum (n_i \cdot C_i) + \sum (n_a \cdot C_a)}{\sum (n_a \cdot C_{a,0})} \cdot 100 \tag{2}$$

$$\text{selectivity:} \quad \varphi_i(\%) = \frac{n_i \cdot C_i}{\sum (n_a \cdot C_{a,0})} \cdot 100 \tag{3}$$

where C is the concentration and n is the number of carbon atoms of i compound or a reactant. The carbon unbalance is assumed to be CO, CO_2, carbonaceous, or condensed compounds (labeled as coke and CO_x).

Carbon deposits were analyzed by temperature-programmed oxidation analyses (TPO) in a Micromeritics Autochem II 2920. Using 0.5% O_2 in helium (20 mL·min^{-1}), with a temperature program of 5 °C·min^{-1} from room temperature up to 700 °C. The CO_2 effluent was analyzed by mass spectrometry (Omnistar GSD301).

RESULTS AND DISCUSSION

Blank Reactions. Initially, the reactivity of the different reactants in absence of catalyst at 500 °C was studied to determine the presence of homogeneous reactions that could interfere in the analysis of the catalytic activity. At these conditions, ethylene and furan show negligible conversions, whereas ethanol produces 1.4% of alkenes (mostly ethylene) and furfural undergoes decarbonylation reactions yielding furan (5.7%) and carbon oxides. Concerning the reactant mixtures, furfural−ethanol produces 0.3% alkenes and 0.9% of furan, with a carbon unbalance of 5.1%. The selectivity distribution is detailed in the Supporting Information (Table S2).

Reactivity of Single Reactants. When the reactants were fed separately to the catalytic bed, ethylene and ethanol reached similar product distributions (Figure 1). The amount of nonreacted ethylene (15.3%) is analogous to the produced ethylene when feeding ethanol (17.9%), with this good correspondence determining all the subsequent products. This fact suggests that ethanol undergoes a fast dehydration to ethylene, in good agreement with the previous literature findings.[36] This fact suggests that the studied reaction follows the same mechanism, regardless of feeding ethanol or ethylene. The only significant difference is the decrease in the carbon balance closure when feeding ethanol instead of ethylene, suggesting that the production of carbon oxides is promoted by the higher oxygen content of the reactant's mixture.
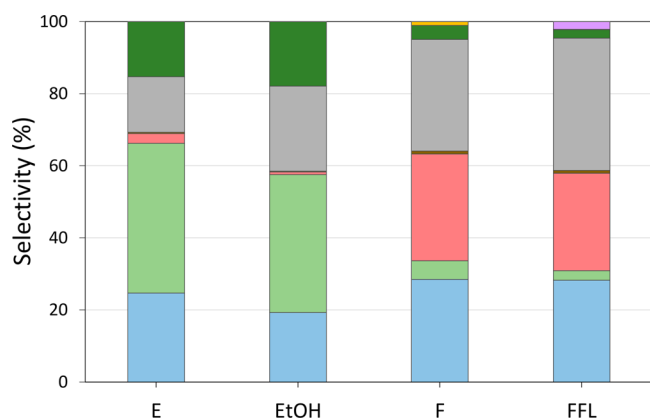
Figure 1. Distribution of selectivities obtained when feeding each reactant separately: ethylene (E), ethanol (EtOH), furan (F), and furfural (FFL). Blue: BTX; Light green: heavy alkenes; Pink: naphthalenes; Brown: indenes; Gray: Coke and CO_x; Dark green: ethylene; Purple: furfural; Yellow: furan. Conditions: 180 mg H-ZSM-5, 500 °C, 3 bar, 20 N mL·min^{-1}, 5% v/v reactant.

In the same way, furan and furfural conversion produces similar amounts of BTX and naphthalenes (both around 28%). This is congruent with a fast and almost total furfural decarbonylation to furan, as proposed by Zhang et al.[37] However, furfural yields lower alkene selectivities (5.0% vs 9.0%) and more coke and CO_x (36.7% vs 31.0%) than feeding furan. This last effect is attributed to the CO released during the decarbonylation reaction. The distributions of product selectivities for all the reactions are detailed in the Supporting Information (Table S2), including the particular selectivity of each isomer of the different families.

