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Co-processing of oxygenated biomass compounds and hydrocarbons for sustainable fuel production

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Climate changes related to global warming impose rapid actions to reduce green house gas releases, especially carbon dioxide emissions. Being one of the main contributors, changes in the transportation sector that are compatible with current technologies can have a strong impact. Focusing on a replacement of fossil fuels by carbon-neutral renewable resources seems very adequate, as this will have immediate impact. Biomass processing is a perspective for the direct production of liquid fuels and chemicals^[1,2].

Currently, the world production of bio-ethanol and bio-diesel from vegetable oils covers a mere 1% of global transport fuels^[3]. This bio-fuel production has doubled over the past 5 years, and reports indicate that if this trend continues bio-fuels could supply at least 35% of US transport fuels and 20-30% of the EU oil use, in the next 25 years^[3,4]. Nevertheless, these bio-fuels have their own environmental and strategic costs, since they are derived from agricultural sources grown in net competition with food production. Given the huge capacities involved in transportation, rapid change can be only achieved using existing infrastructures and guaranteeing the same quality of the final fuels. Thus, it seems natural to investigate first options for introducing biomass components into existing refinery infrastructures. Ideally, bio-fuels production could be almost instantaneously achieved by co-processing of biomass-derived oils in standard units along with conventional crude oil. This co-processing of renewables and hydrocarbons in an existing refinery will be economically more competitive than processes such as Fischer-Tropsch fuels obtained from biomass gasification^[5] and bio-diesels derived from vegetable oils^[6]. In this sense, non-competing lignocellulosic biomass sources derived from forestry and industrial wastes are

cheaper and present the most promising alternative, which will eventually dominate the market in the future^[7]. Up to now, different types of gasification processes commonly perform the conversion of bulky biomass materials into easier treatable intermediates. Pyrolysis, partial oxidation, and steam gasification are the most common ways to obtain gaseous products, but also liquids and solids, from biomass resources^[1,8].

The fast pyrolysis of biomass performed under adequate conditions can yield, besides gaseous and solid products, 75wt.% of a liquid or condensable biomass-derived oil^[9]. Pyrolysis-oils obtained from lignocellulosic biomass are complex mixtures (> 200 components) of mainly oxygenated compounds emulsified in water. Constituents are acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols and phenol derivatives, as well as carbohydrates and derivatives, and a large proportion (20-30 wt.%) of lignin-derived oligomers^[10]. In the last years, demonstrators for upgrading of pyrolysis-oil by catalytic cracking processes were tested, indicating low gasoline production, important amounts of tars, chars and coke, and irreversible catalyst deactivation, mainly due to the high oxygen content in the feed^[11-16]. The transformation of oxygenated model compounds into liquid fuels by cracking over acid catalysts has also been studied^[17,18]. Thus, although these pyrolysis-oils can be used as renewable feedstock for the production of transportation fuels, direct feeding of the entire pyrolysis-oil into standard refinery reactors is not a straightforward task, even after passing compulsory upgrading steps^[19].

As such, it is necessary to achieve the integration of processes in large-scale units (e.g. fluid catalytic cracking (FCC), hydro-treating) that can convert pyrolysis-oils to automotive fuels at a lower cost than small-scale plants dedicated to biomass-processing or transesterification, thus raising with relative low cost public acceptance. In order to elucidate the possibilities of co-processing approaches in FCC refinery units, we focused our study on the co-feeding of hydrocarbon and oxygenated compounds mixtures into a catalytic fixed-bed reactor simulating the FCC conditions in the range of 450-530°C. Equilibrated FCC catalyst formulations, i.e. catalyst having already sustained several FCC cycles, are tested. Acetic acid, acetone, and iso-propanol, chosen as model compounds being representative for the pyrolysis-oil, are co-injected along with iso-octane presenting the hydrocarbon feed (similar trends were observed with dodecane). The use of model compounds is motivated by preliminary results on real feeds that are complex to analyze and by a need for a better fundamental understanding. In fact, the extensive knowledge that exists today on the mechanism of catalytic cracking stems mainly from experiments using small hydrocarbons^[20]. The influence of oxygenates addition on the cracking reaction is evaluated in terms of conversion and product distribution, as well as catalyst stability. A rigorous comparison of data obtained for catalytic hydrocarbon cracking with and without oxygenated molecules allows identifying those classes of oxygenated compounds obligatorily to eliminate from pyrolysis-oils before admission to FCC units.

