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Synergy in the Cracking of a Blend of Bio-oil and Vacuum Gasoil under Fluid Catalytic Cracking Conditions

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Abstract

The catalytic cracking of a blend of raw bio-oil (20 wt%) from black poplar sawdust fast pyrolysis and vacuum gasoil (VGO, 80 wt%) has been studied. The runs have been performed in a riser simulator reactor (RSR) under fluid catalytic cracking (FCC) conditions; that is, 500-560 ºC, catalyst to feed mass ratio of 6 $g_{cat\ (g_{feed})}^{-1}$ on a dry basis, reaction times of 3-10 s and a balanced commercial FCC catalyst. The co-feeding effect has been quantified by comparing the yields of product lumps and individual components in the gaseous fraction and gasoline lump in the cracking of VGO, raw bio-oil and their blend (20% bio-oil/ 80% VGO), at the same conversion values (60-70 wt%). The co-feeding has a favorable synergy because it promotes the formation of C_3-C_4 and gasoline (C_5-C_{12}) hydrocarbon lumps, attenuating the formation of CO_2, CO and also coke formation. In the cracking of the blend (80% VGO/ 20% bio-oil) at 70 wt% conversion, a deoxygenation degree of 95 wt% has been obtained, with a total liquid fuel yield of 52.8 wt% and a gasoline yield of 31.6 wt%, with a low oxygenate fraction (< 4 wt%) containing carboxylic acids, aldehydes, ketones and phenols.

Keywords: fluid catalytic cracking; bio-oil; vacuum gasoil; FCC catalyst; fuel

1. Introduction

The co-feeding of raw bio-oil into the fluid catalytic cracking (FCC) unit with the standard feedstock (vacuum gas oil, VGO) is considered an interesting strategy for fuel production from biomass, given that it reduces oil consumption and global emission of greenhouse gases.[1-3] The co-feeding strategy is encouraged by the considerable technological development of biomass fast pyrolysis[4,5] and the large capacity of FCC units, which are being modified to improve versatility for the processing of heavier streams.[6,7] However, great differences between bio-oil and VGO features cause problems in their co-feeding.

Raw bio-oil is a complex mixture of oxygenates with different functional groups, such as acids, esters, aldehydes, ketones, phenols, alcohols, ethers and sugars.[8-10] Although raw bio-oil has a low N and S content, it has limitations to be used as fuel and be stored.[11] Among these limitations, the following are worth mentioning: low heating value (16-19 MJ kg^{-1}) due to the high H_2O content (15-50 wt%) in the raw bio-oil, high acidity (pH ≈ 2-4) due the high carboxylic acid content, high viscosity (10-100 cP at 40 ºC), thermal and chemically unstable by the presence of phenolic compounds derived from lignin due to their repolymerization when the raw bio-oil is heated.[12]

Most of the studies on oxygenate compound cracking have been performed in fixed bed reactor.[9,13] These studies have shown high conversion of oxygenate compounds under FCC conditions (catalyst, temperature, reaction time). The high temperature and the use of a commercial catalyst with HY zeolite give way to high reactivity. The HY zeolite catalyst (with a matrix containing mesopores and macropores) minimizes oxygenates diffusional restrictions. The presence of oxygenates in the blend (VGO and bio-oil) causes synergistic effects, such as an increase in dry gas yield (C_1-C_2), decrease in C_3-C_4 hydrocarbons[8,14,15] and a change in the gasoline composition (more aromatics and oxygenates). These synergies have been explained in the literature based on two phenomena: i) hydride transfer from hydrocarbons to oxygenates;[14,16,17] and ii) hydrocarbons preferential adsorption on the acid sites of the catalysts.[18,19] Many studies have shown that the co-feeding strategy increases coke yield, but Naik et al.[20] have reported that the cracking of different blends (VGO/acetic acid and VGO/guaiacol) under conditions of high H_2O yield causes a decrease in coke yield compared to VGO cracking. Agblevor et al.[15] observed small differences when bio-oil (15 wt%) was fed

together with VGO at 538 ºC into a fluidized bed reactor, with the more significant facts being a higher aromatic concentration in the product stream and the presence of oxygenates from the bio-oil.

Al-Sabawi et al.[8] attribute certain contradictory results obtained when oxygenates and bio-oil are cracked isolately and blended with VGO to the use of different experimental conditions, and this fact hinders the interpretation of product distribution results and the deactivation study. Bertero & Sedran[13] have obtained a higher hydrocarbon yield and lower coke yield when the bio-oil conditioned by thermal treatment was cracked. Thegarid et al.[21] studied the effect of bio-oil composition and analysed in detail the results obtained for the cracking of different mixtures of VGO and the bio-oil obtained by catalytic pyrolysis or once it has been subjected to hydroprocessing.

