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Technical note

# Products and coke from the conversion of bio-oil acids, esters, aldehydes and ketones over equilibrium FCC catalysts

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ABSTRACT

Reactivity and product distributions in the conversion of five different compounds representing typical species in bio-oils were studied over an equilibrium FCC catalyst at 500 °C during 60 s in a fixed bed reactor. Acetic acid, methyl acetate, furfural, 3-methyl-2-pentanone and 2-hidroxy-3-methylcyclopentenone were dissolved at 5% wt. in water. Thermal conversions were performed under the same conditions with inert SiC in the bed. The test compounds converted very differently, deoxygenation being produced by decarboxylation and dehydration. Furfural and 3-methyl-2-pentanone gave the highest yields of hydrocarbons, with high selectivity to light olefins and, when liquid (case of ketones), to aromatics. Methyl acetate gave the highest yield of oxygenated compounds. Coke yields were important (maximum 12.8% wt., 2-hidroxy-3-methylcyclopentenone). Thermal conversions were similar to the catalytic ones with acetic acid and methyl acetate, and much lower for the other reactants. Compared catalytic experiments, the thermal yields of hydrocarbons were much higher with acetic acid, and the yields of oxygenated higher with methyl acetate ester. Much less hydrocarbons were produced thermally with the other reactants. This information may be useful for predicting contributions if these compounds are to be co-processed in existing FCC units or upgraded over acidic catalysts.



## 1. Introduction

The liquid fraction from the pyrolysis of lignocellulosic biomass is usually referred to as bio-oil, and constitutes an alternative source for the production of fuels and raw materials for the chemical industry [1]. Bio-oils are complex aqueous mixtures of mostly oxygenated compounds, which have different chemical structures and a wide range of molecular weights; for example, bio-oils from different sawdusts contain mainly phenols, furanes, acids, esters, alcohols, aldehydes and ketones, with approximately 35–40% of oxygen, 55–60% of carbon, 15–60% of water, an acidic pH, and a density close to 1.2 g/cm$^3$ [2,3].

In order to transform bio-oils into transportation fuels, an upgrading process to remove oxygen could be performed with the help of catalytic cracking reactions over acidic zeolites, which mainly lead to hydrocarbons in the range of gasoline [3–7]. The conversion of oxygenated model compounds over zeolites and mesoporous materials showed that almost all of them formed hydrocarbons, the various functional groups indicating significantly different reactivities and product distributions [8–13].

Among the various options to upgrade bio-oils, their co-processing in existing industrial processes deserves special consideration, because by means of using present structure, no important process development and investments would be needed. Oil refineries, particularly the processes of thermal or catalytic cracking of hydrocarbons (FCC), might cover such an option, where bio-oils may play the role of non conventional feedstocks [14].

In the case of FCC, where the main component of the catalyst is the Y zeolite, the feasibility of adding bio-oils to the feedstock, which is usually vacuum gas oil, VGO, could be hampered by the high coke forming potential of bio-oils, which tend to polymerize at high temperatures [3–7]. Indeed, present day FCC technologies can handle heavy resid hydrocarbon mixtures, with Conradson Carbon Residue CCR higher than two, yielding more coke than conventional VGOs, by means of particular innovations such as catalyst coolers, two stage regeneration and more efficient strippers, among others [15,16]. In order to facilitate co-processing in FCC, the previous thermal treatment of bio-oils induces important changes in their composition, with reductions between 30 and 50% in the amount of phenols [17], which are assumed to be main coke precursors; as a consequence, up to 30% decrease in the yield of coke was observed with previously treated bio-oils [7,18]. Other possible drawback in the approach is the significant content of water in bio-

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oil and the fact that it may be not possible to dissolve it into VGO; some options were discussed by Corma et al. [19].