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Fig. 1 shows the iso-octane conversion at 530°C for 10 reaction cycles for a catalyst to iso-octane ratio of 15 g/g. During these cycles the catalyst is regenerated by oxygen by keeping the temperature in the catalyst bed at 530°C. The catalyst is stable during all 10 cycles. Low amounts of acetone, acetic acid and iso-propanol, 2 wt.% of the hydrocarbon feed, were co-fed together with iso-octane. The effects of the presence of different oxygenated species on the hydrocarbon conversion during the catalytic cracking steps along several cycles are displayed in Fig. 1. The presence of oxygenated species decreases the conversion. Initially, acetone causes ~17% loss of activity but progressive deactivation raises this value to 32% after 10 reaction cycles. On the contrary, both acetic acid and iso-propanol addition lead to a strong initial catalyst deactivation, however the iso-octane conversion remains constant throughout the cycles. Higher regeneration temperatures led to similar results. Apparently the presence of acetone results in a severe catalyst deactivation, whereas in the presence of acetic acid and iso-propanol the deactivation is partly reversible.

Table 1 reports the yields (wt%) of the main cracking products, the iso-octane conversion and the mass balance for the pure hydrocarbon feed as well as for the addition of the oxygenated compounds. Introduction of the oxygenated compounds always led to higher coke levels. Moreover a larger deficit of the carbon balance was observed as well, maybe due to coke that has not been regenerated completely. Addition of the different oxygenated compounds induces changes in the product distribution. The formation of CO (but no CO₂) is observed that corresponds to a conversion of approximately 50% of the oxygenated compounds. Note that the product distribution depends on the conversion level and the data in Table 1 are not at iso-conversion. To better understand the effect of acetone on the product distribution, the selectivity as a function of the conversion has been compared for the different feeds. The selectivity to light gas, propylene and iso-butane are shown in Fig. 2. Similar trends were observed for the cracking of iso-octane in the TAP reactor^[21]. Adding acetone to the iso-octane feed results in an increase of iso-butane and butene selectivities (Fig. 2) as the conversion increases at the expense of propylene and light gases. In the case of C7, C6, C5 fractions no changes were observed. As iso-butane and butenes are primary cracking products and propylene a secondary product, the effect of acetone appears to suppress the secondary cracking activity. Cracking of iso-butane requires stronger acid sites than iso-octane, thus implying that the cracking of acetone leads to coke that selectively blocks the most acid sites. From these results we conclude that, although co-processing of upgraded pyrolysis-oils in archetypal refineries constitutes a promising route towards greener automotive fuels, bio-oils will present several challenges before introduction into the FCC and upgrading remains a critical step.

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Figure 1. Figure 1. Effect of oxygenated compounds addition on the catalytic cracking of iso-octane over FCC catalyst (1g) at 530°C during 10 reaction cycles (■ iso-octane, ♦ + acetone, ▲ + iso-propanol, ● + acetic acid).

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Figure 2. Effect of acetone addition on the selectivity of cracking products from iso-octane (■ iso-octane, ▲ + acetone).

Product	iso-octane	+ acetone	+ acetic acid	+ i-propanol
light gases	9.6	5.9	4.7	6.3
CO	0.0	0.6	0.7	0.4
propane	0.5	1.0	0.5	1.4
propylene	21.2	11.7	10.5	11.4
iso-butane	11.8	11.6	10.4	7.9
n-butane	0.3	0.2	0.2	0.1
Butenes ^[a]	18.6	16.7	16.8	16.0
C5	7.0	5.6	5.5	5.0
C6-C7	3.0	1.8	2.1	2.0
Coke ^[d]	3.4	7.8	6.1	8.0
Conversion ^[b,c]	73.1 (76.5)	53.5 (61.3)	50.3 (56.4)	50.5 (58.5)
C-balance	99	94	95	98

[a] Addition of n- and iso-butenes. [b] Conversion calculated from GC data as (Total Products Obtained / Remained iso-octane) * 100. [c] In brackets, conversion from GC data + coke. [d] Coke measured as CO₂ + CO produced during the regeneration step.