This paper deals with a study conducted on the synergy of raw bio-oil (20 wt%) and VGO (80 wt%) in the catalytic cracking. The co-feeding results involving conversion and product distribution have been compared with those for the cracking of individual feeds. The use of raw bio-oil avoids the costs associated with the catalyst in the pyrolysis step, in which the catalyst undergoes fast deactivation by coke,[22] and with an additional step of bio-oil hydroprocessing involving high pressure and considerable H_2 consumption.[21] In order to obtain results of industrial interest, runs have been performed in a riser simulator reactor under similar conditions (temperature, reaction time and catalyst/feed mass ratio) as in a FCC unit reactor and using a commercial FCC equilibrium catalyst. Moreover, the synergistic effects caused by the co-feeding have been assessed by comparing the results at the same conversion values within the range of interest in refineries.

2. Experimental

2.1. Feed properties

The feeds used are as follows: vacuum gasoil (VGO), raw bio-oil and a blend of bio-oil (20 wt%) and VGO (80 wt%). The VGO has been provided by Petronor S.A. (Somorrostro, Spain), whereas the raw bio-oil has been supplied by Ikerlan/IK-4 (Vitoria, Spain). The raw bio-oil has been obtained by fast pyrolysis of black poplar sawdust at 440-450 ºC in a 25 kg h^{-1} pilot plant provided with a conical spouted bed

reactor.[23] The feeds have been characterized by means of simulated distillation in a gas chromatograph with FID detector (Agilent 6890 Series GC System with a column Simdis D-2887 Fast/Ext.) and by elemental analysis (Leco TruSpec CHN Macro and additional module TruSpec S) to determine the contents of C, H, N and S, with the content of O been determined by difference. It should be noted that the content of N is insignificant in both the VGO and the bio-oil. The concentrations of the component families in the raw bio-oil have been determined by GC-MS (Shimadzu GC-MS QP2010, column of 50 m x 0.22 mm x 0.25 μm). The water content of the raw bio-oil (46.5 wt%) has been measured by Karl-Fisher method (Metrohm 830 KF Titrino plus). The properties of the feeds are detailed in Tables 1 and 2.

Table 1

Table 2

2.2. Catalyst

A commercial FCC equilibrium catalyst (used in refinery) containing 15 wt% of HY zeolite has been used. The properties of the catalyst (Table 3) have been determined by N_2 adsorption-desorption (Micromeritics ASAP 2010) and the crystal structure by X-ray diffraction (Phillips PW1710, using a radiation of Cu K_α). The acidity and acid strength have been obtained by the isothermal adsorption of NH_3 at 150 ºC. Subsequently, temperature programmed desorption (TPD) of absorbed NH3 has been carried out following a ramp of 5 ºC min^{-1} to 550 ºC (thermobalance, TA Instruments SDT 2960, on-line with a mass spectrometer, MS Thermostar Balzers Instruments). The Brönsted/Lewis ratio has been determined by FTIR spectrophotometry with adsorbed pyridine (Thermo Nicolet 6700).

Table 3

2.3. Reaction equipment and product analysis

The runs have been carried out in a riser simulator designed to operate on a laboratory scale under similar conditions to the FCC unit.[24] The reaction conditions were as follows: 500-560 ºC (the fluidized bed regime ensures isothermicity); reaction time, 3-10 s (once reaction time has elapsed the products are extracted by vacuum, avoiding side reactions); catalyst/feed mass ratio on a dry basis, 6 g_{cat} $(g_{feed})^{-1}$. The

- 4 -

product stream has been analyzed on-line with a gas chromatograph (Agilent Technologies 7890 A, with FID and PFPD detectors). The CO and CO_2 concentrations in the product stream have been quantified (off-line) by means of a gas micro chromatograph (Varian CP-4900). The products have been grouped into lumps: CO_2 and CO, dry gas (C_1-C_2), liquefied petroleum gases (LPG, C_3-C_4), gasoline (C_5-C_{12} and oxygenates in the same boiling point range), light cycle oil (LCO, C_{13}-C_{20}), heavy cycle oil (HCO, C_{20}^+) and coke. The amount of coke has been assessed by combustion in a thermobalance (TGA-Q 5000 de TA Instruments), with a heating rate of 3 ºC min^{-1} from 300 ºC to 550 ºC.

The conversion was calculated subtracting the yields of LCO, HCO and oxygenates from the initial amount of feed on a dry basis:

$$X = 100 - Y_{LCO} - Y_{HCO} - Y_{oxygenates} \tag{1}$$

where Y_{LCO}, Y_{HCO} and $Y_{oxygenates}$ are the yields (in wt %) of light cycle oil, heavy cycle oil and oxygenate compounds, respectively.

The yield of each lump was calculated by:

$$Y_i = \frac{m_i}{m_{feed}} 100 \tag{2}$$

where m_i and m_{feed} are the mass of lump i produced and the mass of the feed without water, respectively.

Similarly the liquid fuel yield was defines as:

$$Y_{liquid\ fuel} = \left(\frac{m_{liquid\ fuel}}{m_{feed}}\right) 100 \tag{3}$$

where $m_{liquid\ fuel}$ is the mass of liquid fuel (hydrocarbons C_5^+ and oxygenates in the same boiling point range).

