



## Full Length Article

## Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production



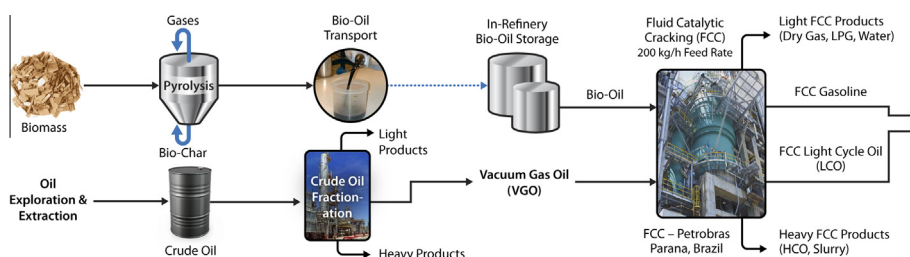
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Raw bio-oil produced from fast pyrolysis of pine woodchips was co-processed with standard Brazilian vacuum gasoil (VGO) and tested in a 200 kg·h<sup>-1</sup> fluid catalytic cracking (FCC) demonstration-scale unit using a commercial FCC equilibrium catalyst. Two different bio-oil/VGO weight ratios were used: 5/95 and 10/90.

Co-processing of raw bio-oil in FCC was shown to be technically feasible. Bio-oil could be directly co-processed with a regular gasoil FCC feed up to 10 wt%. The bio-oil and the conventional gasoil were cracked into valuable liquid products such as gasoline and diesel range products.

Most of the oxygen present in the bio-oil was eliminated as water and carbon monoxide as these yields were always higher than that of carbon dioxide. Product quality analysis shows that trace oxygenates, primarily alkyl phenols, in FCC gasoline and diesel products are present with or without co-processing oxygenated intermediates. The oxygenate concentrations increase with co-processing, but have not resulted in increased concerns with quality of fuel properties.

The presence of renewable carbon was confirmed in gasoline and diesel cuts through <sup>14</sup>C isotopic analysis, showing that renewable carbon is not only being converted into coke, CO, and CO<sub>2</sub>, but also into valuable refining liquid products. Thus, gasoline and diesel could be produced from lignocellulosic raw materials through a conventional refining scheme, which uses the catalytic cracking process. The bio-oil renewable carbon conversion into liquid products (carbon efficiency) was approximately 30%, well above the efficiency found in literature for FCC bio-oil upgrading.

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## 1. Introduction

The fast pyrolysis of lignocellulosic biomass has been gaining relevance in recent years due to its ability to convert raw lignocellulosic biomass into a liquid product, frequently referred to as bio-oil [1]. The use of lignocellulosic materials and processing residues, such as wood processing residues, corn cobs, and sugarcane bagasse, has the advantage of decreasing impacts on food security, because they are not used for human consumption. Additionally, agriculture and forest products economics may improve by using some of these residues, as is the case of pellet fuel market development for the power and heating markets [2].

Fluid catalytic cracking (FCC) is one of the main processes in a petroleum refinery and used worldwide to convert heavy petroleum molecules into valuable products such as gasoline, liquefied petroleum gas or LPG (propyl and butyl products), and light cycle oil or LCO (diesel range product). Finished cracked naphtha produced from the FCC is usually the predominant blendstock in the gasoline pool in most of the refineries in Brazil and the U.S. The use of the FCC units for direct introduction of raw bio-oils, the product of the fast pyrolysis of biomass, has many challenges and limitations reported in the literature, often from small-scale experimentation [3–5]. Bio-oil characteristics, such as low miscibility with hydrocarbons, high acidity [6], high tendency to form coke and poor chemical stability are commonly cited as limitations or even as impediments for its direct use. In one reported example of 3/97 weight ratios of pine bio-oil and vacuum gasoil (VGO) co-processing in a continuous reactor FCC pilot unit, more coke and less gasoline were observed along with production of CO and CO<sub>2</sub>. In this reference, coking and plugging of the feed nozzle was observed [7]. Many researchers concluded that a previous hydrodeoxygenating (HDO) step was necessary to make drop in fuels [8–11] for the current petroleum fuels infrastructure. Multiple technologies are under development to reduce the oxygen content of pyrolysis oils and measuring fuel properties to indicate desirable compositions [12,13].

On the other hand, many tests carried out at FCC lab-scale units with heavy fossil feeds showed that their results do not necessarily reflect behavior obtained at larger scales, especially with respect to coke formation tendency. Coke results obtained in circulating FCC

pilot risers are frequently lower than those observed at lab scales [14].

The use of even larger scales offers additional advantages to better understand bio-oil co-processing. The Petrobras demonstration unit in São Mateus do Sul (State of Paraná, Brazil) has been used intensively for many years to develop its FCC technology. Among its features is the possibility of using one or more multiple feed nozzle injection points positioned along the riser reactor. Therefore, bio-oil and the fossil FCC streams are segregated, dispensing the use of any dispersant agent, and can be introduced separately into the riser reactor.

Fig. 1 shows a possible refining scheme using the FCC process. The bio-oil is directly fed into the FCC unit, without any kind of previous hydroprocessing. The naphtha and LCO produced by the FCC are hydrotreated to remove sulfur, as required to comply with fuels specifications.

In a previous study, it was shown that a bio-oil from pine woodchips, produced in a biomass pyrolysis pilot-scale unit, could be co-processed along with a Brazilian VGO with drastically reduced impacts on coke yield, even when 20 wt.% of bio-oil was used. Moreover, the impacts on coke with 10 wt.% of bio-oil were negligible and feed nozzle or feed line plugging were not observed at demonstration scale [15,16].

In the present work, we co-processed raw bio-oils from pine woodchips from a commercial producer with a standard Brazilian VGO and tested in a 200 kg·h<sup>-1</sup> FCC demonstration-scale unit using a commercial FCC equilibrium catalyst. Two different bio-oil/VGO weight ratios were used - 5/95 and 10/90 - running at a reaction temperature of 540 °C and other conventional operating FCC conditions. Given the current commercial supply of bio-oil relative to the supply of petroleum, a feed addition rate of up to 5/95 bio-oil to VGO is considered to be a reasonable starting point for a typical commercial FCC unit. We investigated the influence on conversion and product yields, such as gasoline. We also conducted a longer test run at 5% bio-oil (uninterrupted for 70 h). The liquid effluent was then distilled to produce 400 gallons of gasoline and 400 gallons of diesel materials for subsequent hydrotreating and studies of the quality of the co-processed biofuels produced using this route. The co-processing of raw pine bio-oil in the FCC unit operating at 200 kg·h<sup>-1</sup> flow rate with vacuum gas oil and 5 or

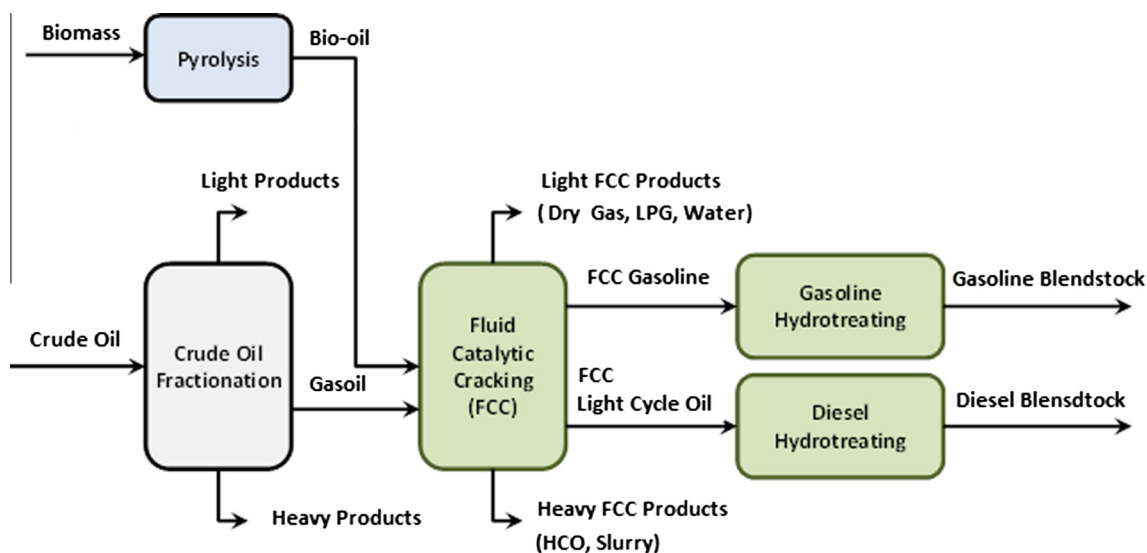


Fig. 1. Refining scheme. Bio-oil is directly co-fed into the FCC unit with VGO. Naphtha (gasoline range cut) and LCO (diesel range cut) are hydrotreated to remove sulfur and comply with fuels specifications.