The study of the reactivity of bio-oil model compounds representing different chemical functionalities over actual, equilibrated commercial FCC catalysts, as well as of the product distributions observed, could provide useful information to predict co-processing details. Particularly, the chemical groups which are responsible of higher coke yields, or which show more efficiency in being converted into hydrocarbons, could be identified. At present that information is scarce. It is the objective of this work to study the conversions and product selectivities of acids, esters, aldehydes and ketones, in terms of model compounds, on an equilibrated commercial FCC catalyst, and compare them with the same observations on an inert material used to represent thermal cracking reactions.

## 2. Experimental

The model compounds (Sigma–Aldrich) used were acetic acid (99.8%, named ACET), methyl acetate (99.5%, MACET), furfural (99%, FUR), 3-methyl-2-pentanone (99%, MP) and 2-hidroxy-3-methylcyclopentenone (98%, HMCP), to represent acids, esters, aldehydes and linear and cyclic ketones, respectively. Each of the reactants was 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 from conventional pyrolysis processes.

The equilibrium FCC catalyst used (E-Cat) was of the octane-barrel type, sampled from a running refinery, its most important characteristics being 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. 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 and carbon balances (recoveries) were higher than 90% in all the cases. Thermal cracking reactions were performed under the same conditions with a bed of inert SiC occupying the same volume as the catalytic bed.

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 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 were 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; water yield was assessed by difference from the mass balance.

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

| | |
|---|---|
| Particle size (μm) | 100–120 |
| UCS (Å) | 24.26 |
| Zeolite load (%) | 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 |

## 3. Results and discussion

The model compounds were selected based on the composition of bio-oil derived from the conventional pyrolysis of pine sawdust [17], selecting compounds that represent some of the most important chemical groups, such as acids and esters (typically present at about 30% wt.) [20], aldehydes and ketones (with typical concentrations from to 2 to 20% wt. and about 7% wt., respectively [20]). Moreover, some of the compounds, such as FUR and HMCP, were the most important in the group they represent.

In their conversion on acidic zeolites, acids, esters, aldehydes and ketones react through a mechanism involving decarbonylation, decarboxylation, dehydration, cracking and aromatization, thus yielding mainly aromatic and aliphatic hydrocarbons and oxygenated compounds covering a wide range of molecular weights [9,10,13,21–23].

In all the cases liquid, gases and solid (coke) products were generated by the catalytic and thermal conversions of the model compounds. The amount of water in the liquid stream represented from 96 to 99% of the liquid fraction, accounting for solvent water and product water from dehydration reactions. Table 2 shows the conversions and the yields of the different product groups, where significant differences can be observed among the five reactants. Most noticeable facts on E-Cat are that under the conditions used the highest conversion and yield of oxygenated product corresponded to MACET (95.1%), while MP and FUR yielded much more hydrocarbons than the other reactants, selectivities being 47% and 41%, respectively. The highest producer of oxygenated compounds was MACET, and HMCP yielded the highest amount of hydrogen (8.1% wt.) and carbon dioxide (35.7% wt). Maximum dehydration was observed with FUR (12.8% wt.).

The published literature about the conversion of these model compounds, or similar, on FCC catalysts or Y zeolite, which is their main component, is very scarce. For example, Hutchings et al. [8]

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

| | ACET | | MACET | | FUR | | MP | | HMCP | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Conversion (%) | 45.0 | 50.4 | 95.3 | 95.1 | 21.6 | 78.2 | 24.9 | 79.6 | 37.7 | 84.5 |
| Yields (%wt.) | | | | | | | | | | |
| Hydrocarbons | 10.4 | 4.2 | 0.4 | 0.9 | 5.3 | 32.1 | 0.3 | 37.6 | 5.0 | 14.0 |
| Oxygenated | 5.0 | 5.2 | 81.6 | 54.5 | 0.7 | 9.0 | 17.9 | 20.7 | 14.4 | 9.4 |
| Hydrogen | 17.5 | 6.6 | 5.2 | 3.7 | 6.7 | 5.7 | 0.6 | 0.5 | 3.7 | 8.1 |
| $CO_2$ | 8.2 | 22.9 | 3.0 | 22.2 | 1.1 | 9.6 | 1.2 | 1.1 | 1.9 | 35.7 |
| CO | | | | | | 1.8 | | | | 1.2 |
| Water | 3.6 | 9.9 | 4.7 | 6.4 | 6.8 | 12.8 | 3.1 | 13.7 | 10.0 | 2.3 |
| Coke | 0.3 | 1.6 | 0.4 | 7.4 | 1.0 | 7.2 | 0.1 | 5.9 | 0.7 | 12.8 |
| Unknown | | | | | | | 1.7 | | 2.0 | 1.0 |