Reaction Mixtures. The reaction results are analyzed in Figure 2, comparing the selectivities of the furfural−ethanol system with the corresponding ones obtained with the well-
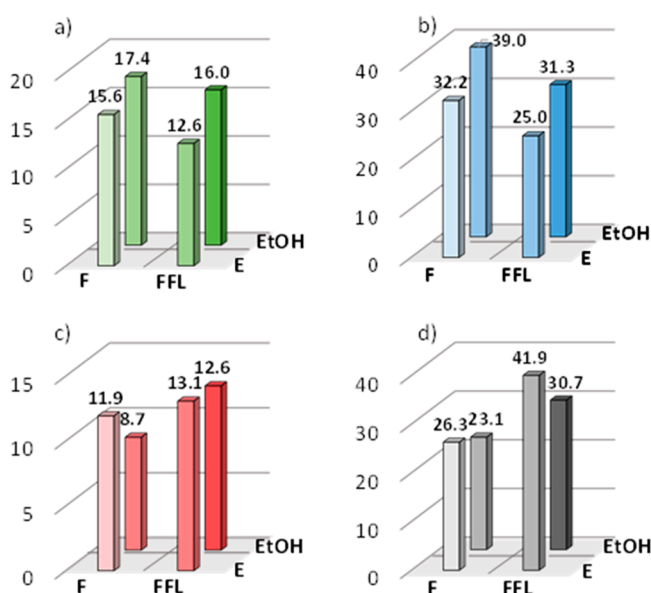

Figure 2. Selectivities obtained in the gas-phase valorization of different binary mixtures involving furan (F), ethylene (E), furfural (FFL), and ethanol (EtOH). Results corresponding to (a) alkenes (except ethylene); (b) BTX; (c) naphthalenes, and (d) coke and CO_x. Conditions: 180 mg H-ZSM-5, 500 °C, 3 bar, total flow 20 N mL·min^{-1}, 5% v/v of each reactant..

studied furan−ethylene mixture, as well as the intermediate combinations: furan−ethanol and furfural−ethylene.

Ethanol yields high selectivities to alkenes (>C2), both using furan and furfural as dienes. The water released during ethanol dehydration promotes the hydrolysis of the furan ring, yielding propylene.[38] The reductive ring-opening of the furan heterocycle is favored in the absence of electrophilic functionalities, justifying the lower values reached with furfural (16.0% vs 17.4% obtained with the furan−ethylene mixture).

Regarding BTX, ethanol promotes their formation, whereas the selectivity observed with furfural is lower than that observed in the presence of furan. The balance between these two opposite effects results in a similar selectivity with furan−ethylene and furfural−ethanol systems (around 32%), whereas the maximum aromatics production (39%) is obtained with the furan−ethanol mixture.

The presence of ethanol hinders the subsequent condensations, yielding heavy compounds (naphthalenes and coke), whereas furfural promotes these reactions. The condensation capacity of furfural (larger than the corresponding to furan, for both self- and cross-condensations)[39] explains these results, whereas the water released in dehydration reactions hinders these condensations by competitive adsorption on the active sites. This second effect prevails in the furfural−ethanol mixture in such a way that the sum of both effects contributes to a similar selectivity of naphthalenes (from 11.9 to 12.6%) for ethanol−furfural mixtures.

In global terms, the product's distribution obtained when working with the furfural−ethanol mixture is quite similar to the one obtained with the furan−ethylene mixture, defining a similar mechanism, depicted in Scheme 1. The good correspondence represents a relevant result since ethanol and furfural are primary bioplatform molecules, whereas ethylene and furan are manufactured from these bioplatform molecules or obtained by petrochemical routes.

Catalyst Stability. Regarding the stability, the catalyst presents a stable performance when feeding either ethylene or ethanol for more than 8 h time-on-stream (TOS). On the contrary, the continuous deactivation observed in the presence of furan or furfural suggests that these reactants play a key role in the formation of heavy compounds by oligomerization, yielding naphthalenes and coke and, hence, lead to catalyst deactivation by pore blockage (Figures S1 and S2).

