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# Upgrading of bio-oils over equilibrium FCC catalysts. Contribution from alcohols, phenols and aromatic ethers

Melisa Bertero, Ulises Sedran*

*Instituto de Investigaciones en Catálisis y Petroquímica INCAPE (FIQ, UNL–CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina*

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ABSTRACT

The conversions of oxygenated compounds of bio-oils (alcohols, phenols and aromatic ethers) on a equilibrium FCC catalyst were studied at 500 °C during 60 s in a fixed bed laboratory reactor. Methanol, phenol and 2,6-dimethoxyphenol were dissolved in water and 1,2,4-trimethoxybenzene in benzene at 5 %wt. Identical experiments were performed over inert SiC. Conversions were very different, the highest one being that of 1,2,4-trimethoxybenzene (95.7 %wt.), followed by 2,6-dimethoxyphenol (75.0 %wt.), methanol (60.8 %wt.) and phenol (54.9 %wt.). Deoxygenation in all the reactants was from dehydration and decarboxylation. The highest yield of hydrocarbons (47.1 %wt.) and coke (16.0 %wt.) were from 1,2,4-trimethoxybenzene, which, together with methanol, yielded mainly aromatics in the gasoline range. On the contrary, phenol and syringol yielded C4-hydrocarbons with high content of olefins. The highest amounts of oxygenated compounds were produced by 2,6-dimethoxyphenol. The thermal conversions were similar to the catalytic ones in the only case of 1,2,4-trimethoxybenzene, but much lower with the other reactants. In comparison to the catalytic experiments, thermal tests yielded much more hydrocarbons with 1,2,4-trimethoxybenzene, and oxygenated compounds with 2,6-dimethoxyphenol, than the other reactants. These tests could help in the prediction of specific contributions by these reactants if bio-oils are co-processed in FCC units or upgraded over acidic catalysts.



## 1. Introduction

Bio-oil is the usual designation for the liquid fraction from the pyrolysis of lignocellulosic biomass, which constitutes an interesting alternative source for the production of fuels and chemical products [1]. Bio-oils are very complex aqueous mixtures of a large number of oxygenated compounds, which have different chemical functionalities with a wide range of molecular weights. As an example, bio-oils from different sawdusts contain phenols, furans, acids, esters, ethers, alcohols, aldehydes and ketones, which account for the approximate contents of 35–40% of oxygen, 55–60% of carbon and 15–60% of water in bio-oils, and the acidic pH and density close to 1.2 g/cm$^3$ [2–4].

The catalytic conversion over acidic zeolites, which mainly lead to hydrocarbons in the range of gasoline [3,5–8], is one of the options to upgrade bio-oils into transportation fuels by removing oxygen, following a mechanism overall similar to that of the conversion of alcohols into hydrocarbons [9,10]. The conversion of oxygenated model compounds representing various functional groups present in bio-oils over zeolites and mesoporous materials demonstrated that almost all of them, even though with different reactivities and product distributions [11–16], formed hydrocarbons.

Another option to use these biomass derived oils is to co-process them into conventional petroleum refineries [17], integrating them in the running refining schemes, where they can act as non conventional feedstocks, taking advantage of existing processes and infrastructures. The catalytic cracking of hydrocarbons (FCC) is an attractive possibility, because the catalyst used in the process, which is mainly composed by Y zeolite, is potentially useful for this approach [5,14]. In this way, bio-oils could be added to vacuum gas oil, VGO, which is the usual feedstock to the process. However, this option has to consider probable problems like those, for example, derived from the high coke forming potential of bio-oils, which tend to polymerize at high temperatures [3,5–8]. At present, the higher coke yields when residual hydrocarbon feedstocks, e.g., with Conradson Carbon Residue (CCR) higher than two, are processed in FCC, are handled through technological innovations such as catalyst coolers, two stage regeneration steps and more efficient strippers, among others [18,19]. Other possible drawbacks in the approach are the high content of water in bio-oil and the fact that it may be not possible to dissolve it into VGO; some options were discussed by Corma et al. [17]. Recent studies discuss some technical, economical and environmental issues in the upgrading of bio-oils to liquid transportation fuels, considering design and operation parameters [20–22].