**Table 1**  
FCC equilibrium catalyst properties.

Physical properties	CAT1	CAT2
Collected in	11/27/12	04/15/13
Surface area (m <sup>2</sup> /g)	155	158
Mesopore area (m <sup>2</sup> /g)	53	61
Micropore volume (m <sup>2</sup> /g)	0.048	0.045
X-ray diffraction (%)	18.7	17.4
<i>Chemical analysis</i>		
Al <sub>2</sub> O <sub>3</sub> (wt.%)	44.9	45.1
Na <sub>2</sub> O (wt.%)	0.33	0.29
RE <sub>2</sub> O <sub>3</sub> (wt.%) <sup>a</sup>	1.9	2.2
V (mg/kg)	1047	899
Ni (mg/kg)	1560	1705

<sup>a</sup> Sum of rare earth elements.

10 wt.% bio-oil reached a cumulative operation time of 400 h over nearly 18 months.

## 2. Experimental

### 2.1. Materials

The catalyst used in this study was a commercial FCC equilibrium catalyst produced by FCC S.A. (Rio de Janeiro, Brazil) and collected in an industrial FCC unit located in one of the Petrobras refineries. Table 1 shows the physicochemical characteristics of two equilibrium catalyst samples of the same product (grade) collected in different days, CAT1 and CAT2.

A commercial bio-oil, produced in March 2013 from pine woodchips in a fast pyrolysis commercial RTP<sup>TM</sup> unit, was provided by Ensyn Corp. (Canada) and used as feedstock in the experiments described in this paper. Ensyn Corp. already supplies pyrolysis oil liquid biofuels for heating and boiler applications [17]. For these applications in the U.S., biomass pyrolysis oil fuels need to conform to ASTM D7544-10 developed through the International Energy Agency Bioenergy Pyrolysis Task #34 [18,19]. The bio-oil characterisation is reported in Table 2. Properties are similar to those found in literature for low and very low solids bio-oils [20–22].

A typical Brazilian vacuum gasoil (VGO) commercially processed in Petrobras FCC units was used as reference feed (Table 3).

**Table 2**  
Pine bio-oil properties.

Density (g/cm <sup>3</sup> , 20 °C)	1.204
Sulfur (wt.%)	<0.3
Flash point (°C)	63.5
<i>Elemental analysis (wt.%) – wet as received</i>	
Carbon	41.8
Hydrogen	7.5
Oxygen (by difference)	50.7
Acidity (mg/KOH g)	128
Ash (wt.%)	0.17
<i>Metals (mg/kg)</i>	
Na	4.8
K	160
Mg	130
Ca	400
Si	23
Fe	31
Mn	33
Cr	<0.5
Solids (wt.%)	0.006
Water (wt.%)	31.9
Viscosity at 60 °C (mm <sup>2</sup> /s)	6.7

**Table 3**  
Reference feed (VGO) properties.

	VGO
Density (g/cm <sup>3</sup> , 20 °C)	0.9362–0.9374
Sulfur, wt.%	0.59–0.67
Total nitrogen, wt.%	0.33–0.34
Basic nitrogen, mg/kg	1194–1260
Aniline point, °C	74.7–76.0
Ramsbottom carbon residue, wt.%	1.19–1.49
<i>Simulated distillation (mass recovery:°C)</i>	
Initial	199.0–206.4
10%	331.2–330.2
30%	402.0–403.0
50%	443.4–444.4
70%	486.2–490.4
90%	563.8–567.6
Final	715.0–737.8

### 2.2. Set-up

The work was conducted in two test series between December 2013 and December 2014:

- Test series 1 (December 2013/January 2014): 18 tests with a 3-h run length and an additional test, with 5% bio-oil, using a longer run length (70 h), was performed to produce a large batch of liquid effluent. Afterwards, this liquid effluent was distilled to obtain gasoline (naphtha), diesel (LCO), and bottoms cuts. The pine woodchip bio-oil (9-months-old) was co-processed with the VGO reference feed using catalyst CAT1.
- Test series 2 (November/December 2014): 16 tests performed with a 2-h run length. The pine woodchip bio-oil (21-months-old) was co-processed with the VGO reference feed (see Table 3) using catalyst CAT2.

The demonstration-scale FCC unit is equipped with a pseudo-adiabatic riser reactor and a continuous catalyst regenerator, operating under steady state conditions (Fig. 2). The catalyst inventory is 450 kg. The total feed rate was controlled at 200 kg·h<sup>-1</sup>. The catalyst circulation rate may be adjusted by changing the feed pre-heater temperature to achieve the set reactor outlet temperature (reaction temperature), i.e., changing feed temperature will result in a change in catalyst circulation to maintain reactor outlet temperature.

Two different bio-oil/VGO weight ratios were used: 5/95 and 10/90. Bio-oil and regular petroleum streams are totally immiscible due to the high polarity of the bio-oil. Therefore, bio-oil and VGO were introduced at two different axial positions in the FCC riser reactor, which consists of an 18-meter-high cylindrical tube. The bio-oil cannot be heated above 50 °C because its heating accelerates polymerisation reactions and coke formation, which cause feed line obstruction [20,21]. Therefore, the main feed (VGO) and the bio-oil were injected into the riser reactor at two different axial positions as described in previous studies [15,16]. The bio-oil feed temperature was kept around 30 °C in all experiments, while the VGO temperatures were kept between 220 °C and 320 °C. For the pure VGO experiments, feed was divided between the two feed nozzle levels. Thus, the introduction of the bio-oil through a separate feed nozzle below the VGO feed line permits the heating of the VGO up to 320 °C, as carried out in regular FCC commercial operations. The heating of the fossil feed decreases its viscosity and improves the feed dispersion.

The experiments were carried out at a reaction temperature of 540 °C and the total reactor pressure was maintained at 2.7 bar. The regenerated catalyst temperature was kept at 690 °C. These operating conditions are adequate, and currently used, to process the Brazilian VGO reference feed in FCC commercial units.