The comparison of products and reactants evolution for the different systems allows suggesting a two-step deactivation: a first disappearance of Diels−Alder products (BTX, naphthalenes), furan, and ethylene being the only products detected after this phenomenon; and a second deactivation step related to the complete decrease in the conversion. Figure 3 compares the temporal evolution of the different considered systems, in terms of the TOS required to observe the absence of target compounds (first deactivation step), and the TOS to reach negligible furan/furfural transformation (second and final deactivation step, reduction to 10% of the initial conversion values).

When furan is the only reactant, the catalyst deactivation (disappearance of the reaction products) takes place after 2.4 h TOS. In this case, there is an almost total correspondence between this TOS and the lack of conversion (2.4 h), as shown in Figure S1. This result discards the furan oligomerization as the main deactivation route, with a predominant effect of the Diels−Alder pathway. This fact suggests a prevalence of furan

Scheme 1. Suggested Reaction Pathway of Furfural and Ethanol Aromatization over Acid Zeolites[a]
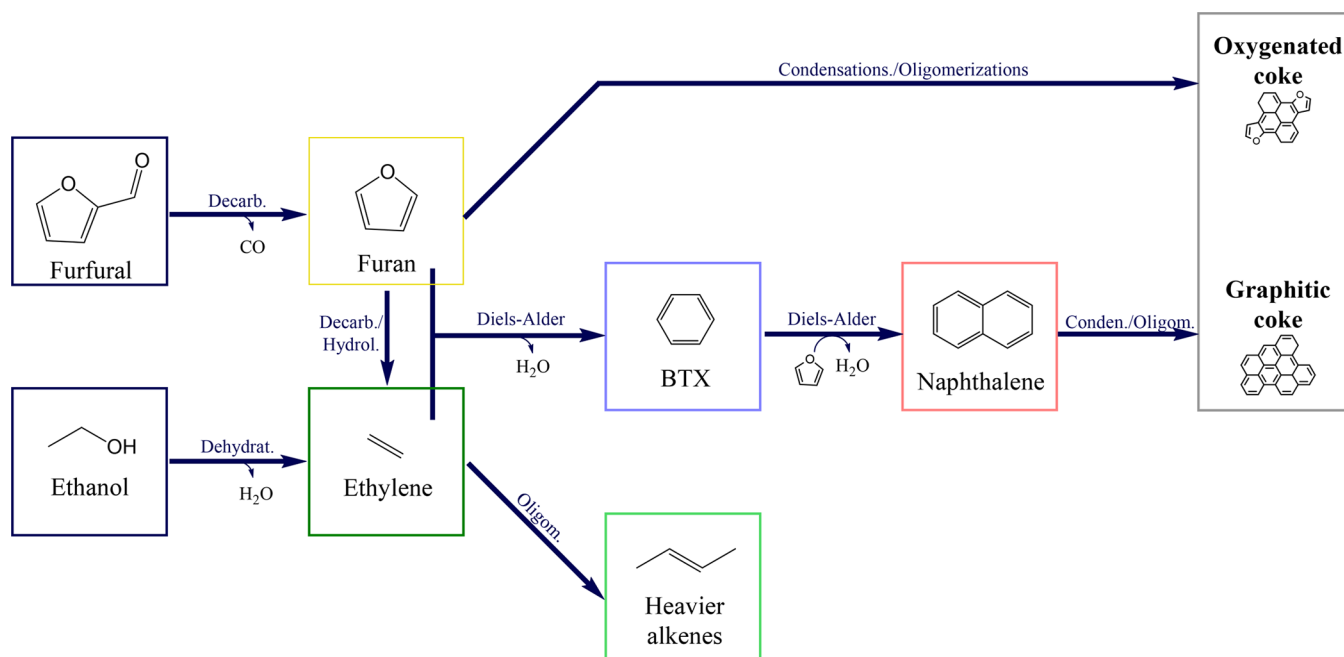
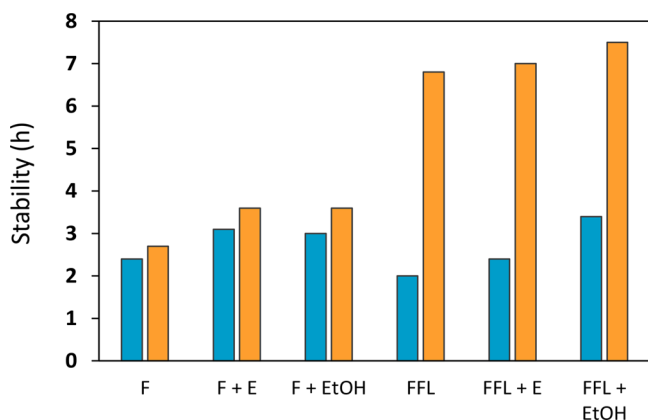[a]BTX and naphthalenes include their structural isomers.