* Corresponding author. Tel.: +54 342 452 6082; fax: +54 342 453 1068.
*E-mail address:* usedran@fiq.unl.edu.ar (U. Sedran).

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**Table 1**
Properties of the catalyst E-Cat.

| | |
|---|---|
| Particle size (μm) | 100–120 |
| UCS (Å) | 24.26 |
| Zeolite content (%) | 18.0 |
| Specific surface area ($m^2$/g) | 158.0 |
| *t*-Plot micropore volume ($cm^3$/g) | 0.046 |
| Fe (%wt.) | 0.35 |
| Ni (%wt.) | 0.06 |

The prediction of some important details in co-processing (e.g. coke and product distribution issues) could be assisted with observations about the reactivity of bio-oil model compounds representing different chemical functionalities. Particularly, the chemical groups responsible of higher coke yields, or which show more efficiency in their catalytic conversion into hydrocarbons over an acidic catalyst such as that of FCC, could be identified. Although this approach has been followed by some researchers [14,17,23,24] at present that information is scarce.

In particular, among the many components in bio-oils, both phenols [25] and cyclic ketones [12], which are present in significant amounts, are considered to be main coke precursors. It was shown that thermal pre-treatments of bio-oils can facilitate their co-processing in FCC, because very important changes in their compositions are produced, with reductions from 30 to 50% in the amount of phenols and cyclic ketones [26]. Then, up to 30% decrease in the yield of coke was observed when previously treated bio-oils were converted over ZSM-5 catalysts [8,27].

It is the objective of this work to study the product distributions generated by alcohols, phenols (phenol and phenolic ethers) and aromatic ethers, as represented by model compounds, on an equilibrium commercial FCC catalyst, and to compare them with results from the purely thermal cracking reactions. This information could be useful to understand the chemistry of these compounds under conditions of catalytic cracking and predict their specific contributions to the products if bio-oils are co-processed in FCC, or upgraded over acidic catalysts.

## 2. Materials and methods

The reactants were purchased from Sigma–Aldrich; they were methanol (99.8%), phenol (99.5%), 2,6-dimethoxyphenol (99.0%, also known as syringol) and 1,2,4-trimethoxybenzene (97.0%), to represent alcohols, phenols, phenolic ethers and aromatic ethers, respectively. The reactants methanol, phenol and syringol were dissolved in water with a concentration of 5 %wt., as an approximation to the conditions observed for the respective chemical groups in typical bio-oils, while 1,2,4-trimethoxybenzene was dissolved in benzene (which is adequate as a solvent due to its low reactivity under FCC conditions [28]) with the same concentration.

The catalyst used was an equilibrium commercial FCC (E-Cat). It was of the octane-barrel type, provided by a refinery, and its most important characteristics are shown in Table 1.

The conversion experiments were performed in a stainless steel MAT (ASTM D-3907/03)-type fixed bed reactor of 15.6 mm diameter and 400 mm length, which has a porous metal plate in its mid position to support the 2 g catalyst bed. The reactor was heated in an electrical furnace up to the reaction temperature of 500 °C under nitrogen flow of 30 mL/min. The reactants were fed by means of a SAGE Instruments Model 3414 pump, with flows of 0.7 mL/min in the case of aqueous solutions and 0.8 mL/min in the case of the benzene solution in order to achieve a $W/F_0$ relationship of 0.9 h. Reactor effluents were passed through an ice-water condenser where most of the liquids were retained, and gases were collected and quantified by displacement of water in a glass column. In all the cases the time on stream was 60 s, after which a sweeping flow of 30 mL/min of nitrogen was passed during 7 min. Mass, carbon and oxygen balances (recoveries) were higher than 90% in all the cases. Thermal cracking reactions were performed with a bed of inert SiC occupying the same volume as the catalytic bed, all the other conditions being the same.