The degree of deoxygenation has been determined from the O contents in the liquid product and the feed, as:

$$DOD = \left(1 - \frac{O_{in\ product}}{O_{in\ feed}}\right) 100 \tag{4}$$

3. Results

3.1. Conversion and product yields

Figure 1 shows the effect temperature and reaction time have on the conversion of the VGO and the blend. The blend conversions are higher than the VGO ones over the whole operating range. Furthermore, conversion increases as temperature is increased. It should be noted that under these conditions (standard in FCC) the reaction is fast and, although conversion increases as reaction time is increased, it has already reached a high value for a reaction time of 3 s. This result shows the advantage of using reaction equipment that allows operating with short reaction times, similar to those in the industrial operation, which allows assessing the effect of this variable.

Figure 1

The different reactivity of the blend (hydrocarbons from VGO and oxygenates from bio-oil) and the synergistic effect of the joint cracking contribute to the higher conversion of the VGO/bio-oil blend. The relevance of these factors is revealed by comparing (Figure 2) the evolution of product yields with conversion for the cracking of the VGO/bio-oil and the individual feeds. The use of conversion as variable allows monitoring the evolution of the results with the reaction extent. Although the results correspond to different temperatures, the range of this variable is narrow and a change in the cracking mechanism is not expected.

The yield of CO_2+CO (Figure 2a) is significant in the cracking of raw bio-oil and VGO/bio-oil blend, which is due to the enhancement of decarboxylation and decarbonylation reactions as temperature is increased (a high conversion in Figure 2a). The yield of CO_2+CO in the cracking of VGO/bio-oil blend is lower than expected for the blend composition (20 wt% bio-oil), given that it should be in the 2.5-3 wt% range when it is calculated as a contribution of the cracking of the individual feeds (VGO and bio-oil). This lower yield evidences that the cracking of the hydrocarbons in the VGO delays the decarboxylation and decarbonylation reactions of the oxygenates in the raw bio-oil. A fact contributing to this result is the different partial pressure of the components in the reaction medium depending on the feed to be cracked (mixture or individual feeds) and, specifically, the lower partial pressure of the bio-oil oxygenates when they are fed in the blend.

Figure 2

The dry gas yield is higher in the cracking of the raw bio-oil (Figure 2b) than in the cracking of the VGO and increases exponentially as conversion increases (temperature is also raised), which is due to the methane and ethane produced by the thermal cracking of oxygenates from the raw bio-oil. The value of dry gas yield for the blend is consistent with the one expected considering the cracking of the individual feeds.

The LPG yield for the cracking of both the blend and the VGO does not increase exponentially with temperature, which would be the case for a lump formed exclusively by primary cracking products, but rather linearly (Figure 2c), which is due to the cracking of heavy molecular weight components leading to the compounds in this lump, as well as those in the dry gas. The LPG yield in the cracking of the raw bio-oil is lower than in cracking of the VGO due to the instability of the light oxygenates in the raw bio-oil for the production of dry gas, CO_2 and CO. Figure 2c shows that the LPG yield in the cracking of the blend is higher than expected based on the cracking of the individual feeds of VGO and bio-oil. This result is consistent with the aforementioned ones; that is, the co-feeding strategy attenuates the formation of CO_2 and CO and selectively encourages the formation of the LPG lump.

The gasoline yield peaks (Figure 2d) and in the cracking of the raw bio-oil corresponds to a lower conversion (57 wt%) than in the cracking of the VGO (about 65 wt%) and the blend (60-65 wt%) because just above this value the overcracking of this fraction is promoted (cracking of heavy component), giving rise to the formation of CO_2, CO, dry gas and LPG. The higher gasoline yield in the cracking of VGO/bio-oil blend compared to VGO is a result of the contribution of unreacted oxygenates and hydrocarbons produced in the bio-oil transformation, specially the former.

The LCO yield (Figure 2e) also peaks for a conversion of 60-62 wt % for pure VGO and for a higher conversion (65-67 wt%) for VGO/bio-oil blend because just above this value the overcracking of this fraction to gasoline, LPG and dry gas is promoted rather than its formation from HCO. It is observed that the HCO lump yield (Figure 2f), which is only present in the case of VGO, decreases as the cracking advances, without synergistic effects when bio-oil is in the feed.

Figure 2g shows the evolution of coke yield with conversion in the cracking of the different feeds. The coke yield increases with conversion in the cracking of both VGO and VGO/bio-oil blend because under the conditions studied an increase in temperature and reaction time promotes mainly coke formation reactions by heavy volatile condensation rather than the cracking of these volatile compounds that are intermediates in coke formation. The highest yield of coke is obtained in the cracking of the raw bio-oil at conversions under 63 wt%, which is consistent with the well-known capacity for coke formation by the polymerization of the phenolic compounds in the bio-oil, i.e., lignin derivatives in the biomass.[25-28] Nevertheless, coke formation is attenuated by increasing conversion (increasing temperature) in the cracking of raw bio-oil because it promotes the cracking of intermediate oligomers rather than the condensation reactions of bio-oil compounds.[29,30]