Figure 3. Comparison of the stability of different systems analyzed in this work: ethylene (E), ethanol (EtOH), furan (F), and furfural (FFL). Analysis in terms of time producing aromatics (blue lines) and time for a total deactivation. Conditions: 180 mg H-ZSM-5, 500 °C, 3 bar, total flow 20 N mL·min^{-1}, 5% v/v of each reactant..

cracking over oligomerization since ethylene must be produced.

These 2.4 h obtained with only furan increase up to 3−3.1 h when ethylene or ethanol are cofed (Figures S3 and S4). This soft increase is also observed for the total deactivation, reaching values of 3.6 h. These results are congruent with the previous ones, highlighting the improvement in the main route once the ethylene is not the limiting reactant. Considering the correspondence between the two deactivation steps observed with these systems, it can be concluded that the furan oligomerization relative weight is stable, being congruent with the constant 20−25% of coke and CO_2 fraction observed with the three configurations analyzed. The comparative analysis of the results with ethanol and ethylene discards any role of the water released during the ethanol dehydration in the stability,

this step being so fast that both systems (ethanol and ethylene) have the same behavior.

The period of stable production of Diels−Alder condensed adducts when feeding only furfural is lower (2 h) than the corresponding value using furan (Figure S2). Once these products are not detected, the furan conversion remains almost total during a long period, requiring a TOS higher than 8 h to observe decreases to conversions lower than 20%. During this second step, furan is observed with selectivities higher than 50%, with almost 40% of carbon unbalances, values supported by the presence of CO from the decarbonylation and possible solid deposits by the furfural oligomerization. The analysis of the spent catalysts is discussed below. These two well-marked phases indicate that the activity related to furfural decarbonylation is mainly a surface process less influenced by the pore blockage than the Diels−Alder condensation, requiring a high deposition of organic solids on the surface to observe significant decreases on the decarbonylation activity.

The effect of cofeeding dienophiles is more evident in the case of configurations involving furfural, mainly when introducing ethanol, observing BTX products during the 3.4 h. This TOS implies an improvement of 70% in comparison to feeding only furfural and an increase in the stability higher than 13% if the well-studied furan−ethylene system is considered. Previous literature demonstrate that the presence of ethanol reduces the benzofuran production,[29] one of the main precursors of the oxygenated coke, being a probable reason for this improvement in selectivity.