Liquid and gas products were analyzed by conventional capillary gas chromatography in an Agilent 6890N gas chromatograph equipped with a 30 m length, 0.25 mm i.d. and 0.25 μm phase thickness HP-1 column and FID detection. Gases were also analyzed with a 30 m length, 0.53 mm i.d. and 3.0 μm phase thickness GS-CARBONPLOT column and TCD detection. Products were identified by means of the use of standards and the GC–MS technique. The calibration of the chromatographic areas was performed by using separate response factors for each of the chemical groups, assessed from mixtures of standards and a reference compound (tetralin for liquids and methane for gases). Unidentified peaks, each representing less than 0.5% of the total chromatographic area was assigned an average response factor.

The amount of water in the liquid products was determined by means of the Karl–Fischer method (IRAM 21320). The amount of coke on the reactor bed was assessed with a combined method of thermal programmed oxidation (initial temperature, 250 °C during 15 min; heating ramp, 16 °C/min; final temperature, 700 °C, during 16 min) and further conversion of the carbon oxides formed to methane on a Ni catalyst, which was quantified with a FID detector. The various product yields were calculated as the relationship between the corresponding mass of product and the mass of reactant, and water yield was assessed by difference from the mass balance. Deoxygenation was determined as the amount of oxygen in the reactant removed as carbon dioxide, carbon monoxide and water.

## 3. Results and discussion

The various model compounds were chosen according to the composition of a bio-oil derived from the conventional pyrolysis of pine sawdust [26], selecting compounds that represent some of the most important chemical groups, such as alcohols, (which are present typically at about 2–6 %wt. [29]), phenols and phenolic ethers (with typical concentrations up to 12 %wt. [12]), and aromatic ethers (about 3 %wt. [26]). Furthermore, some of the compounds, such as methanol and 1,2,4-trimethoxybenzene, were the most important in the group they represent. The behaviors of other important groups in bio-oils, such as acids, esters, aldehydes and ketones, were reported elsewhere (unpublished results).

Alcohols react over acidic zeolites following a mechanism involving dehydration, aromatization and cracking, yielding hydrocarbons in the C1–C12 range, with a high proportion of aromatics in the gasoline boiling range [9,12]. On the other hand, phenols and aromatic ethers are subjected to cracking, alkylation and condensation, yielding mainly hydrocarbons and alkylated phenols [12,13,15,30].

The conversion of the model compounds used in this work, or similar, on Y zeolite or FCC catalysts was reported scarcely in the literature. Concerning alcohols, Hutchings et al. [11] observed mainly hydrocarbons in the conversion of methanol over pure Y zeolite at reaction temperatures between 320 and 420 °C, with conversions as high as 78%. Domine et al. [31] converted isopropylic alcohol dissolved into isooctane over a FCC catalyst, observing hydrocarbons and carbon monoxide as the most important products. Corma et al. [17] used glycerol and sorbitol at 50 %wt. in water over FCC catalysts, REUSY and Y zeolite, and reported conversions of up to 80%, mainly to hydrocarbons and carbon oxides. Prasomsri et al. [32] converted methoxybenzene dissolved into different hydrocarbons (tetralin, benzene and n-decane) over HY zeolite at 400 °C

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and reported phenol and alkylated phenols as the main products; hydrogen donor solvents, such as tetralin increased methoxybenzene conversion. Samolada et al. [14] produced a synthetic bio-oil composed by acetic acid, furfural, cyclohexanone, guaiacol, vainillin and 42.8 %wt. of water, to obtain conversions close to 63% over a pure REUSY zeolite, the main product yields being those of water (42.7 %wt.), hydrocarbons (8.5 %wt.) and oxygenated compounds (4 %wt.). Other authors dissolved the model compounds directly into VGO; for example, Graça et al. [23,24] reported that hydrocarbons, oxygenated compounds and water were the major products in the conversion of phenol and guaiacol dissolved in VGO at 10 %wt. and 12.8 %wt., respectively, over an equilibrium FCC catalyst in a fixed-fluidized-bed reactor at 535 °C. With the exception of this last report, all the other ones were produced using fixed bed reactors.

On the contrary, the behavior of ZSM-5 zeolites with these or similar model oxygenated compounds was studied more extensively. For example, reports were published for methanol [13,30,33], propanol and butanol [15], phenol [12,15,30], guaiacol [15,30], syringol [30], eugenol [5,30], methoxybenzene [12,13,30], and ethoxybenzene [12]. The conversions of the alcohols and the aromatic ethers were high, between 60 and 90%, with significant hydrocarbon yields in the case of methanol and of oxygenated compounds in the case of aromatic ethers. In contrast, phenols converted to a much lower extent, conversions ranging from 10 to 30% and oxygenated compounds being the main products. In all the cases water and carbon dioxide were produced significantly.