reacted pure methanol over pure HY zeolite at 370 °C with conversions up to 78% and mostly hydrocarbons among products. Samolada et al. [11] produced a synthetic bio-oil made up of acetic acid, furfural, cyclohexanone, vainillin and water (42.8% wt.) which was converted to 63% over pure REUSY zeolite in a fixed-bed reactor, to yield 8.5% wt. of hydrocarbons and 4% wt. of oxygenated compounds. Domine et al. [24] converted acetic acid, isopropylic alcohol and acetone added to isooctane at 2% wt. on an FCC catalyst, and observed hydrocarbons and carbon monoxide among products. Other authors made use of model compounds dissolved directly into VGO. Graça et al. [25] reported that light hydrocarbons $C4^-$ and carbon oxides were the most important products of the conversion of a mixture of 6.6% wt. of acetic acid − VGO on equilibrium FCC catalysts.

On the contrary, ZSM-5 zeolite was tested much more extensively in the conversion of some of these types of oxygenated compounds (e.g. acetic acid and methyl acetate [22]; furfural [10,23], methylcyclopentanone [9] and 2-butanone [13]). Some observations could be taken into account and compared to results from FCC catalysts. In all the cases conversions were higher than 90%, with considerable yields of hydrocarbons in the cases of linear and cyclic ketones (about 60–70% wt.), and of oxygenates in the case of furfural (about 50% wt.). Water and carbon dioxide were produced in significant amounts in all the cases (between 20 and 30% wt.), and acetic acid and methyl acetate yielded mainly oxygenated compounds (between 14 and 20% wt.).

All the reactants showed that decarboxylation and dehydration reactions existed in their catalytic conversions, and FUR and HMCP also showed decarbonilation (see Table 2). These reactions accounted for the observed deoxygenation of about 80% in the cases of ketones HMCP and MP, of about 60% in the case of aldehyde FUR and of about 45% in the cases of acid and ester ACET and MACET, respectively. Deoxygenation had been coincidently noticed on zeolite ZSM-5 to be due to decarboxylation and dehydration in the cases of acids and esters [22], decarbonilation being observed with ketones and aldehydes [9,10,25]. Graça et al. [25] had reported that carbon dioxide and water were the most important products in the deoxygenation of acetic acid over equilibrium FCC catalysts. This can be contrasted with reports from Domine et al. [24], who observed mainly carbon monoxide in the conversion of acetic acid over FCC catalysts.

The extents of the thermal conversions for ACET and MACET were similar to those in the catalytic processes, while the other model compounds showed thermal conversions between two to three times smaller. However, the product distributions in the thermal and catalytic conversions were always very different (refer to Table 2); particularly, in the thermal processes, much higher hydrocarbon and hydrogen yields were observed with ACET, as well as a much higher yield of oxygenated compounds with MACET. In the cases of FUR, MP and HMCP, the thermal processes yielded much less hydrocarbons than the catalytic ones; HMCP also yielded more water and oxygenated compounds.

Moreover, the overall deoxygenations induced by the thermal processes (about 35% for HMCP and about 20% for the other reactants) were in all the cases much lower than the corresponding catalytic one.