The spent catalysts were recovered after each test, analyzing the carbon deposits by TPO. Results shown in Figure 4 compare the total amount of CO_2 per gram of catalyst recovered as well as the strength distribution of these deposits as a function of their oxidizing temperature (in all the cases, a white catalyst was recovered after the thermal treatment). This strength distribution is determined by comparing the TPO profiles, being in good agreement with previous literature in
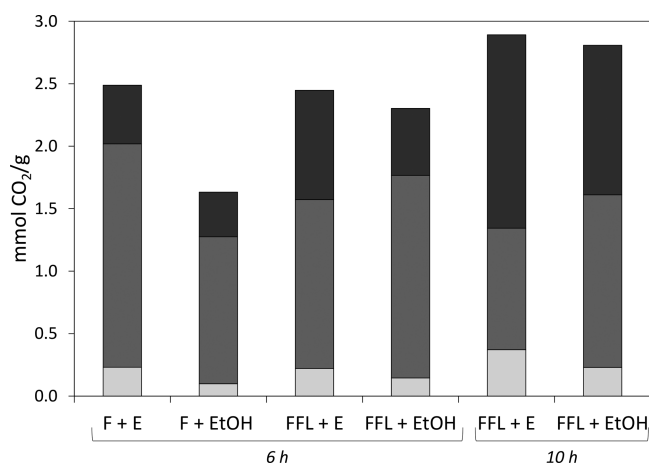
Figure 4. Decomposition of carbon deposits by TPO of the spent materials after 6 and 10 h TOS. Catalysts recovered after reactions with different mixtures involving ethylene (E), ethanol (EtOH), furan (F), and furfural (FFL). Results correspond to light carbon deposits (light gray, <500 °C), medium (gray, 500−600 °C), and heavy ones (dark gray, 600−650 °C).

which the same ranges are proposed (<500, 500−600, and >600 °C), establishing a direct effect of coke structure and the oxidizing temperature.[40]

Considering the total amount of carbon fed in these systems, these deposits represent less than 0.5% in all the cases, demonstrating an almost total prevalence of permanent gases on the "coke and CO_x" fraction (mainly CO and CO_2 produced by cracking and decarbonylation). The low percentages of CO_2 present in these deposits and their high effect on the stability confirm that most of the active sites are inside the microporous, a small amount of coke being enough to produce their total blockage.

The differences in stability seem to contradict the TPO analyses, highlighting the relevance of the structure of these organic solids. The carbonaceous deposits represent 0.44% of the total carbon in the system furan−ethylene, and 0.37% in the furfural−ethanol. However, the furan−ethylene is totally deactivated after only 3 h of TOS, whereas the ZSM-5 is still active after 6 h when feeding furfural. This is explained by the relative weight of these deposits, light and medium ones being predominant in reactions involving furan, whereas higher temperatures are required to oxidize most of the carbon deposits produced in the presence of furfural. These differences suggest that the coke produced from furan is less organized than the one from furfural, a typical characteristic of the oxygenated coke, producing the simultaneous blockage of most of the pores. However, the profiles obtained with furfural suggest the prevalence of graphitic and more complex structures with less anchoring points, with a remaining fraction of pores still active for the catalytic activity. In good agreement, when the TPO are extended to materials recovered after a 10 h TOS, the relative weight of this heavy fraction increases, but not the total amount of carbon (0.28 and 0.27% with ethylene and ethanol, respectively), corroborating the stable production of furan by furfural decarbonylation.

To sum up, the use of furfural and ethanol is a promising sustainable configuration to obtain aromatics, not only from the point of view of selectivity of the process but also since the stability is improved by the synergetic presence of these more oxygenated compounds. All these systems are affected by a fast deactivation produced by coke deposits that can be totally oxidized at temperatures lower than 700 °C, suggesting a fluidized-bed configuration as the best strategy for a future scale-up.

■ CONCLUSIONS

Furfural−ethanol mixtures are promising reactants to obtain aromatics through the acid-catalyzed Diels−Alder condensation. Monoaromatics (BTX) and naphthalenes are obtained at 500 °C, using H-ZSM-5. At these conditions, both reactants are fast transformed into furan and ethylene, by decarbonylation and dehydration, respectively. These reactions are so fast that the product distribution is not affected by them, being enriched in BTX (32%) and naphthalenes (9%). The stability of the system is also improved, reducing the relevance of the deactivation by oxygenated deposits.

These results corroborate the possibility to develop a green route to obtain aromatics by the direct substitution of traditional precursors (oil-based ones) by green platforms selectively produced by the valorization of waste lignocellulosic biomass, implying a double benefit in terms of sustainability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02285.

> Table S1 summarizes the bulk, Knudsen and effective diffusional coefficients; Table S2 details the selectivity distribution obtained for all the experiments; Figure S1 shows the experimental setup; Figures S2−S6 illustrate the conversion and selectivity evolution with the time for each experiment (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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