Studies on the conversion of bio-oils over equilibrium FCC catalysts are scarce, and typically limited to their co-processing with hydrocarbon feedstocks after hydrotreating the bio-oils [34–37]. These approaches have also been reviewed by Al-Sabawi et al. [38]. The most important conclusions were that C1–C2 hydrocarbons increased and that C3–C4 hydrocarbons decreased their yields. Gasoline and LCO yields were not affected significantly, although the proportion of aromatics in gasoline increased and some oxygenated aromatic compounds such as phenol and alkylphenols were observed in this boiling range. As expected, coke yield was higher when bio-oil was present, and bio-oil deoxygenation lead to significant amounts of water and carbon dioxide.

Contrastingly, zeolite HZSM-5 has been extensively studied in the conversion of bio-oils [3,6,39], conversions and hydrocarbon yields ranging up to 90% and 26%, respectively; then, commercial FCC catalysts which contain ZSM-5 zeolite as an additive to maximize olefin yields could be appropriate to co-process bio-oils. The high coke yields from bio-oils could be managed by using resid FCC catalysts, which have low coke selectivity.

### 3.1. Conversions in the thermal and catalytic experiments

All the catalytic and thermal transformations over catalyst E-Cat and inert SiC, respectively, produced three product streams: gases, liquids and coke. In the cases of methanol, phenol and syringol, the amount of water in the liquid fraction was 96–97 %wt., considering both the product from dehydration and solvent water. Table 2 shows the conversions and the yields of the different product groups, with significant differences among the four reactants. In the particular case of 1,2,4-trimethoxybenzene, which was dissolved into benzene, the pure solvent was fed to the catalytic bed under the same conditions in order to consider its own conversion and contribution to the products. Diluting the reactant with benzene does not affect significantly the product distribution in the conversion of aromatic ethers over Y zeolite, as reported by Prasomsri et al. [32]. The observed conversion of the pure solvent was 5.5 %wt., the main products being toluene and biphenyl, both with selectivities of 32%, and naphthalene. Coke yield was 0.05 %wt. These results were considered in order to assess product distributions from 1,2,4-trimethoxybenzene.

Most noticeable facts in the experiments with E-Cat are that under the conditions used the highest conversion and yield of hydrocarbon products corresponded to 1,2,4-trimethoxybenzene (95.7 %wt. and 47.1 %wt., respectively), while the highest yield of oxygenated products (32.5 %wt.) and hydrogen (4.1 %wt.) corresponded to syringol. Carbon dioxide was produced most significantly in the catalytic conversion of syringol and 1,2,4-trimethoxybenzene (22.9 and 29.8 %wt, respectively), while the highest dehydration was achieved with methanol (27 %wt.).

Particularly, the resulting deoxygenation effect was due to dehydration in the cases of methanol and phenol and to decarboxylation in the cases of syringol and 1,2,4-trimethoxybenzene. Essentially all the oxygen was removed from 1,2,4-trimethoxybenzene, about 60% in the cases of methanol and syringol and about 37% in the case of phenol. These results are coincident with observations on HZSM-5 zeolites, where methanol and phenol also deoxygenated mainly through dehydration [30,33], while methoxybenzene yielded mainly carbon oxides and dehydration was nil [12,13].

The extent of the thermal conversions of the model compounds resulted much smaller than the catalytic ones (particularly in the case of phenol, which is thermally very stable [40]), with the exception of 1,2,4-trimethoxybenzene, in whose case they were similar. Moreover, the distributions of products in the thermal and catalytic processes were very different (see Table 2). In effect, in the thermal processes, 1,2,4-trimethoxybenzene produced more hydrocarbons and oxygenated compounds than in the catalytic cracking, while methanol, phenol and syringol produced much less hydrocarbons. As expected, the thermal dehydration of methanol was important [40] and the total deoxygenation produced by the thermal effect was similar to the catalytic one in the case of 1,2,4-trimethoxybenzene (97.5%) and lower for the other reactants (23% in the case of methanol, 20% in the case of phenol and 45% in the case of syringol).