### 3.1. Distribution of oxygenated products in thermal and catalytic conversions

Table 3 shows the distributions of oxygenated products in the thermal and catalytic conversions of the various model compounds. Methanol and acetone were always present among the products, formic acid was particularly present in the case of FUR and acetic acid in the case of MACET. HMCP showed the more extended oxygenated distribution, which included ketones, furans and alcohols. These observations are consistent with some known facts. For example, it is known that acetone can be obtained from the dehydration of both acetic acid and methyl acetate [21,26] and from the thermal decomposition of low molecular weight linear ketones, such as MP [27]. As well, the hydrolysis of methyl acetate leads to acetic acid [28] and the thermal decomposition of furanic compounds such as FUR produce oxygenated fragments such as HCO· that may lead, for example, to formic acid [29].

The selectivity to acetone was higher in the thermal experiments than in the catalytic ones in the cases of ACET, MACET and HMCP, and much lower in the cases of FUR and MP. The selectivity to methanol was lower in the thermal experiments in all the cases except with MACET, which was similar.

The catalytic conversion of HMCP produced mainly ketones (88% selectivity), particularly methylcyclopentenone, following the behavior typical of cyclopentanones over HZSM-5 zeolites [9,10].

**Table 3**
Thermal and catalytic conversions of the model compounds. Distribution of oxygenated products. Temperature: 500 °C.

| | ACET | | MACET | | FUR | | MP | | HMCP | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Formic acid | Traces | Traces | 2.6 | | 48.4 | 5.0 | | | 0.7 | 1.2 |
| Acetic acid | | | 27.5 | 35.2 | | | | | | |
| Acetaldehyde | | 0.6 | | | | | | | | |
| Acetone | 96.0 | 85.8 | 7.1 | 6.3 | 8.8 | 44.8 | 26.7 | 63.5 | 0.4 | 0.2 |
| 4-Hydroxy-3-methylbutanone | | | | | | | 48.3 | | | |
| 2,3-Pentadione | | | | | | | | | | 0.2 |
| 4-Hydroxy-4-methylpentanone | | | | | | | | | 0.7 | 0.8 |
| Cyclopentanone | | | | | | | | | 1.5 | 0.3 |
| Cyclopentenone | | | | | | | | | 0.3 | 1.2 |
| Methylcyclopentenone | | | | | | | | | 78.4 | 72.4 |
| Cyclohexenone | | | | | | | | | 3.2 | 2.4 |
| Methylcyclohexanone | | | | | | | | | | 3.5 |
| Methylfuranone | | | | | | | | | 0.3 | 0.8 |
| Ethylfuranone | | | | | | | | | 4.5 | 6.2 |
| Methylfuran | | | | | | | | | 1.7 | 1.7 |
| Dibenzofuran | | | | | | | | | 0.3 | 0.2 |
| Methanol | 4.0 | 13.6 | 62.8 | 58.5 | 42.8 | 50.2 | 25.0 | 36.5 | 0.7 | 1.5 |
| Ethanol | | | | | | | | | | 0.3 |
| Phenol | | | | | | | | | 4.0 | 2.1 |
| Dimethylphenol | | | | | | | | | | 1.1 |
| Ethoxybenzene | | | | | | | | | 3.3 | 3.9 |

Phenol, ethoxybenzene, methanol and formic acid were also produced, but with much lower selectivity. In general terms, the thermal conversion of HMCP yielded a similar distribution of oxygenated compounds, but yields were 50% higher since the further conversion of oxygenated into hydrocarbons could not proceed without catalytic active sites.

### 3.2. Distribution of hydrocarbon products in the thermal and catalytic conversions

Table 4 shows the distribution of hydrocarbon products in the thermal and catalytic conversions of the model compounds. It can be seen that C1–C4 gases were always present in both processes, and that liquid products were also obtained in the experiments with FUR, MP and HMCP.