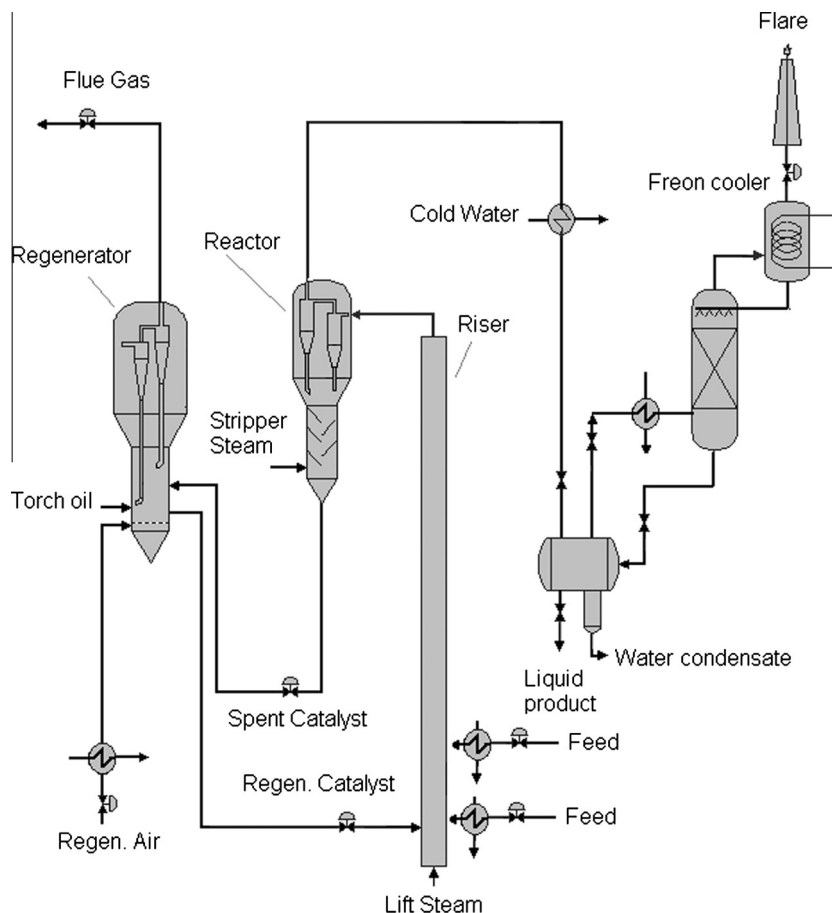


Fig. 2. FCC demonstration-scale schematic drawing. Total feed rate (renewable and fossil) controlled at  $200 \text{ kg} \cdot \text{h}^{-1}$ .

Catalyst-to-oil ratio (CTO) was calculated by dividing the coke yield by the difference between the coke in the spent catalyst and the coke in the regenerated catalyst. A correction factor is applied to take into account the light hydrocarbons lost from the spent catalyst when it is collected from the stripper.

### 2.3. Analysis

Coke-free product yields were calculated and normalised (i.e., the coke yield was excluded from the normalisation) into main groups defined as: dry gas (C1, C2 hydrocarbons, and hydrogen), liquefied petroleum gas (LPG: C3 and C4 hydrocarbons), gasoline (C5–220 °C boiling point), light cycle oil (LCO: 220–343 °C boiling point), bottoms (boiling point above 343 °C), coke, carbon monoxide, carbon dioxide, and water. The yield of each fraction is given by

$$\text{Yield of fraction } i \text{ (\%)} = \frac{\text{mass of fraction } i}{\text{total mass in the feed}} \times 100 \quad (1)$$

The coke yield was calculated from the flue gas (produced in the regenerator from the combustion of the coke deposited on the catalyst) mass flow rate and the chromatographic composition of its constituents.

Gaseous products collected in gasbags during the experiments were analysed by using an Agilent 7890 micro gas chromatography unit equipped with three columns, two thermal conductivity detectors, and one flame ionisation detector.

The water was calculated from the difference between the total water added into the unit (catalyst lifting, feed dispersion, catalyst stripping, and the catalyst separation device) and the water collected at the end of each experiment.

The conversion is defined as the sum of the dry gas, LPG, gasoline, coke, carbon monoxide, carbon dioxide, and water, i.e.,  $100 - \text{LCO (wt.\%)} - \text{bottoms (wt.\%)}$ .

Liquid samples were collected and analysed by simulated distillation (ASTM D2887) according to their boiling point range.

The liquid effluents were submitted to a gas chromatography – flame ionisation detector (paraffins, isoparaffins, aromatics, naphthenes, and olefins - PIANO) in order to obtain a detailed characterisation of the gasoline fraction composition in terms of n-paraffins, i-paraffins, aromatics, naphthenes, i-olefins and n-olefins up to a boiling range of 220 °C. An Agilent 6890 N gas chromatograph was used with a HP PONA methyl silicone column and a flame ionisation detector. The water content in the liquids was measured using the volumetric Karl Fischer method.

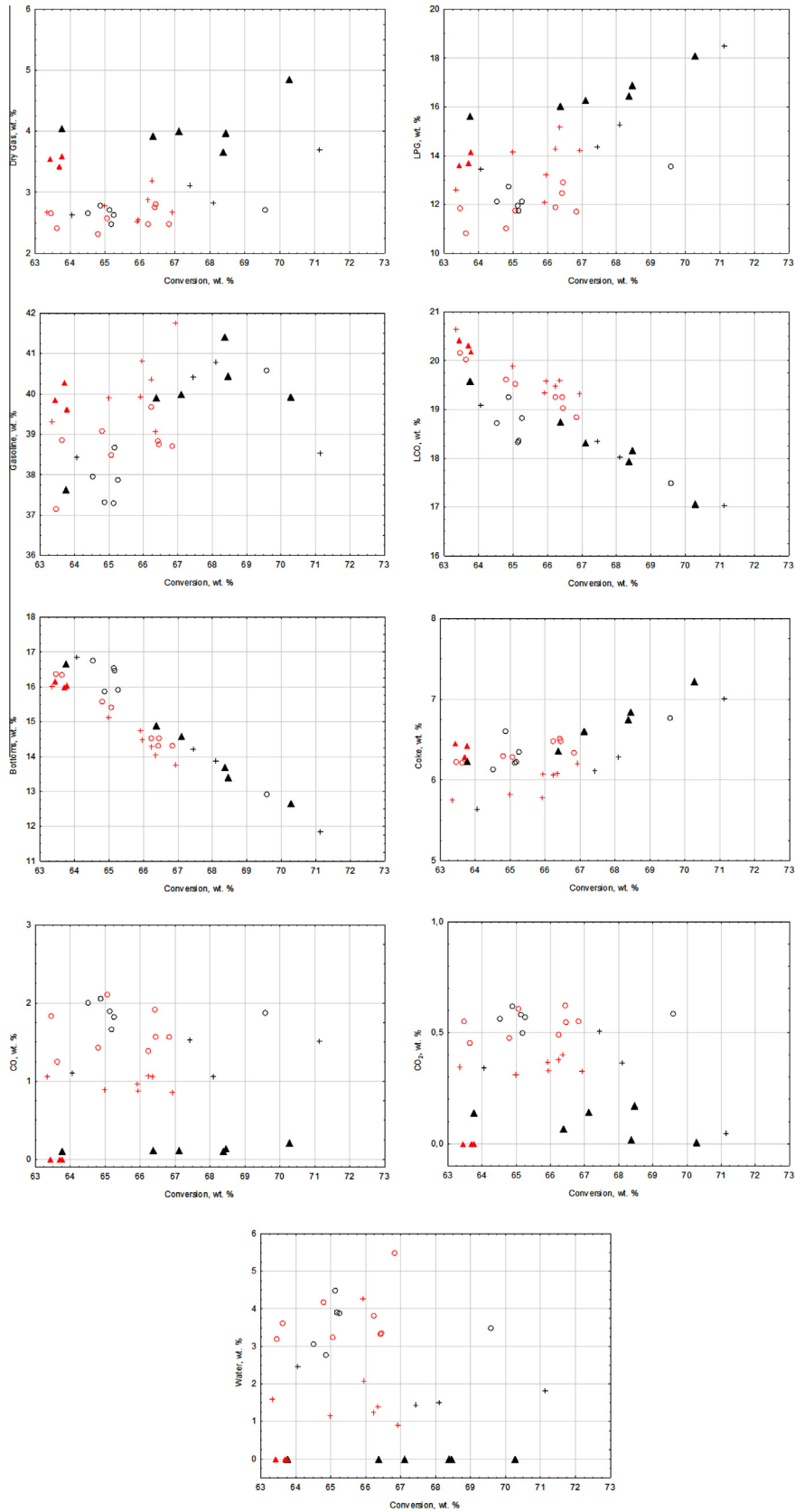
The  $^{14}\text{C}$  (renewable carbon) concentrations in the gasoline and LCO fractions were determined by accelerator mass spectrometry (AMS) combined with isotope ratio mass spectrometry using the ASTM D6866-12 method at Beta Analytic Inc. laboratories in Miami, Florida, USA.