### 3.2. Oxygenated products in the thermal and catalytic conversions

Table 3 shows the distributions of oxygenated products obtained in the thermal and catalytic conversions of the various model compounds. It has to be noted that during its catalytic conversion phenol yielded a single oxygenated compound, methanol, and that alkylated phenols and acetone were always present among the products of all the other model compounds. For the case of syringol, methanol and phenol were important products, and for the case of 1,2,4-trimethoxybenzene, the aromatic oxygenated compounds, such as benzofurans and benzophenones (see Table 3). The catalytic conversion of methanol showed the most extended distribution of oxygenated products, including acetic acid, dimethylether, ketones, dibenzofuran and furfural among others.

In the thermal experiments, methanol yielded only formic acid. In the cases of syringol and 1,2,4-trimethoxybenzene the yield and selectivity of alkylated phenols (e.g. phenol, cresol and dimethylphenol) was much higher than in the catalytic experiments, while the yield and selectivity of the other aromatic oxygenated compounds, if present, was much higher in the catalytic conversion.

These observations are consistent with recognized facts. For example, it is well known that dimethylether is the product of the catalytic dehydration of methanol [9], and that phenol and methanol are the products from the thermal and catalytic hydrolysis of phenolic ethers such as guaiacol and syringol [12,30,41], which is favored by water in the medium [41]. Alkylated phenols are the consequence of phenol alkylation reactions by methanol [30] and of the molecular reordering in the products

**Table 2**
Thermal and catalytic conversions and product yields from the model compounds. Temperature: 500 °C.

| | Methanol | | Phenol | | Syringol | | Trimethoxybenzene | |
|---|---|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Conversion (%wt.) | 22.6 | 60.8 | 8.2 | 54.9 | 56.7 | 75.0 | 97.1 | 95.7 |
| Yields (%wt.) | | | | | | | | |
| Hydrocarbons | 0.2 | 7.1 | 0.2 | 34.9 | 0.4 | 2.1 | 57.8 | 47.1 |
| Oxygenated | 5.4 | 4.0 | | 2.0 | 39.0 | 32.5 | 3.4 | 0.2 |
| Hydrogen | 2.4 | 3.5 | 1.1 | 1.6 | 3.0 | 4.1 | 2.3 | 2.3 |
| $CO_2$ | 0.8 | 12.2 | 4.0 | 4.0 | 7.5 | 22.9 | 32.9 | 29.8 |
| CO | | | | | | | 0.3 | 0.3 |
| Water | 13.6 | 27.0 | 2.8 | 8.0 | 6.0 | 4.9 | | |
| Coke | 0.2 | 5.5 | 0.1 | 4.4 | 0.8 | 8.5 | 0.4 | 16.0 |
| Unknown | | 1.7 | | | | | | |

from disproportionation reactions of aromatic ethers, such as trimethoxybenzene [32,42].

### 3.3. Hydrocarbon products in the thermal and catalytic conversions

The distributions of hydrocarbon products obtained in the thermal and catalytic conversions of the model compounds are shown in Table 4. It can be seen that phenol and syringol produced mainly light C1–C4 hydrocarbons, while methanol and 1,2,4-trimethoxybenzene produced almost exclusively liquid products in the C5–C15 range.

The conversion of methanol over the catalyst was 60.8 %wt., yielding mainly hydrocarbons in the range of gasoline (selectivity 98 %wt.), with a high content of aromatics (selectivity 59% in gasoline) and very low content of olefins (selectivity 1 %wt.). This is consistent with the classic observations by Chang and Silvestri [9] who showed that the more extended the methanol conversion reaction pathway, the less dimethylether and olefins among products. Most important hydrocarbons were xylenes and C9 aromatics (propylbenzene, methylethylbenzenes and trimethylbenzenes), and C5 + linear and branched paraffins. Naphthalene, phenanthrene and their alkylated homologous compounds represented only 5% of the aromatic hydrocarbons. The thermal conversion of methanol produced only C3- hydrocarbons, particularly methane and ethylene, which were produced much more significantly than in the catalytic experiments.