ACET and MACET did not extend their conversion importantly, producing only $C4^-$ hydrocarbons with a high proportion of olefins. The most important hydrocarbons in the catalytic conversion of ACET were methane and butenes, both with selectivities of 38%, while the thermal cracking of this compound generated methane, ethylene and propylene as the most important products, as also observed by Mackie and Doolan [30]. The conversion of MACET on catalyst E-Cat produced about three times more C1–C2 hydrocarbons than C3–C4 hydrocarbons, C2–C4 olefins representing 39% in the $C4^-$ group. This proportion was about two times the one observed in the thermal process, where methane was by far the most important product. An important yield of C4 olefins from the aldol condensation of acetone (which was formed significantly in this work, see Table 3), was observed on HZSM-5 zeolite by Chang and Silvestri [21] and Hutchings et al. [8].

The catalytic conversion of aldehyde FUR showed that among gas products the C3–C4 hydrocarbons were predominant, and that liquid products (74.5% selectivity) were composed almost exclusively by C5 olefins. This distribution is different from the one observed with HZSM-5, where aromatics (particularly alkylbenzenes) and naphthalene and alkylated homologous compounds were the most important liquid products [10,23]. The thermal conversion of FUR produced mainly methane, C2–C3 light olefins and C5 olefins, in coincidence with reports from Moldoveanu [29].

Ketones showed a more extended catalytic pathway, aromatics being the most important liquid hydrocarbon products. The selectivity to hydrocarbons in the gasoline range was 90% in the case of MP, with 70% of aromatics in the cut; in turn, naphthalene and alkylated homologous were the most important individual products in aromatics. C5–C9 aliphatic hydrocarbons, mainly 3-methylpentane, were observed. Contrary to ACET, MACET and FUR, the selectivities to C1–C2 and C3–C4 hydrocarbons observed in the conversion of ketones were very low, smaller than 1%. The thermal cracking of MP produced light hydrocarbons C5 − (highly olefinic, particularly butenes) and methane, in coincidence with reports from Barry and Walters [27].

The selectivity to hydrocarbons in the gasoline range was not as high (32%) in the case of the catalytic conversion of the cyclic ketone HMCP, aromatics being the most important compounds in the range (about 60%), followed by C5 olefins (20%) and i-pentane (16%). The family of naphthalene was prevailing among aromatics. High yields of C1–C2 (40% of ethylene) and C3–C4 hydrocarbons (97% of olefins) were observed (see Table 4), in correspondence to reports about the conversion of cyclopentanones over HZSM-5 [10,23]. The thermal cracking of HMCP showed a high selectivity to olefinic C4 hydrocarbons, in coincidence with reports from Dao et al. [23], which can further support the high yield of aromatic hydrocarbons observed [29].

### 3.3. Coke yields in the thermal and catalytic conversions

Coke formed in the conversion of oxygenated compounds or their mixtures over acidic catalysts has both thermal and catalytic sources [4,7,10,12,13]. In the case of compound catalysts, such as those used in FCC, where the main component (the Y zeolite) is loaded on a matrix, coke from thermal origin generally deposits on the matrix, thus having a less important effect on catalyst activity than the catalytic coke, which forms on the active sites or block pores [31].

The yield of coke was very important in most of the cases, above approximately 6% wt. (see Table 2), considering that water was present in high concentrations, a fact that may attenuate coke yield from oxygenated compounds [12]. The lowest yield was observed

**Table 4**
Thermal and catalytic conversions of the model compounds. Distribution (%wt.) of hydrocarbon products. Temperature: 500 °C.