Experimental Section

Set-up. Experiments were performed in a fixed-bed quartz reactor (ID = 12mm, L = 34mm) at 1 bar. A thermocouple was located inside the catalyst bed. Reactants were vaporized (at 140-250°C) before introduction into the reactor. Argon was used as carrier gas (flow = 100 ml/min), the Ar/HC feed volume ratio was around 19. One reaction cycle consists of 2.5 minutes cracking, 20 minutes stripping, 15 minutes regeneration under 20 vol.% of O₂ in Ar and a 12.5 minutes purge. Multiple reaction cycles were performed during several hours in order to evaluate the catalyst regeneration ability. Gases were analyzed by mass spectrometry continuously and during cracking steps simultaneously by two on-line HP6890 gas chromatographs. One equipped with a flame ionization detector to quantify the C₁-C₁₂ hydrocarbons on an ATTM-1 column (30m). The other one equipped with two thermal conductivity detectors used in parallel to quantify light oxygenated compounds on a Poraplot Q column (30m) and to analyze permanent gases on a back-flush protected molecular sieve 5A column (30m). The amount of coke formed on the catalyst was estimated from the carbon dioxide production during the regeneration period.

Catalyst. An industrial FCC catalyst was used that has been equilibrated in a FCC unit^[21]. The sample contains 32wt% Y-zeolite, 1.5wt% rare earth oxides, 700 ppm of Ni and 1500 ppm of V. It has a BET of 172 m²/g. The average size of zeolite crystallites was estimated to be 2 nm, with an overall Si/Al atomic ratio of 2.5.

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Keywords: bio-fuels, catalysis, co-processing, cracking, pyrolysis oil, zeolites

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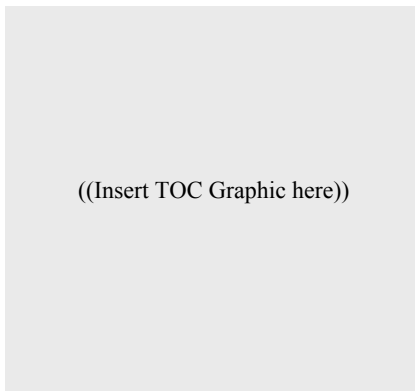
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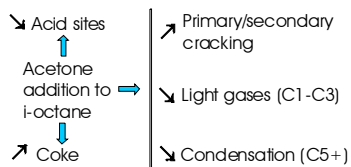
*Marcelo E. Domine, Andre C. van Veen,
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Page No. – Page No.

Co-processing: Model compounds, representative of fast pyrolysis oil, are co-fed to iso-octane in a simulated FCC unit.