The catalytic production of hydrocarbons from phenol and syringol had a highly olefinic character. For example, the most important products in the conversion of phenol were propylene and butylenes (selectivities 49 %wt.), as also observed by Gayubo et al. [15] and Graça et al. [23]. The thermal conversion of phenol produced mainly methane, ethylene and propylene, representing about 86 %wt. of the products, in coincidence with observations by Moldoveanu [40].

The conversion of syringol over the catalyst yielded two times more C1–C2 hydrocarbons than C3–C4 hydrocarbons, which in turn were exclusively olefins. Some alkylbenzene aromatic compounds were produced with selectivity about 23 %wt. among hydrocarbons. These observations are consistent with reports about the catalytic conversion of syringol and other phenolic ethers over HZSM-5 zeolite and a FCC catalyst [12,24,30]. The distribution of hydrocarbons in the thermal experiment with syringol was similar to that of phenol.

Only aromatic hydrocarbons were produced in both the catalytic and thermal conversion of 1,2,4-trimethoxybenzene; biphenyl was the most important product, with a higher selectivity in the thermal experiments. Polyaromatic hydrocarbons such as naphthalene,

**Table 3**
Selectivity of oxygenated products (%wt.) in the thermal and catalytic conversions of the model compounds. Reaction temperature 500 °C.

| | Methanol | | Syringol | | Trimethoxybenzene | |
|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Conversion (%wt.) | 22.6 | 60.8 | 56.7 | 75.0 | 97.1 | 95.7 |
| Oxygenated compounds yields (%wt.) | 5.4 | 4.0 | 39.0 | 32.5 | 3.4 | 0.2 |
| Selectivity (%wt.) | | | | | | |
| Formic acid | 100.0 | | | | | |
| Acetic acid | | 7.3 | | | | |
| Acetaldehyde | | | | 5.7 | | |
| Acetone | | 8.3 | 0.1 | 0.5 | | 10.7 |
| Cyclopentanone | | 2.8 | | | | |
| 2-Hydroxy-3-methylcyclopentenone | | 2.0 | | | | |
| Furfural | | 1.0 | | | | |
| Ethylfuranone | | 1.2 | | | | |
| Dimethylether | | 2.7 | | | | |
| Methanol | | | 3.2 | 22.2 | | |
| Phenol | | 0.7 | 68.0 | 56.5 | | |
| Cresol | | 1.1 | 13.5 | 12.9 | 6.9 | 23.1 |
| Dimethylphenol | | 35.5 | 6.0 | | 8.0 | |
| Trimethylphenol | | 0.6 | 7.5 | | 20.4 | |
| Ethylphenol | | 0.6 | | | | |
| Ethylmethylphenol | | | 1.3 | 1.2 | 24.9 | |
| Ethylbenzenediol | | 1.2 | 0.4 | 1.0 | | |
| Cinnamaldehyde | | 3.3 | | | | |
| Benzofuran | | 30.5 | | | | 33.7 |
| Dibenzofuran | | 1.3 | | | 19.7 | |
| Dimethylbenzophenone | | | | | 13.0 | 32.5 |
| Methoxybenzene | | | | | 7.1 | |

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**Table 4**
Selectivity of hydrocarbon products (%wt.) in the thermal and catalytic conversions of the model compounds. Reaction temperature: 500 °C.