| | ACET | | MACET | | FUR | | MP | | HMCP | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat | SiC | E-Cat |
| Conversion (%) | 45.0 | 50.4 | 95.3 | 95.1 | 21.6 | 78.2 | 24.9 | 79.6 | 37.7 | 84.5 |
| Hydrocarbons C1–C2 | 87.4 | 47.2 | 89.8 | 75.8 | 13.1 | 5.5 | 32.1 | 0.2 | 7.4 | 16.4 |
| Methane | 75.0 | 38.4 | 83.2 | 57.5 | 8.2 | 2.5 | 14.7 | 0.1 | 4.4 | 8.8 |
| Ethane | | | 0.9 | 2.6 | | | | | 0.3 | 0.9 |
| Ethylene | 12.4 | 8.8 | 5.7 | 15.7 | 4.9 | 3.0 | 17.4 | 0.1 | 2.7 | 6.7 |
| Hydrocarbons C3–C4 | 12.6 | 52.8 | 10.2 | 24.2 | 15.2 | 19.3 | 56.5 | 0.8 | 41.4 | 51.7 |
| Propylene | 7.5 | 12.4 | 2.7 | 12.8 | 13.5 | 14.0 | 16.9 | 0.5 | 3.2 | 18.5 |
| n-Butane | | 1.1 | | | 1.2 | 1.1 | 2.0 | | | 0.3 |
| Isobutane | | 1.0 | | 1.0 | | 2.0 | 0.3 | 0.1 | 1.9 | 1.2 |
| Butenes | 5.1 | 38.3 | 7.5 | 10.4 | 0.5 | 2.2 | 37.3 | 0.2 | 36.3 | 31.7 |
| Hydrocarbons C5–C9 | | | | | 71.7 | 74.5 | 11.4 | 31.2 | 7.2 | 13.3 |
| i-Pentane | | | | | | 0.6 | | 1.4 | 0.5 | 5.0 |
| n-Pentane | | | | | | 3.6 | 2.8 | | 0.8 | 1.3 |
| Pentenes | | | | | 71.7 | 69.3 | 8.6 | 0.1 | 3.8 | 6.3 |
| C6+ aliphatics | | | | | | 1.0 | | 25.9 | 1.4 | 0.3 |
| C6+ Cycloparafins and naftenics | | | | | | | | 3.8 | 0.7 | 0.4 |
| Aromatics | | | | | | 0.7 | | 67.8 | 44.0 | 18.6 |
| Benzene | | | | | | 0.7 | | 4.3 | | 4.0 |
| Toluene | | | | | | | | 2.8 | | |
| Ethylbenzene | | | | | | | | | 6.8 | 3.2 |
| Aromatics C9 | | | | | | | | | 8.7 | 0.8 |
| Aromatics C10 | | | | | | | | | | 2.1 |
| Aromatics C11+ | | | | | | | | 60.7 | 28.5 | 8.5 |

with ACET, 1.6% wt., and the highest with HMCP, 12.8% wt. In all the cases the yield of coke when the catalyst was present was much higher than in the thermal experiments. High coke yields were also observed in the conversion of these reactants, or structurally similar oxygenated compounds, over HZSM-5 catalysts [10,13,22].

Fig. 1 shows the combustion profiles of the coke formed on the catalyst by the various oxygenated compounds. The profiles corresponding to the coke formed in the thermal conversion experiments (not shown for the sake of clarity) showed a single, very small peak located in the range from 450 (ACET and MACET) to 500 °C (FUR and ketones). Two peaks can be seen in the cases of the coke from ACET and MACET; the first one would correspond to a less condensed coke that could be associated to thermal sources only [13], assuming that it is possible to uncouple the processes and that no interaction between reactants and products. The first peak in the coke from ACET locates at approximately 375 °C and the one from MACET at approximately 390 °C. The second peak would correspond to a more dehydrogenated coke from catalytic source, with a maximum at approximately 630 °C in both cases.

A single peak was observed in the cases of the catalytic conversion of the aldehyde FUR and the linear and cyclic ketones MP and HMCP. This peak represented a highly condensed coke in the case of the ketones with the maximum located at about 700 °C, a characteristic that could be associated to the important production of aromatics among products (refer to Table 4). The coke from FUR showed its maximum at about 500 °C; both thermal polymerization [13,23] and aldol condensation reactions in the reaction medium [9] were pointed as the sources of coke in the conversion of aldehydes over HZSM-5.