The liquid effluents were also analysed using an adapted UV technique from UOP (UOP 262-59) to measure the phenolic content of different distillation cuts.

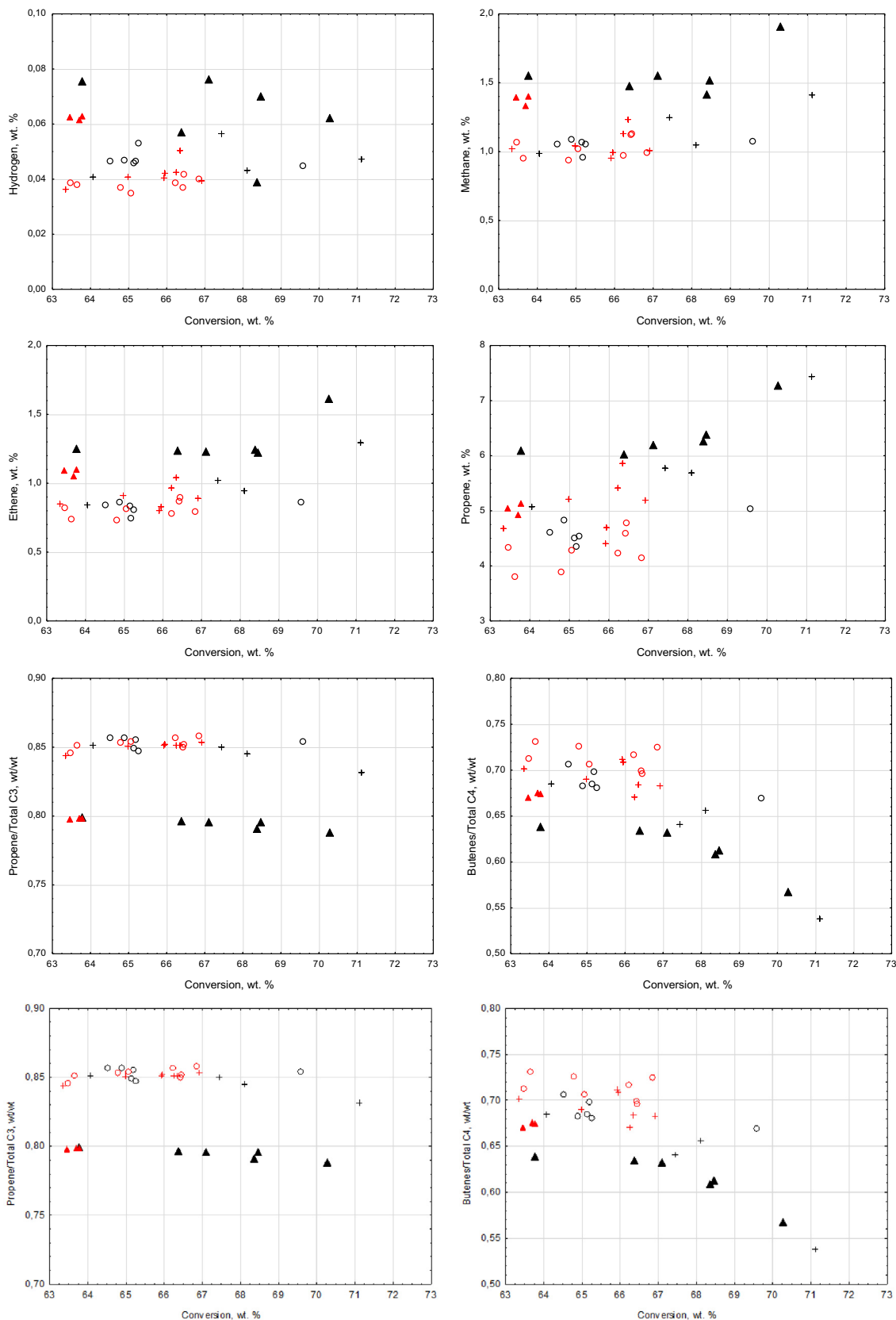
Further chemical information on the gasoline samples was obtained by ion chromatography to identify and quantify phenolic compounds present compared to just those present in the VGO only processing.

### 3. Results

A set of graphs (Figs. 3 and 4) includes 34 experiments and shows the product yields as a function of the conversion extent.



**Fig. 3.** Effect of the feed on the yields at different conversion levels: VGO cracking 1<sup>st</sup> test series (▲), VGO/Bio-oil cracking 95/5 1<sup>st</sup> test series (+), VGO/Bio-oil 90/10 1<sup>st</sup> test series (○), VGO cracking 2<sup>nd</sup> test series (▲), VGO/Bio-oil cracking 95/5 2<sup>nd</sup> test series (+), VGO/Bio-oil 90/10 2<sup>nd</sup> test series (○).



**Fig. 4.** Gas phase yields at different conversion levels: VGO cracking 1<sup>st</sup> test series (▲), VGO/Bio-oil cracking 95/5 1<sup>st</sup> test series (+), VGO/Bio-oil 90/10 1<sup>st</sup> test series (○), VGO cracking 2<sup>nd</sup> test series (▲), VGO/Bio-oil cracking 95/5 2<sup>nd</sup> test series (+), VGO/Bio-oil 90/10 2<sup>nd</sup> test series (○).



Both test series were included: the first one, carried out in December 2013/January 2014 with 18 experiments, and the second in November/December 2014 with 16 experiments. Although test sequences in 2014 were performed with similar VGO feeds and FCC equilibrium catalysts, in the second experimental test series the bio-oil had aged an additional 10 months by the time it was used. Fig. 3 shows the main group of products, dry gas, LPG, gasoline, LCO, bottoms, coke, carbon monoxide, carbon dioxide and water. These yields add up 100% (in weight). Four other products of interest, such as hydrogen, methane, propene, and ethene, can be found in Fig. 4. Co-processing tests with 5% and 10% of bio-oil were carried out in alternate times. The mass balance closure was between 96 wt.% and 100 wt.%.

Despite the different bio-oil ages, the resulting product yields were again very similar to those found in other studies with bio-oil from pine woodchips [15,16]. Although the cracking of pure VGO does not produce any CO, CO<sub>2</sub>, or water, some CO and CO<sub>2</sub> formed in the regenerator could be observed in the products due to their entrainment in the regenerated catalyst. Catalytic cracking has shown a great ability to remove O-compounds from the bio-oil and primarily convert them into water, followed by CO and then by CO<sub>2</sub>, indicating a predominance of dehydration reactions due to the FCC catalyst acidity (Fig. 3).

CO formation prevailed over CO<sub>2</sub> in the co-processing of bio-oil, indicating the predominance of decarbonylation reactions over decarboxylation. In other studies in literature performed using hydrodeoxygenated bio-oil or catalytic pyrolysis oil [8,23] at laboratory scale, the CO<sub>2</sub> yields are higher than CO yields. On the other hand, a previous study using this same experimental FCC unit obtained the same proportion of oxygenated products, i.e., prevalence of decarbonylation reaction over decarboxylation [16].

A clear decrease in the dry gas yields was obtained when bio-oil was processed. Hydrogen, methane, and ethene yield decreased significantly (Fig. 4), which compensates, to some extent, for the higher CO and CO<sub>2</sub> yields. Likewise, there is some decrease in LPG yields. The C3 and C4 olefinicity increased. According to Corma et al., complex reaction pathways are involved in the catalytic cracking of biomass. Olefins and paraffins present in the gas-phase are formed by three main catalytic pathways: dehydration reactions, hydrogen-producing reactions, and hydrogen-consuming reactions [24]. The higher C3 and C4 olefinicity would be the consequence of the predominance of hydrogen-consuming over hydrogen-producing reactions and bio-oil H-deficiency.