| | Methanol | | Phenol | | Syringol | | Trimethoxybenzene | |
|---|---|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Conversion (%wt.) | 22.6 | 60.8 | 8.2 | 54.9 | 56.7 | 75.0 | 97.1 | 95.7 |
| Hydrocarbons yield (%wt.) | 0.2 | 7.1 | 0.2 | 34.9 | 0.4 | 2.1 | 57.8 | 47.1 |
| Selectivity (%wt.) | | | | | | | | |
| Hydrocarbons C1–C2 | 98.7 | 2.0 | 74.5 | 12.8 | 85.3 | 50.0 | 0.4 | 0.1 |
| Methane | 55.5 | 1.6 | 38.4 | 4.6 | 56.0 | 34.5 | 0.2 | 0.1 |
| Ethane | 5.4 | 0.1 | 6.8 | 2.6 | 8.5 | 4.7 | 0.1 | |
| Ethylene | 37.8 | 0.3 | 29.3 | 5.6 | 20.8 | 10.8 | 0.1 | |
| Hydrocarbons C3–C4 | 1.3 | 0.3 | 25.6 | 82.2 | 14.7 | 25.0 | 0.2 | |
| Propane | | | | 13.6 | | | | |
| Propylene | 1.3 | 0.2 | 17.9 | 38.0 | 10.1 | 15.6 | 0.1 | |
| n-Butane | | | | 7.6 | | | | |
| Isobutane | | 0.05 | 1.7 | 12.0 | | | | |
| Butenes | | 0.05 | 6.0 | 11.0 | 4.6 | 9.4 | 0.1 | |
| Hydrocarbons C5–C9 | | 38.7 | | 5.0 | | 2.0 | | |
| i-Pentane | | 1.5 | | 4.9 | | | | |
| n-Pentane | | 2.1 | | | | | | |
| Pentenes | | 0.6 | | | | | | |
| C6 + Aliphatics | | 30.9 | | | | | | |
| C6 + Cycloparaffins and Naphthenics | | 3.6 | | 0.1 | | 2.0 | | |
| Aromatics | | 58.9 | | 0.7 | | 23.0 | 99.6 | 99.9 |
| Benzene | | 0.8 | | 0.7 | | 6.5 | | |
| Toluene | | 9.7 | | | | | 8.8 | 27.6 |
| Xylenes | | 21.3 | | | | | 1.5 | 0.9 |
| Ethylbenzene | | 3.9 | | | | | 1.6 | 2.8 |
| Aromatics C9 | | 14.0 | | | | | 2.8 | 1.8 |
| Aromatics C10 | | 7.6 | | | | 8.7 | 3.1 | 3.4 |
| Aromatics C11+ | | 1.6 | | | | 7.8 | 81.8 | 63.4 |

flourene, pyrene and their alkylated homologous compounds represented about 25% of the aromatic hydrocarbons in the catalytic conversion and about 11% in the thermal conversion. These observations are in line with reports for the thermal and catalytic conversion of methoxybenzene over HZSM-5 zeolite [13,30,43].

### 3.4. Analysis of the coke yields in the thermal and catalytic conversions

Both thermal and catalytic sources for coke can be identified in the conversion of oxygenated compounds over acidic catalysts [5,13,15,16]. Particularly in compound catalysts such as those used in the FCC process, formulated with the Y zeolite deposited on a matrix with different characteristics, and which sometimes is not active, the coke formed by the effect of temperature tends to deposit on the matrix and consequently its impact on the catalytic activity is less significant than the coke derived from the catalytic activity, which forms on the own zeolite active sites.

The yields of coke were very different (see Table 2), ranging from 4.4 %wt. in the case of phenol to the very high yield of 16 %wt. observed with 1,2,4-trimethoxybenzene. In all the cases the yield of coke in the catalytic experiments was much higher than in the thermal experiments. These values indicate a significant coke forming trend in these oxygenated compounds, particularly considering that they were contacted with the catalyst under a high dilution in water, a factor which attenuates coke yield [15]. The reaction of these reactants, or similar, over HZSM-5 catalysts [13,30] also produced high amounts of coke ranging from 3 to up to 12 %wt. (case of methoxybenzene [13]).

In case of co-processing bio-oils at the commercial scale, the yield of coke in riser units will be necessarily lower, due to significant differences in design and operation, than those in laboratory fixed bed reactors. Moreover, in the conversion of pine sawdust bio-oil performed in a laboratory CREC Riser Simulator unit [44], which closely mimics the fluidynamics of commercial riser reactors [45], the yields of coke and hydrocarbons were lower and the yield of oxygenated compounds were higher than the corresponding yields in a fixed bed reactor.