The yield of coke in the cracking of VGO/bio-oil blend is lower than in the cracking of the individual feeds, which evidences a complex synergistic effect giving way to the attenuation of coke formation by the joint feed. This result has been explained based on two combined effects in the co-feeding strategy: i) the role of the water contained in the bio-oil by attenuating the rate of the condensation reactions involving the coke precursors in the VGO, which are mainly polyaromatic components from the HCO lump. It is well-established that H_2O competes with coke precursors in its adsorption on the catalyst acid sites, attenuating the condensation reactions;[25,31-33] and ii) the capacity for hydrogen transfer from the hydrocarbons in the VGO to the phenolic intermediates derived from the bio-oil, enabling a lower deposition of coke.[34-36] These hypotheses are in line with the coke analysis for the three feeds used in this study,[37] which evidences the different nature of the coke deposited on the catalyst in the cracking of VGO and bio-oil, and the relationship between the coke formation mechanisms from the two feeds. Furthermore, a good performance has been observed for the commercial FCC catalyst, which is designed with a hierarchical porous structure in order to minimize the effect the deposition of the coke derived from the bio-oil has on the deactivation because most of the coke is retained in the mesopores and macropores of the matrix, avoiding the blockage of the acid sites of the microporous HY zeolite crystals.[37]

Figure 3 compares the yields for different product lumps corresponding to the cracking of VGO/bio-oil blend and each of the individual feeds to assess quantitatively

the synergy when co-feeding. The results shown as an example correspond to 500 ºC and 6 s.

Figure 3

As observed, the dry gas, LPG, gasoline and LCO yields for the cracking of the blend are halfway between those corresponding to the individual feeds. Nevertheless, the yield of the dry gas is lower than that expected based on the blend concentration and ignoring the synergistic effects between the cracking mechanisms for the hydrocarbons in the VGO and oxygenates in the bio-oil. This result is consistent with the higher gasoline yield than expected for the blend cracking, as well as with the slightly higher LPG yield. Consequently, the co-feeding attenuates gasoline overcracking reactions and, to a lesser extent, the LPG cracking ones. The H_2O in the bio-oil contributes to this result by attenuating the cracking reactions.

It should be noted that the values for CO_2 and CO yield are much lower than expected, which evidences the attenuating effect of decarboxylation and decarbonylation reactions involving the oxygenates in the bio-oil. Moreover, as mentioned above, the coke yield is lower in the cracking of VGO/bio-oil blend than in the cracking of VGO and raw bio-oil isolately, which is due to the synergy between the coke formation mechanisms involving hydrocarbons and oxygenates. As a consequence of this synergistic effect, the coke yield is lower than expected, and therefore a higher residual catalyst activity is promoted. This higher activity contributes to a lower CO and CO_2 yield by hindering the thermal reactions (independent of catalyst deactivation state), such as decarboxylation and decarbonylation of the oxygenates in the bio-oil.

Apart from increasing the yield of gasoline, the co-feeding strategy modifies the component distribution in the lump. Figure 4 compares the yields of component families in the gasoline lump for the cracking of the mixture and individual feeds of VGO and bio-oil. The results show that oxygenates cracking in the blend (mainly ketones, carboxylic acids and phenols) is enhanced, and therefore their presence in the gasoline lump is lower than expected. Moreover, the yield of naphthenes, linear and branched paraffins and olefins is higher than expected, whereas the aromatics yield is similar.

The aforementioned results show that co-feeding promotes selective cracking of oxygenates in the gasoline to produce dry gas and LPG, attenuating the CO and CO_2

formation. The higher reactivity of oxygenates than VGO hydrocarbons under FCC conditions is consistent with the results by Doronin et al.[38] who conducted joint cracking of vegetal oil with VGO.

Figure 4

3.2. Product distributions

Given that this is a process with an industrial perspective, the cracking results should be compared for the same reaction extent (conversion).

3.2.1. Gases

Table 4 shows the yields of individual gaseous components obtained from the cracking of VGO and the blend for three conversion values (60, 65 and 70 wt%) at the standard operating range in FCC units. The gases in the cracking of VGO are hydrocarbons from C_1 to C_4 (dry gas and LPG lumps). LPG is main gaseous lump obtained from VGO cracking, with propylene being the main component for a conversion of 60 wt%. In the dry gas lump, ethylene is the main component. It is also observed that an increase in conversion (temperature and/or reaction time) gives way to an increase in the yield of both lumps (dry gas and LPG) due to the increase in the yield of all the olefins, whereas an increase in temperature lightly enhances propane yield, but hinders that of butenes. Therefore, the cracking of heavy molecular weight lumps is favored by increasing conversion. High conversions are associated with high temperatures (500-560 ºC range), which hinder hydride transfer reactions, and therefore the paraffin/olefin ratio in the product stream.

Table 4

In the cracking of the blend, the oxygenates in the bio-oil produce CO_2 and CO, whose yield values increase by increasing temperature, which in the case of CO_2 are 10 times higher than CO and increase to 1.76 wt% for 70 wt% conversion. There are no remarkable differences between the product yields obtained by cracking the VGO or the blend. The dry gas yield is higher and that of LPG lower in the cracking of the blend.