The decrease in the hydrogen, dry gas (except CO and CO<sub>2</sub>), and LPG may preserve or slightly decrease the wet gas compressor feed rate, i.e., the net effect would be a similar gas feed rate to the FCC wet gas compressor.

In the first test series, the gasoline overcracking (maximum of gasoline) was not reached for the pure VGO processing and the gasoline yield for 5% bio-oil was practically the same as was obtained with VGO, while some decrease was observed at 10 wt.%. However, in the second test series, the gasoline overcracking region was reached for all feeds, including the VGO. Gasoline yield was maximized at a conversion between 68 wt.% and 69 wt.%, and these maximum values were approximately the same (Fig. 3) for all the feeds studied. Likewise, LCO yields, which were the same level for pure VGO and 5%, slightly decreased at 10% bio-oil. On the other hand, bottoms yields increased slightly when 5% or 10% bio-oil was added to the feed (Fig. 3).

In both sequences, separated by a period of 10 months, a clear drop in coke yield was observed at 5 wt.% bio-oil when compared with pure VGO and it increased back again to the level obtained with pure VGO when 10% of bio-oil was added to the feed. It is probable that, at 5% of bio-oil, dilution effects caused by the presence of water and oxygen in the bio-oil prevail over its pronounced coke formation tendency. At a 10% bio-oil level, the more pro-

nounced bio-oil trend to promote coke formation caused the return to the coke level originally obtained by the pure VGO.

In an industrial FCC unit, metals present in an FCC fossil feed, such as Na, Ni, V and Fe, cause deactivation of the catalyst, so fresh catalyst is constantly added and equilibrium catalyst is removed to keep the FCC equilibrium catalyst activity. The industrial catalyst make-up rate is usually around 1.0 kg catalyst·m<sup>-3</sup> feed. The alkaline metals present in the bio-oil, such as Na, K, Ca and Mg may also cause catalyst deactivation (zeolite destruction). Equilibrium FCC catalyst was used in these experiments, instead of fresh FCC catalyst, and catalysts samples were collected during the first co-processing test series. Samples were collected after approximately 22 h, using a 1.0 kg·m<sup>-3</sup> feed catalyst make-up rate and metals content and textural properties of the catalyst were analysed. Increases in K (from 271 ppm to 650 ppm) and Ca (936 ppm to 1287 ppm) in the catalyst were observed under these conditions. Despite the evident increase in alkaline metals, it was not possible to observe a clear drop in surface area or micropore volume. Therefore, longer run tests, without catalyst make-up, would be necessary to assess the impact of alkaline metals on the FCC catalyst.

### 3.1. Oxygen balance

There was no detectable difference in the water content in the liquid effluents produced from bio-oil and those produced from pure gasoil. All liquid effluents contained approximately 400 ppm wt. of water. Likewise, elemental analysis did not indicate the presence of oxygen (obtained by difference) in the liquid effluents.

The oxygen mass balance was calculated based on the oxygen content in the feed (50.7 wt.% of oxygen, as shown in Table 2) and in the products: CO, CO<sub>2</sub>, water, liquid products and other components not classified in coke or gaseous fraction (Table 4). As observed in literature in oxygen balances obtained with HDO, water is the main oxygenated product [6]. However, contrary to what is observed with HDO, CO formation and decarbonylation reactions prevail over decarboxylation and CO<sub>2</sub> formation.

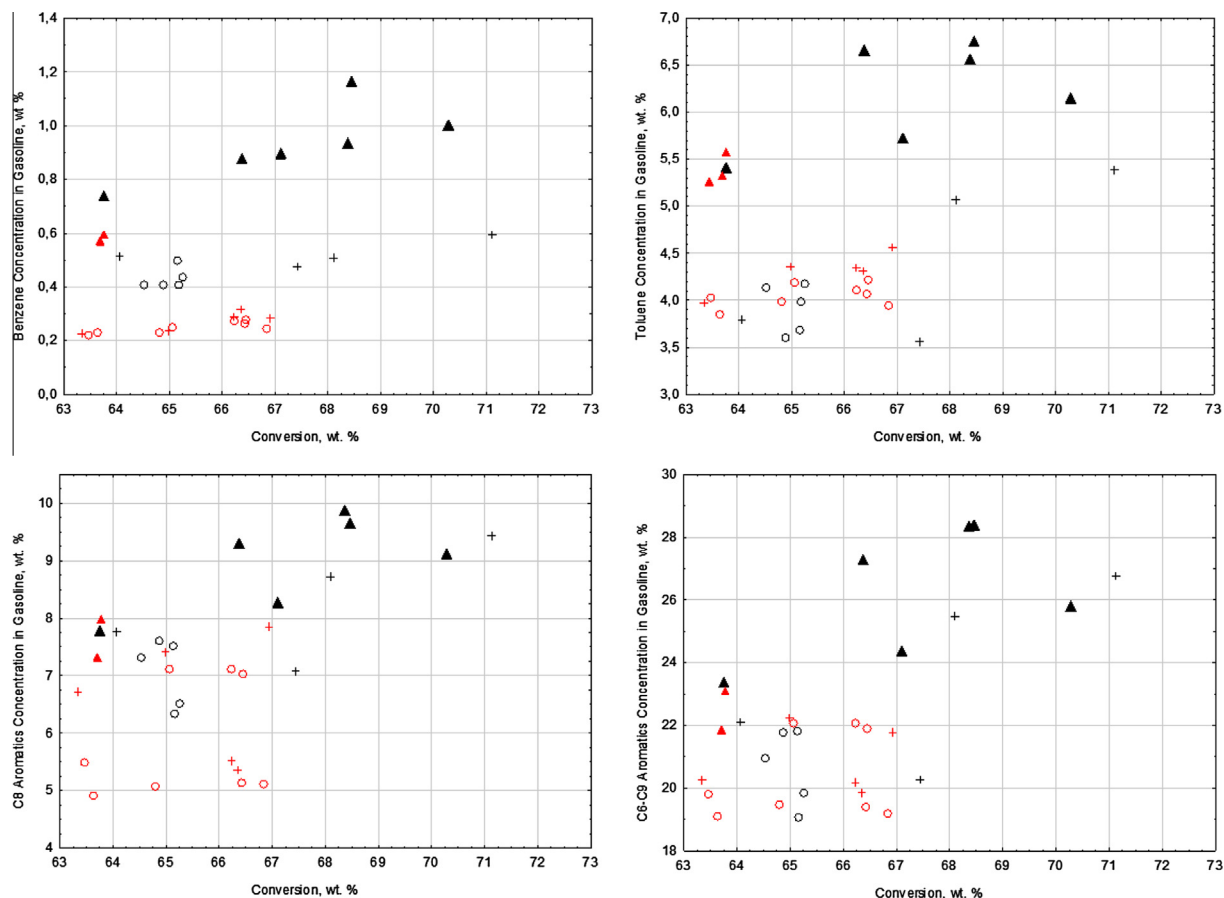
### 3.2. Quality of the gasoline, LCO, and bottoms

The PIANO analysis was used to explore the gasoline fraction in detail. Compared at the same conversion level, the benzene, toluene, and C8 aromatics concentrations in gasoline were lower when pure VGO was used (Fig. 5). Contrary to what was observed in literature from the co-processing of 20 wt.% HDO and 80 wt.% VGO, monoaromatics formation increased with the increase of the conversion [10].