**Co-processing of oxygenated
biomass compounds and
hydrocarbons for sustainable fuel
production**

From biomass, via pyrolysis oil, to tomorrow's biofuels



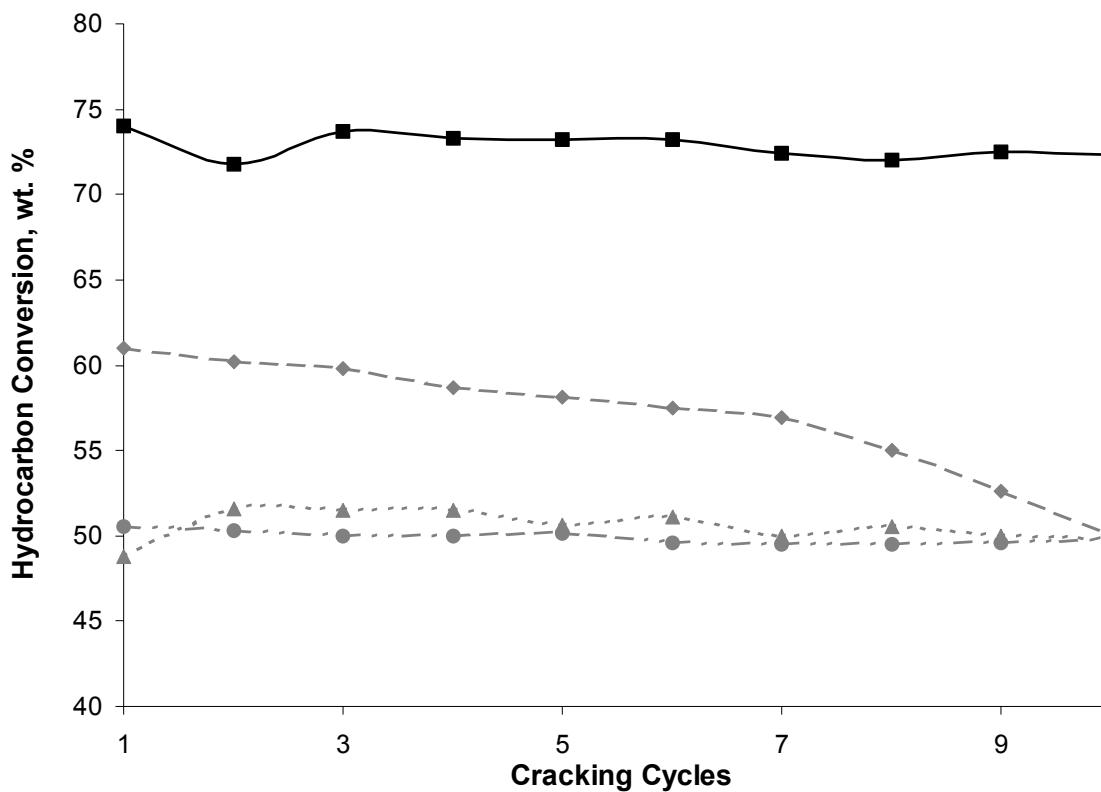


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acetic acid).

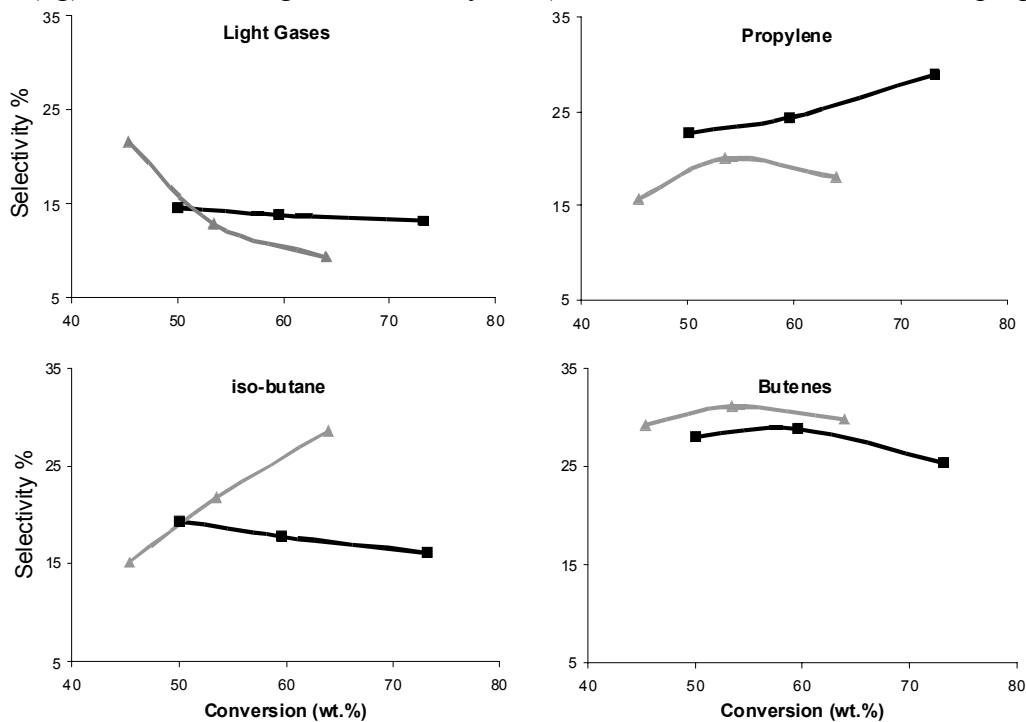


Figure 2. Effect of acetone addition on the selectivity of cracking products from iso-octane (■ iso-octane, ▲+ acetone).

From biomass, via pyrolysis oil, to tomorrow's biofuels

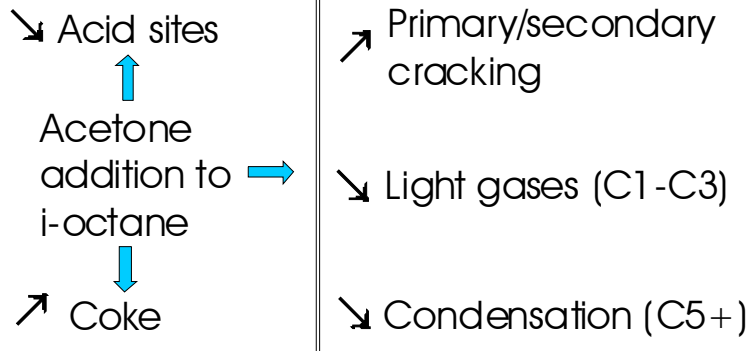


Table of Content Graphic