3.2.2. Liquid

As explained above when discussing the results in Figure 2d, the co-feeding of bio-oil has a remarkable synergistic effect (increases the gasoline yield). Table 5 sets out the yields of component families in the gasoline for the blend and the VGO at different conversions. The higher gasoline yield for the blend (Figure 2d) is explained by both the presence of oxygenates in the bio-oil and the slightly higher hydrocarbon yields. Moreover, this increase in the hydrocarbon yield is promoted by a remarkable synergistic effect. Thus, the presence of H_2O in the reaction medium and the different state of catalyst deactivation may play an opposite role in the cracking capacity of the catalyst. On the one hand, water attenuates the cracking reactions of the gasoline components to dry gas and LPG, such as side hydride transfer and condensation reactions to produce aromatics. On the other hand, the lower catalyst deactivation in the blend cracking will promote overcracking side reactions due to a higher number of active sites. Furthermore, the cracking of the components in the blend is conditioned by other specific factors involving the cracking of complex feeds like VGO, whose significance has been reported in the joint cracking of oxygenates and VGO.[14,16-19] Among these factors, the following are worth mentioning: i) hydride transfer from hydrocarbons to oxygenates; and ii) competitive adsorption of feed components on the catalyst acid sites.

Table 5

Based on the effects mentioned, the hydrocarbon fraction in the gasoline lump (Table 5) obtained from the cracking of the blend has a higher content of paraffins (linear and branched) than the gasoline from VGO cracking. The yields of aromatics and i-paraffins decrease by increasing conversion (Table 5), whereas the yields of olefins increase because hydride transfer reactions (reversible and exothermic) are greatly disfavored. Furthermore, an increase in conversion involves an increase in the olefin yield by β excision of side chains in the LCO and HCO fractions, which is reported in the literature for FCC[39,40] and clearly observed in Table 5 for conversions above 65 wt%.

The yield of oxygenates is small in the cracking of the blend and decreases as conversion is increased (2.1 wt% for 70 wt% conversion), which evidences that oxygenate conversion is significant. These oxygenates are carboxylic acids (mainly acetic acid), aldehydes, ketones and phenols (Table 5), whose low reactivity in the

cracking has been reported in literature.[9,13,41,42] The role of these compounds in the refinery gasoline pool may be a problem, but in this case the yield of phenol (remarkable polymerization capacity) is rather low.

The presence of unconverted oxygenate compounds in the gasoline lump is due to their low reactivity. Nevertheless, as shown in Table 6, the degree of deoxygenation of the bio-oil is very high, 95 wt% for 70 wt% conversion, which corresponds to an oxygen content of 0.08 by mass unit of carbon in the liquid fuel. Although the gasoline yield obtained by cracking the blend is higher than those obtained by cracking the individual feeds, the total liquid yield is lower than that obtained by VGO cracking, which is because the contents of HCO (absent in bio-oil) and LCO are lower in the blend.

Table 6

Furthermore, the presence de water in the liquid fuel should be noted, whose content is enhanced by the fast dehydration of the oxygenates in the bio-oil. Water yield increases by increasing conversion, until 2.5 wt% for 70 wt% conversion. Consequently, the liquid fuel described in Tables 5 and 6 without considering water is in fact a mixture of hydrocarbons, oxygenates and water, with the content of the latter being 12 wt% (from the raw bio-oil and formed by dehydration reactions). The water content in the product stream should not be a problem because the VGO is injected in the FCC unit together with steam in order to favor the vaporization of the reactants. Furthermore, steam is also injected in the stripping to remove the coke volatile compounds adsorbed on the catalyst and thus control coke combustion in the regeneration section.

4. Conclusions

A comparison of the results for the cracking of the blend (20 wt% raw bio-oil and 80 wt% VGO) with those for the cracking of the individual feeds of VGO and bio-oil for the same conversion values evidences the existence of a relationship between the mechanisms for the cracking of the hydrocarbons in the VGO and oxygenates in the bio-oil. This interaction has great impact on the yields and lump concentrations. A favorable synergistic effect is observed on the LPG and gasoline yields (higher values than expected in the absence of synergy), and the formation of CO_2 and CO is lowered.

Moreover, co-feeding prevents coke formation, which lowers catalytic deactivation, and therefore selectively promotes the catalytic cracking reactions instead of the thermal ones of decarboxylation and decarbonylation.

In order to explain these synergies between the cracking mechanisms, the significance of different factors should be considered, i.e., the competitive adsorption of hydrocarbons and oxygenates in the feed and the role of H_2O on the selectivity of the cracking reactions.

The cracking of a mixture of 20 wt% raw bio-oil with 80 wt% VGO (under FCC conditions) is effective for achieving a high degree of deoxygenation, 95 wt% at 70 wt% conversion, which corresponds to an oxygen mass fraction in the liquid fuel of 0.08 by mass unit of carbon. In addition, the synergy promoted by co-feeding disfavors the presence of oxygenates in the gasoline lump (mainly ketones, carboxylic acids and phenols). Furthermore, co-feeding gives way to a higher yield of naphthenes, linear and branched paraffins and olefins, with the aromatic one being similar to the value expected in the absence of synergy.