A long uninterrupted test was carried out, co-processing 5% of bio-oil at 540 °C in the FCC unit. The liquid effluent was distilled to produce gasoline, diesel range (LCO), and bottoms cuts (see Table 5). Between parentheses are typical property values obtained at the same reaction temperature and VGO feed quality. As observed in literature with HDO-oil, bio-hydrocarbon products were obtained with very little oxygen [11]. Only phenolic compounds were observed in the products when bio-oil was used as feed. Other studies have also observed that co-processing of either

**Table 4**  
Oxygen balance during co-processing (kg of oxygen/100 kg of feed) - feed temperature = 280 °C.

	5% bio-oil	10% bio-oil
Initial	2.54	5.07
CO	0.57	0.97
CO <sub>2</sub>	0.29	0.44
Water	1.24	3.11
Not classified	0.44	0.55



**Fig. 5.** Benzene, toluene, C8 aromatics and C6–C9 aromatics concentration in gasoline at different conversion levels: VGO cracking 1<sup>st</sup> test series (▲), VGO/Bio-oil cracking 95/5 1<sup>st</sup> test series (+), VGO/Bio-oil cracking 90/10 1<sup>st</sup> test series (○), VGO cracking 2<sup>nd</sup> test series (▲), VGO/Bio-oil cracking 95/5 2<sup>nd</sup> test series (+), VGO/Bio-oil cracking 90/10 2<sup>nd</sup> test series (○).

**Table 5**

FCC naphtha (gasoline range), LCO (diesel range), and bottoms properties produced from 5% bio-oil co-processing at 540 °C. Values between parentheses represent the fossil fuel obtained from a typical Brazilian VGO.

	Gasoline	LCO	Bottoms
Density (g/cm <sup>3</sup> , 20 °C)	0.7755 <sup>a</sup> (0.73–0.76)	0.9125 (0.92–0.96)	1.0997 (1.04–1.20)
Carbon (C), wt.%	85.60	87.00	n.a.
Hydrogen (H), wt.%	12.68	10.79	n.a.
Sulfur, wt.%	936 (700–1200 mg/kg)	0.56 (0.50–0.70)	0.88 (0.70–0.90)
Nitrogen, wt.%	166 (150–250 mg/kg)	0.10 (0.14–0.24)	n.a.
RVP, kPa	48.1 (50.0–60.0)	14.0	n.a.
Water, mg/kg	120 (50–200)	256	n.a.
Biocarbon, wt.%	1 (0)	1 (0)	n.a.
Phenols, mg/kg	4636 (2000–3300)	n.a.	n.a.
Thiophenols, mg/kg	96 (20–50)	n.a.	n.a.
Phenols + Thiophenols, mg/kg	4732	3364	n.a.
BSW, wt.%	n.a.	n.a.	0.0
Ashes, wt.%	n.a.	n.a.	<0.001 (0.10–0.40)
Viscosity at 60 °C, mm <sup>2</sup> /s	n.a.	n.a.	342.1
Viscosity at 82.2 °C, mm <sup>2</sup> /s	n.a.	n.a.	68.46
Viscosity at 100 °C, mm <sup>2</sup> /s	n.a.	n.a.	29.18
<i>Simulated distillation (mass recovery: °C)</i>			
Initial	–20.6 (–20.0 to 0.0)	34.9	334.0
5%	39.4 (10.0–30.0)	144.4	340.5
10%	61.2 (25–40)	202.2	348.1
30%	100.1 (60–80)	234.7	379.0
50%	134.2 (90–130)	255.3 (250.0–270.0)	410.5
70%	161.2 (150–170)	275.8	444.0
90%	194.9 (160–190)	299.8	491.8
95%	202.5 (180–200)	310.1	511.2
Final	220.7 (200.0–240.0)	343.7 (340.0–390.0)	526.2

n.a. – not available.

<sup>a</sup> Higher value may have been caused by the lower RVP required to transport samples.



hydrodeoxygenated oil and vacuum gasoil or catalytic pyrolysis oil and vacuum gasoil [6,23] or model compounds, such as guaiacol [25], led to the presence of phenol and alkylphenols in the gasoline fraction. However, phenol and alkylphenols are also found in the gasoline obtained from the VGO formed from the reaction in the riser between the oxygen entrained in regenerated catalyst and the hydrocarbon feed [26,27]. This value is typically around 3000 ppm wt. Phenolic compounds were identified and quantified by using ion chromatography (see Table 6) obtained from a fossil feed (VGO), 5% of bio-oil, and 10% of bio-oil. Phenol and alkylphenols increased steadily with the bio-carbon content in the feed.

Phenolic compounds are also observed in shale oils [28], which have been widely processed in many FCC units. Therefore, U.S. refineries are not unfamiliar with high phenolic content feedstocks. Phenolics have been mentioned in literature as gasoline octane boosters and antioxidant additives for gasoline, jet fuel or diesel range products [29–31]. However, the possible effect of the phenolic molecules produced from the bio-oil in the catalytic cracking on gasoline stability is yet to be determined.

McCormick and co-workers [13] examined the fuel properties of phenols, guaiacols, anisoles, and other compounds that could be present in upgraded biomass-pyrolysis oils. At low blend levels the phenolics slightly increased octane number and reduced gum formation. However, phenol and the cresol isomers exhibit poor solubility in hydrocarbons, especially at low ambient temperatures. In addition, cresol boils at 202 °C, well above the T90 (90% volume recovered temperature) limit in U.S., European, and many other gasoline standard specifications (185 °C or 190 °C). Boiling point increases with increasing number and length of alkyl chains, with propyl phenol, for example, boiling at 232 °C, well above the end point limit of 225 °C for gasoline. The T90 and end point limits severely constrain the quantity of alkyl phenols that can be blended into gasoline. If present at low levels in diesel fuels, the phenolic compounds improved conductivity, lubricity, and oxidation stability, but have very low cetane number limiting their presence to a few wt.%.

Baumgardner et al. [32] showed that residual diesel blends containing phenolic compounds that can be obtained from pyrolysis oils show slightly positive effects at low percentages (2 vol.%) and some tradeoffs. At higher blend levels properties deteriorate. The authors suggest that phenolics should be limited to 2%. It was observed that, below this limit, reduced in-cylinder temperatures lead to lower NO<sub>x</sub> levels while slightly increasing CO and CH<sub>2</sub>O (negative effects) and inhibit PM10 (particle matter below 10 μm) generation, arguably, in favor of increased total hydrocarbons emissions. In the 5–6 vol.% level directionally negative effects occur such as in-cylinder temperatures appear to rise, reducing CO emissions but raising NO<sub>x</sub> emissions. Thermal efficiency also declines as the fuel additives have greater impact on the combustion timing and overall energy release of the total blend.

**Table 6**  
Phenols (ppm wt.) in the gasoline range by ion chromatography.

	From VGO	From 5% bio-oil	From 10% bio-oil
Phenol	362	844	1681
p-Methoxyphenol	36	0	0
4-MePhenol	562	724	1338
2-MePhenol	526	652	1087
3,4-DiMePhenol	55	122	213
3,5-DiMePhenol	90	413	597
2,3/2,6-DiMePhenol	235	127	1175
2,4/2,5-DiMePhenol	399	439	566
Benzene-1,4-diol	0	0	0
Benzene-1,2-diol	0	0	0
Total phenols	2265	3321	6657

The partially renewable gasoline and light cycle oil (400 gallons each) were sent to the United States and hydrotreated. The properties of the resulting fuels after the hydrotreatment met specifications pursuant to Title 40 CFR Part 79 promulgated by the Clean Air Act required for the sale of renewable fuels into U.S. commerce and Ensyn Corp. was granted regulatory approval from the U.S. Environmental Protection Agency (EPA) for both gasoline and diesel products with renewable content [33]. The same pathways were also approved by the California Air Resources Board under the Low Carbon Fuel Standard program [34]. Description of the U.S. specifications will be provided in a companion paper along with the techno-economic assessment and lifecycle analyses results [35].

#### 4. Discussion

It is frequently reported, based on FCC laboratory and pilot-scale results, that coke production in the FCC units is excessively high when raw (untreated) bio-oil is used as feed [5]. In small-scale units, even low bio-oil amounts or hydrogenated bio-oils may cause a considerable increase in coke yield, operational instabilities, and plugging by coke formation. However, some characteristics inherent to small-scale units may explain the differences in yields obtained in the present study performed at a much larger scale unit (feed rate unit 200 kg·h<sup>-1</sup>).