The coke yields observed with the model compounds do not suggest to be a significant problem in co-processing bio-oils in FCC together with conventional feedstocks, considering that MAT-type reactors tend to produce higher coke yields, that these particular reactants would be much reduced in concentration when co-processing bio-oils and that, eventually, technologies exist which can process heavily coking feedstocks, such as resids. Besides some differences in the experimental approaches and feedstocks used, slight increases in coke yields have been reported when bio-oils were converted together with hydrocarbon cuts [32,33].

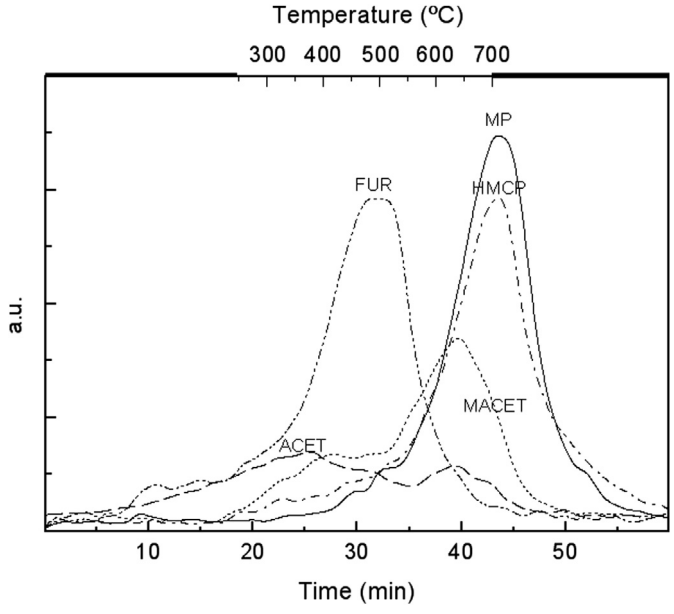


**Fig. 1.** Combustion profiles of the coke on catalyst E-Cat. Lines: dash, ACET; dot, MACET; dash–dot–dot, FUR; solid, MP; dash–dot, HMCP.

## 4. Conclusions

The catalytic conversions of oxygenated compounds representing some of the most important groups present in bio-oils, achieved over an equilibrium FCC catalyst under the existence of high concentrations of water, were different according to the functional group (acid, ester, aldehyde, ketone). The highest conversion (95.1%) corresponded to methyl acetate ester, and the lowest (50.4%) to acetic acid.

Deoxygenation, which proceeded through the production of carbon oxides, particularly carbon dioxide, and water, was very important in all the cases, between 50 and 80%.

Product distributions were different, according to the reactant. For example, acids and esters showed to yield significant amounts of oxygenated compounds and light C1–C4 hydrocarbons, particularly olefins. Aldehydes and ketones produced hydrocarbons in the gasoline boiling range: furfural yielded a very high proportion of C5 olefins, and the ketones yielded predominantly aromatics.

The experimental information addressed the important issue of coke yield, showing that it can be very important in the case of the cyclic ketones (12.8% wt.), most of the other compounds showing yields in the 6 to 7.5% wt. range.

Although the experiments did not fully reproduce the conditions of the FCC process, this information may be useful in predicting the contributions from these types of compounds, which are present in significant concentrations in bio-oils, if they are to be co-processed in existing FCC units, or upgraded over acidic catalysts. In case of co-processing in FCC, possible increases in coke yields and $CO_2$ emissions, and oxygenated compounds in the gasoline boiling range, do not to seem to represent an important problem.

The experiments of thermal cracking of these compounds showed conversions similar to those with the catalyst in the cases of acetic acid and methyl acetate ester, and much lower for the other reactants. Deoxygenations in the thermal conversions were in all the cases much lower than catalytic ones.

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