Acknowledgements

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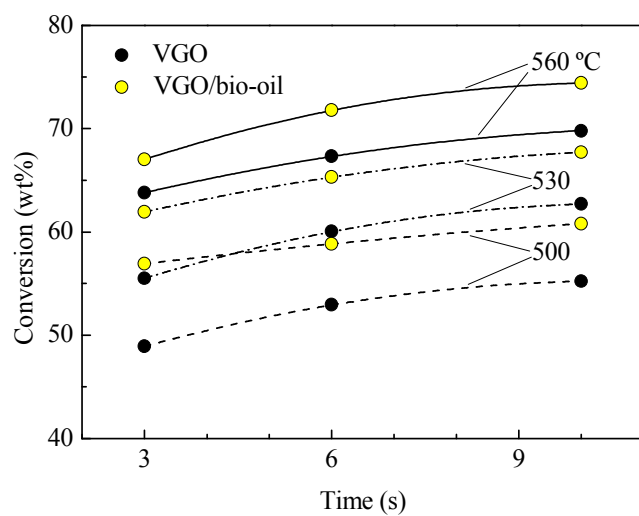
Figure 1.
Evolution of the conversion with the reaction time in the catalytic cracking of VGO and
VGO/bio-oil (20 wt% in bio-oil) at different temperatures.
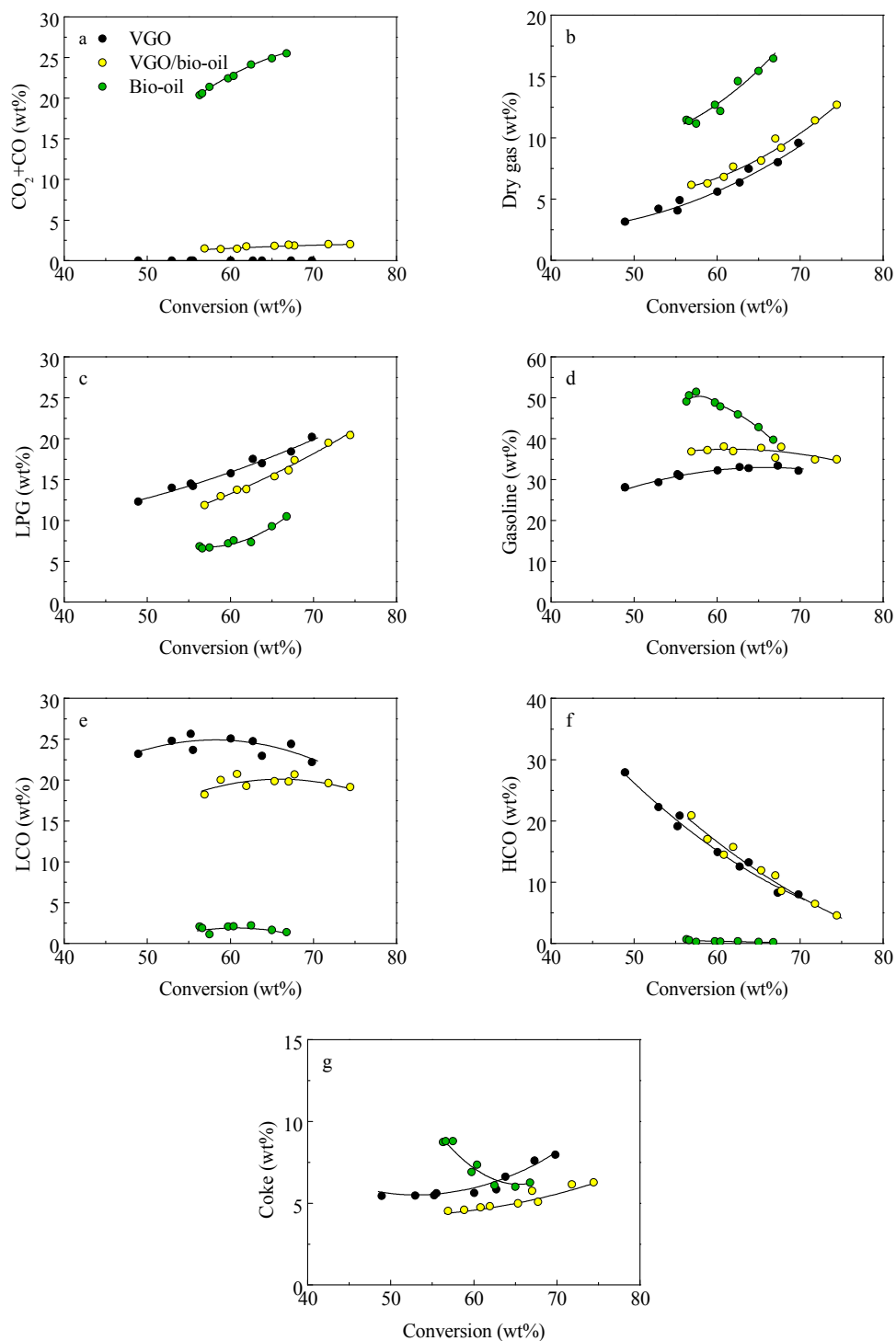
Figure 2.
Evolution of product yields with conversion in the catalytic cracking of VGO, bio-oil and VGO/bio-oil (20 wt% in bio-oil).
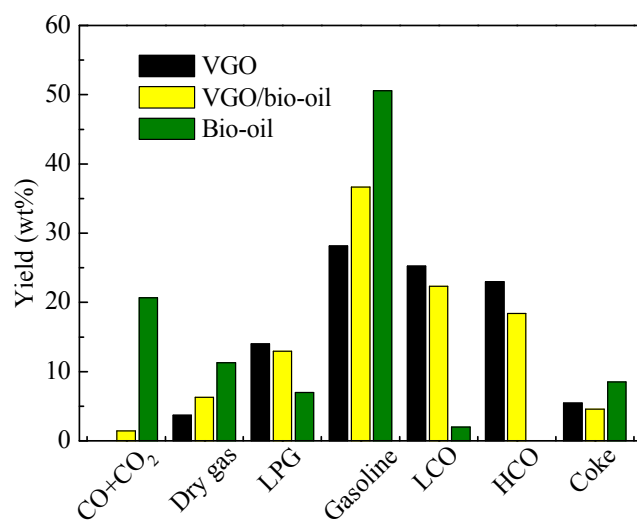
Figure 3.