##### 4.1. Feeding a lignocellulosic stream into the FCC riser reactor

Most FCC lab-scale units, such as ACE (advanced cracking evaluation) and MAT (microactivity test) apparatuses, use a single line to introduce the feed. Co-processing studies in laboratory-scale units require the blending of different feeds in the unit feeding vessel. However, bio-oils and fossil streams are not miscible due to differences in their polarities. Therefore, FCC co-processing experiments necessitate the use of some emulsifier. In some studies 1 wt.% of emulsifier was used to blend 10 wt.% of bio-oil with the fossil feed. In the experiments reported in this work, an emulsifier was not necessary, because the fossil and the renewable feeds were segregated and injected at different heights in the demonstration-scale FCC unit, minimizing or possibly avoiding these problems in optimized systems.

In a commercial FCC unit, separated feed lines and tanks would be necessary for bio-oil introduction due to its high acidity, which requires proper stainless steel materials to minimize corrosion. Moreover, feed segregation would allow bio-oil operation to be discontinued, in case the economics are no longer attractive or if there are pyrolysis oil supply discontinuities, without impairing regular FCC operation.

The pyrolysis oil or other oxygenated feeds need to be maintained below 50 °C. Excessive heating promotes severe coke plugging in the feed lines. For instance, even pure ethanol rapidly dehydrates, polymerises and forms coke in feed lines when heated above 50 °C. On the other hand, fossil feeds, such as VGO and ATR (atmospheric residue, bottom of the atmospheric residue distillation tower), are heated in a commercial FCC unit at temperatures between 180 °C and 320 °C to reduce their viscosity, obtaining proper feed atomisation and dispersion through the feed nozzles. Feed dispersion is of the utmost importance to decrease coke yields and the selectivity of the cracking reactions. Therefore, there are different adequate feed temperatures for the bio-oil and the regular FCC feed. In laboratory-scale, the main concern in FCC co-processing studies is avoiding coke plugging and ensuring the feed line is kept below 50 °C, which affects the fossil feed dispersion and increases coke yields beyond the values that would be caused solely by the bio-oil.

Again, the segregation between the fossil and renewable feeds using larger scales allows the operation at optimum temperature

for each feed. In the present study, the bio-oil was kept below 50 °C, while the VGO was heated between 220 °C and 320 °C, making it possible to obtain an optimum feed dispersion through the nozzles for both feeds.

#### 4.2. Temperature profile in an FCC reactor

The raw lignocellulosic biomass includes mainly different types of macromolecules: cellulose, hemi-cellulose, and lignin. Cellulose is a linear polysaccharide, composed only of glucose, while hemi-cellulose is a more complex polysaccharide of multiple six- (hexoses) and five-carbon sugars (pentoses) [36,37]. Likewise, lignin is an interpenetrating, mostly mononuclear, aromatic polymer with some oxygen functionalities (ethers being predominant). Although these macromolecules widely break apart in biomass fast pyrolysis reactors, the bio-oil still contains some amount of high molecular weight molecules [37].

FCC reactors are commonly used to break large molecules into smaller ones, generating LPG, gasoline, and diesel range products from liquid streams as heavy as atmospheric residues. Industrial riser reactors temperatures are usually set between 500 °C and 550 °C. However, the heaviest part of the residues distillation curve is well above these temperatures; usually at least 15 wt.% of it is above 550 °C. In the industrial FCC unit, the set reactor temperature represents the temperature at the top of the riser reactor, when most of the cracking reaction had already taken place. Nevertheless, the temperature varies widely along the riser reactor height. Higher temperatures are found in the bottom of the riser and the temperature decreases along the riser height until reaching the temperature set for the reaction at the top. At the bottom, the hot catalyst from the regenerator is around 700 °C. A thermal shock takes place when the hot catalyst contacts the liquid bio-oil feed inside the reactor. Some heat vaporises the feed and heat also breaks large molecules into smaller ones, so that these smaller molecules penetrate into the catalyst pores. Therefore, the real temperature in the feed nozzle reactor region, where the contact between the catalyst and the feed occurs, is around 600 °C, well above the set reaction temperature. The temperature then decays due to the endothermic reactions occurring along the reactor. If such an axial temperature profile did not exist, the heaviest fraction of the liquid feed would not vaporise and would be instantaneously transformed into coke, which would deposit on the catalyst and abate the selectivity of the catalyst, causing deterioration in the yields profile.

Nevertheless, most of laboratory-scale FCC reactors, including MAT reactors or fluidised ACE units, are designed to operate isothermally, do not present any temperature profile and are often maintained at the desired reactor temperature during the whole experiment.

These differences explain much of the divergent results from laboratory, pilot, and commercial scales when heavy feeds are used. A comparison between a laboratory-scale and a pilot riser unit was carried out using a typical Brazilian VGO and atmospheric residues [14]. The laboratory unit (ACE) produced more than eight absolute points of coke for atmospheric residues compared to the pilot riser, while coke yields were practically the same in both scales when a VGO feed was used. As in an FCC commercial unit, in the pilot riser the catalyst-feed mixing zone temperature is at least 100 °C higher than the temperature at the top of the riser reactor, contrary to what happens in ACE units, where the entire reactor is kept at the same temperature. Therefore, the coke yields obtained from ACE increase significantly when the heavy end fractions of the feed distillation curve increases, suggesting that the non-vaporised portion of the feed remains as a liquid and is transformed directly into coke.

Bio-oils distillation curves can be generated with thermogravimetric analysis (TGA) [38]. As in ATR, bio-oils present high amounts of heavy distillation fractions, which do not vaporise or break unless they are submitted to extremely high temperatures, suggesting that their behaviour in laboratory-scale would be similar to the one found with ATR feeds.

In the reactor riser profile obtained in the experiments described in this paper, the temperature drops from 690 °C to approximately 660 °C after contacts with the renewable feed and decreases again to less than 580 °C due to the contact with the VGO feedstock and to the endothermic reactions that take place in the riser until reaching the final reaction temperature of 540 °C.

The bio-oil injection in the demonstration-scale reactor before the VGO benefited from the high regenerated catalyst temperature at the base of the riser reactor and the thermal shock between bio-oil large molecules and the hot catalyst. Moreover, the local catalyst-to-bio-oil ratio in the base of the riser is higher than the average catalyst-to-oil ratio (CTO) considering the entire reactor. The total CTO is approximately 6–9 in a regular FCC riser reactor, while the local CTO for the bio-oil was much higher at the bottom of the riser. For a 10 wt.% bio-oil injection at the bottom of the riser reactor, the local CTO ratio is approximately 10 times higher and the catalyst temperature is approximately 690 °C, helping to thermally break and vaporise the heaviest fraction of the bio-oil.

#### 4.3. Bio-oil ageing

Fig. 6a shows the pressure drop trends measured along several tests carried out in January 2014, right after the bio-oil was received. Although the variations in the test conditions (5–10 wt.% of bio-oil, and different feed temperatures) alternate in time,