The TPO combustion profiles of the coke deposits in the catalytic experiments also exhibited differences among reactants, as shown in Fig. 1. Two peaks can be distinguished in the case of methanol, the first one corresponding to less condensed coke, which peaked at about 500 °C, and the other one at about 630 °C, corresponding to a more condensed coke. The profile observed for the case of phenol was very similar. The combustion of the coke formed by the other reactants in the catalytic experiments showed a single peak. In the case of 1,2,4-trimethoxybenzene, this peak was located at very high

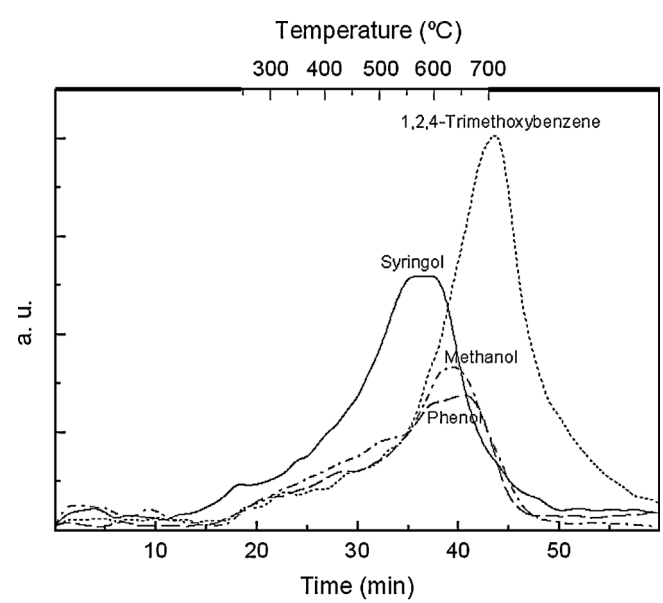


**Fig. 1.** Combustion profiles of the coke on catalyst E-Cat. Lines: dash-dot, methanol; dash, phenol; solid, syringol; dot, 1,2,4-trimethoxybenzene.

temperature (700 °C) and was the largest, probably due to the high yield of mono- and, particularly, diaromatic hydrocarbons observed with this reactant (see Table 4).

The analysis performed with the coke deposited on the SiC bed in the thermal experiments (results not shown) all showed a very small peak, consistent with the low coke yields reported in Table 2, located at about 450 °C.

## 4. Conclusions

Model oxygenated compounds which represent typical chemical groups present in bio-oils, which could be co-processed in conventional oil refineries, showed very different conversions over a commercial equilibrium FCC catalyst in the presence of large amounts of water, according to their chemical functionality. The highest conversion corresponded to 1,2,4-trimethoxybenzene (95.7 %wt.) and the lowest to phenol (54.9 %wt.). The catalytic deoxygenation was between 37 (case of phenol) and 99.5 %wt. (case of 1,2,4-trimethoxybenzene) and mainly achieved through dehydration and decarboxylation reactions.

According to the reactants, the distributions of hydrocarbon products were different. Phenol and syringol yielded olefinic C4-light hydrocarbons and also aromatic hydrocarbons in the case of syringol. Methanol and 1,2,4-trimethoxybenzene yielded mainly aromatics in the range of gasoline.

It was shown that the yield of coke can be very high in the case of 1,2,4-trimethoxybenzene (16 %wt.) and relatively lower, though important, with the other reactants, from 4.4 to 8.5 %wt.

The thermal conversions of the model compounds were much less important than the catalytic ones, particularly in the case of phenol, with the exception of 1,2,4-trimethoxybenzene, which was similar to the catalytic conversion. The thermal deoxygenation produced was similar to the catalytic one in the case of trimethoxybenzene (97.5%) and lower for the other reactants (23% in the case of methanol, 20% in the case of phenol and 45% in the case of syringol).

Even though the experiments did not reproduce completely the conditions of the FCC process, which is a serious candidate process for bio-oil co-processing in refineries, this information could be useful to predict specific contributions to the products from this type of oxygenated compounds, which are present in significant concentrations in typical bio-oils, or assist in predictions for bio-oil upgrading over acidic catalysts. However, when hydrocarbons are present, they may play an important role in hydrogen redistribution. Under the conditions used, this typical FCC catalyst showed capacity to deoxygenate and convert these model oxygenated compounds into hydrocarbons, together with a high coke yield, particularly in the case of aromatic ethers.

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