Comparison of product fractions yields in the cracking of the feeds (VGO, bio-oil and VGO-bio-oil with 20 wt% bio-oil) at 500 ºC and 6 s.
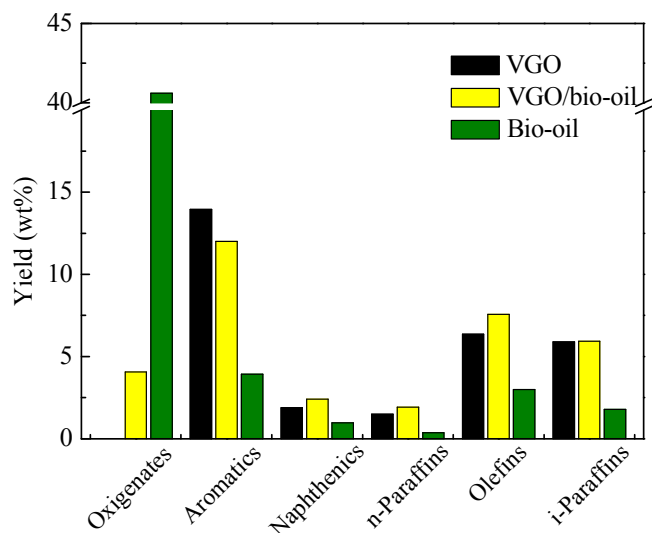
Figure 4.
Comparison of gasoline fraction yields in the cracking of the feeds (VGO, bio-oil and
VGO-bio-oil with 20 wt% bio-oil) at 500 ºC and 6 s.

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Table 1.
Composition of the raw bio-oil.

Elemental composition (wt%)	
C	55.1
H	6.3
S	-
O	38.6
Water content (wt%)	**46.5**
Composition (wt%)	
Acids and esters	21.6
Acetic acid	15.5
Aldehydes	19.4
Hydroxy-acetaldehyde	7.8
Ketones	16.3
1-Hydroxy-2-propanone	6.5
Phenols	5.1
Alcohols	9.7
Ethers	2.8
Sugars	24.1
Levoglucosan	21.6
Non identified	1.0
Simulated Distillation (ºC), D-2887	
Initial boiling point	35
5 wt%	55
25 wt%	74
50 wt%	154
90 wt%	263
Final boiling point	335

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Table 2.

Composition of the vacuum gasoil (VGO).

Density (g cm^{-3})	0.918
Average molecular weight (g mol^{-1})	370.3
Elemental composition (wt %)	
C	85.4
H	11.8
S	2.5
O	-
Composition (wt %)	
Aliphatics	47.2
Aromatics	43.1
Sulfur compounds	9.7
Simulated Distillation (ºC), D-2887	
Initial boiling point	184
5 wt %	367
25 wt %	432
50 wt %	474
90 wt %	533
Final boiling point	614

Table 3.

Properties of the commercial equilibrated catalyst.

Physical properties	
S_{BET} (m^2 g^{-1})	122
V_p (cm^3 g^{-1})	0.15
$d_{p\ mesopores}$ (Å)	117.3
Unit cell size (Å)	24.3
Acid properties	
Zeolite percentage (wt %)	15
Total acidity (μmol g^{-1})	30
Average acid strength (kJ mol^{-1})	100
Brönsted/Lewis (mol mol^{-1})	0.75

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Table 4.