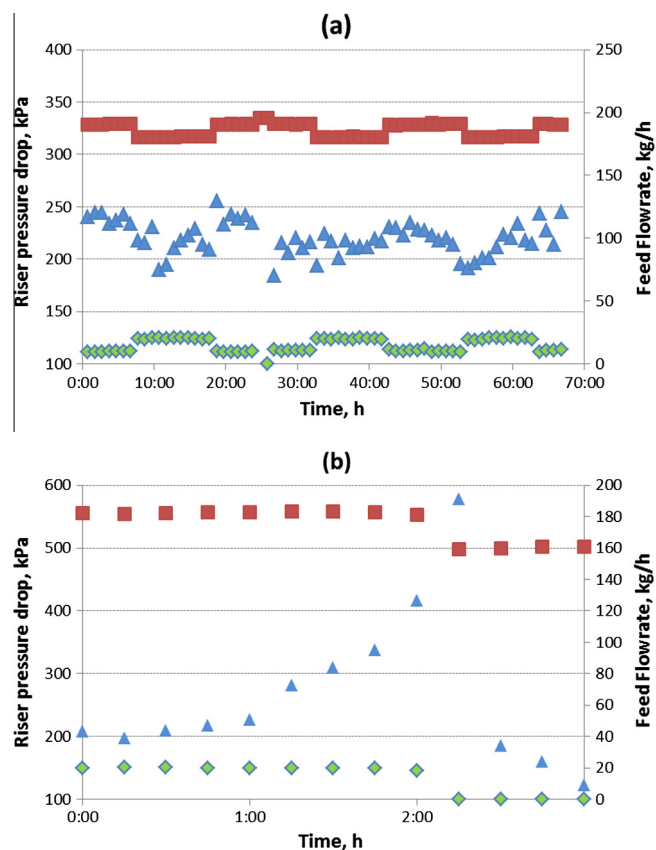


Fig. 6. Riser pressure drop, bio-oil feed rate and VGO feed rate vs. time (a) 9-month-old bio-oil with 67 h of operation, 5 wt.% and 10 wt.% of bio-oil alternately, (b) 21-month-old bio-oil: primary axis (on the left) riser pressure drop ( $\blacktriangle$ ), secondary axis (on the right) VGO feed rate ( $\blacksquare$ ) and bio-oil feed rate ( $\blacklozenge$ ).

the riser pressure drop varied between 200 kPa and 250 kPa over 69 h until all the planned tests with bio-oil were finished in the first test series. It is worth noting that this bio-oil was already 9-months-old when it was finally used.

The same bio-oil was used again in December 2014. Although the product yield profiles were not altered, the pressure drop in the riser increased very fast along each test as shown in Fig. 6b, which represents operating conditions during one of the tests carried out with the aged bio-oil. The clean-up of the deposits inside the reactor could be carried out by allowing some catalyst circulation without any feed introduction during some minutes. This stop-and-go operation indicates some bio-oil deterioration 11 months after the first trials and that, as any other renewable material, bio-oil has an “expiration date” for this application, which is a function of production and storage conditions. This situation is analogous to that of biomass pyrolysis oils intended for use in various types of fuel-burning equipment under various climatic and operating conditions. There are several standard specifications of properties covered by the ASTM D7544.

#### 4.4. Renewable carbon content in the liquid products

Specific bio-oil characteristics, such as its tendency to separate into two test series and become heterogeneous, require the use of  $^{14}\text{C}$  technique to assure that the quality and amount of the bio-oil fed in the FCC unit is the one initially expected. Thus,  $^{14}\text{C}$  isotopic analysis must be conducted to calculate renewable carbon mass balances and the amount of renewable carbon contained in the FCC products.

The renewable carbon content in the gasoline and LCO range were measured by  $^{14}\text{C}$  analysis and compared with another study in literature, which processed 10 wt.% and 20 wt.% of bio-oil produced from pinewood [16]. Fig. 7 represents renewable carbon content versus the % of bio-oil in the feed. Liquid product contained 2 wt.% and 5 wt.% of renewable carbon when 10 wt.% and 20 wt.% of bio-oil was used, respectively. In the present work, liquid products contained 1 wt.% of renewable carbon from 5 wt.% bio-oil (see also Table 5). Therefore, for a similar reference feed (VGO), FCC conditions, and bio-oil origin, approximately 30% of the renewable carbon from the bio-oil ends up in the liquid products for a bio-oil usage between 5 wt.% up to 20 wt.%. This efficiency is in the range estimated by Talmadge et al. [36] for hydroprocessing, where approximately 30–50 wt.% of the carbon in the feed is converted into carbon in the upgraded oil. However, contrary to the hydroprocessing route, the FCC has the advantage of not requiring

the use of an external source of hydrogen to produce gasoline or diesel range blendstocks.

The putative product yields from a virtual 100 wt.% bio-oil processing can be calculated from the linear extrapolation via 100 wt.% VGO and at 5 wt.% bio-oil/95 wt.% VGO, or at 10 wt.% bio-oil/90 wt.% VGO. The linear extrapolation yields are higher than those calculated via  $^{14}\text{C}$  (approximately 60 wt.% against 30 wt.%). De Miguel Mercader et al. [11] co-processed 20 wt.% HDO oil/80 wt.% Long Residue in a laboratory-scale unit and compared with the result obtained from 100 wt.% HDO oil. Similarly, putative yields profile obtained via linear extrapolation give better results (more gasoline, less coke) than the results obtained from pure HDO oil. The authors suggested internal hydrogen transfer and reduction in coke precursor concentration during the co-processing of the renewable and the fossil feed as potentially operative mechanisms to explain these results. However, they concluded that, to date, it is not possible to determine which mechanism causes the changes in the yield profile.

## 5. Conclusions

This paper demonstrates the technical feasibility of co-processing raw bio-oil with VGO, a fossil feedstock, in the fluid catalytic cracking. Different feeding strategies for integrating the bio-oil into the FCC unit were necessary due to its low miscibility with petroleum streams. Up to 10% of bio-oil having an oxygen content of approximately 50% was directly fed into a demonstration-scale FCC riser reactor that had multiple feed injection points.

The tests conducted with the same bio-oil in two different experimental test series showed that while a 9-month-old bio-oil did not cause operating problems in the FCC unit, a 21-month aged bio-oil may affect operating conditions.

The oxygen present in the bio-oil was almost completely removed through catalytic cracking, mostly as water and as CO or  $\text{CO}_2$  to a lesser extent. However, the oxygenated compounds concentrations, especially alkyl phenols, increased in co-processed gasoline and diesel products compared to the amounts present in processing of VGO alone.

The presence of renewable carbon was confirmed in gasoline and diesel cuts through  $^{14}\text{C}$  isotopic analysis, showing that renewable carbon is not only being converted into coke, CO, and  $\text{CO}_2$ , but also into valuable refined liquid products. Thus, gasoline and diesel could be produced from lignocellulosic raw materials through a conventional refining scheme, which uses the versatile catalytic cracking process.

The bio-oil renewable carbon conversion into liquid products (carbon efficiency) was approximately 30%, well above the efficiency found in literature for FCC bio-oil upgrading from laboratory-scale equipment, whose characteristics enhance coke formation in the reactor and deteriorate the yields profile.

The successful demonstration of raw pyrolysis oil (50 wt.% oxygen) co-processing suggests that it would also be feasible to co-process partially-upgraded bio-oils as well. This also suggests there would be an optimal hand-off point between the biorefinery and the petroleum refinery. More data for co-processing partially upgraded pyrolysis oils are needed to further investigate this optimisation.

Future studies must also be dedicated to address catalyst deactivation caused by alkaline metals present in bio-oils, which may require an increased catalyst make-up rate.

Subsequent analysis and publications will present the economic feasibility and lifecycle analysis of the co-processing strategy.

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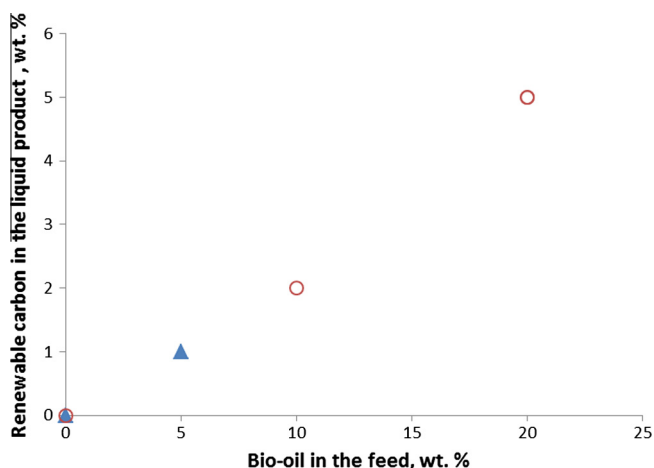


Fig. 7. Renewable carbon content in the liquid product at different bio-oil feed percentages: present study (▲), Literature [16] (◻).

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