Distribution of the gaseous products (wt%) in the cracking of VGO and VGO-bio-oil (20 wt% bio-oil) at the same conversion: 60, 65 and 70 wt%.

Feed	VGO			VGO-bio-oil		
Conversion (wt%)	60	65	70	60	65	70
CO_2+CO	-	-	-	1.54	1.75	1.90
CO_2	-	-	-	1.38	1.57	1.76
CO	-	-	-	0.15	0.18	0.15
Dry gas	5.62	7.30	9.33	6.71	8.25	10.35
C_1	1.81	2.02	2.59	2.56	2.79	3.12
C_2	0.98	1.26	1.88	1.52	1.85	2.51
Ethylene	2.83	4.02	4.86	2.63	3.61	4.72
LPG	15.89	17.78	19.90	13.25	15.55	18.17
C_3	1.90	2.34	2.64	1.66	1.98	2.64
Propylene	6.28	7.89	8.12	5.06	6.59	6.95
C_4 paraffins	4.16	2.64	2.86	2.53	2.45	3.10
C_4 olefins	3.54	4.91	6.28	4.01	4.53	5.47

Table 5.

Distribution of the gasoline fraction (wt %) in the cracking of VGO and VGO-bio-oil (20 wt% bio-oil) at the same conversion: 60, 65 and 70 wt%.

Feed	VGO			VGO-Bio-oil		
Conversion (wt %)	60	65	70	60	65	70
Oxygenates						
Carboxylic acids	-	-	-	**0.56**	**0.51**	**0.40**
acetic acid				0.30	0.42	0.27
Aldehydes	-	-	-	**1.28**	**0.67**	**0.58**
acetaldehyde				0.36	0.18	0.05
Ketones	-	-	-	**1.04**	**1.10**	**0.33**
acetone				0.20	0.14	0.11
Phenols	-	-	-	**0.82**	**0.44**	**0.54**
Others	-	-	-	**0.26**	**0.18**	**0.25**
Hydrocarbons						
Aromatics	**11.7**	**11.5**	**10.8**	**11.8**	**11.3**	**10.4**
C_6	0.86	0.99	0.98	0.62	0.57	0.74
C_7	2.22	2.26	2.23	1.61	1.87	2.00
C_8	3.01	3.00	2.80	3.20	3.10	3.09
C_9	2.26	1.95	1.76	3.09	2.88	2.02
C_{10}-C_{11}	3.34	3.28	3.04	3.32	2.92	2.56
Naphthenics	**2.2**	**2.5**	**2.8**	**2.4**	**2.6**	**2.6**
n-paraffins	**1.3**	**1.2**	**1.2**	**1.8**	**1.7**	**1.7**
C_5	0.34	0.29	0.27	0.37	0.35	0.35
C_6	0.18	0.17	0.16	0.33	0.26	0.22
C_7	0.14	0.14	0.13	0.17	0.19	0.14
C_8	0.11	0.12	0.12	0.22	0.20	0.14
C_9	0.10	0.08	0.08	0.14	0.12	0.12
C_{10}	0.12	0.12	0.12	0.14	0.17	0.15
C_{11}-C_{12}	0.31	0.34	0.35	0.40	0.41	0.56
Olefins	**8.5**	**10.1**	**11.3**	**8.5**	**10.3**	**11.4**
C_5	3.10	3.45	4.03	3.26	3.88	4.16
C_6	2.31	2.82	3.16	2.68	3.07	3.37
C_7	1.33	1.68	1.72	1.23	1.43	1.65
C_8	0.80	1.00	1.09	0.71	0.95	1.11
C_9	0.25	0.31	0.29	0.10	0.17	0.18
C_{10}	0.72	0.85	1.01	0.56	0.84	0.96
i-paraffins	**5.4**	**4.3**	**2.8**	**5.9**	**4.8**	**3.4**
C_5	2.95	1.93	1.30	2.99	2.52	1.93
C_6	1.17	0.72	0.45	1.51	1.03	0.67
C_7	0.66	0.80	0.34	0.78	0.62	0.33
C_8	0.33	0.43	0.40	0.34	0.39	0.37
C_9	0.14	0.20	0.14	0.06	0.07	0.00
C_{10}	0.11	0.08	0.07	0.12	0.11	0.07
C_{11}	0.08	0.10	0.09	0.07	0.09	0.08

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Table 6.

Parameters in the cracking of VGO and VGO-bio-oil (20 wt% bio-oil) at the same conversion: 60, 65 and 70 wt%.

Feed	VGO			VGO-Bio-oil		
Conversion (wt %)	60	65	70	60	65	70
DOD (wt %)	-	-	-	91.3	93.0	95.0
$Y_{liquid\ fuel}$ (wt %)	72.3	68.0	62.7	62.0	58.1	52.8
Ox./C ($g_{Ox.}$ $(g_C)^{-1}$)	0	0	0	0.10	0.09	0.08
Water produced (wt %)	-	-	-	2.3	2.3	2.5

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GRAPHICAL ABSTRACT