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Co-processing raw bio-oil and gasoil in an FCC Unit

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ABSTRACT

Bio-oil is a complex blend of oxygenated compounds, such as acetic acid, hydroxyacetone and phenols, and is produced from the fast pyrolysis of raw biomass. A raw bio-oil produced from pine woodchips was co-processed with standard gasoil and tested in a 150 kg/h fluid catalytic cracking (FCC) demonstration-scale unit. The bio-oil was cracked into valuable products, such as gasoline and LCO, with similar product yields obtained from the base FCC feed when up to 10% bio-oil was used. However, some deterioration was observed when 20% bio-oil was added. ^{14}C isotopic analyses were performed to determine the renewable carbon content in the FCC liquid products. When 20% bio-oil was co-processed, the renewable carbon content in the gasoline cuts varied between 3% and 5%. For 10% bio-oil in the feed, 2% renewable carbon was obtained in the total liquid product. Large amounts of phenolic compounds were detected in the naphtha produced by the FCC. The FCC carbon efficiency, which is defined as the amount of carbon in bio-oil converted to carbon in the total liquid products, was approximately 30%, well above the values found in the literature for FCC bio-oil upgrading (15%–20%) when using laboratory scale units.

1. Introduction

In recent years, the use of renewable fuels has attracted great attention, and vegetable oils from triglyceride plants have been intensively explored in Europe and South America to produce a renewable diesel oil substitute by transesterification (biodiesel). Due to their long side carbon chains and absence of aromatic rings, these oils can also be successfully processed in a fluid catalytic cracking unit (FCC) to produce gasoline or light olefins [1]. A commercial test in an FCC unit was carried out in the 1980s with 10% of soybean oil. Although technically successful [2], this operation has two disadvantages: i) it is not economically attractive due to the high prices of the vegetable oil, and ii) the use of crops for biofuel production diverts resources from production for human consumption. In this context, the use of lignocellulosic waste, such as wood chips and sugarcane bagasse would not impair food security. Actually, this usage may even improve agriculture economics and contribute to decreasing food prices. However, transforming lignocellulosic materials into fuels, and doing it economically, is still a challenge.

Biomass fast pyrolysis is the leading method to increase cellulosic waste density and produce a liquid intermediate, the so-called bio-oil [3]. This offers the advantage of using the entire plant material so that practically any biomass form can be considered for pyrolysis. However, bio-oil chemical properties are significantly different from that of petroleum feedstocks. Indeed, bio-oils are a complex mixture of different oxygen-containing molecules [4–6], including phenols, sugars, carboxylic acids and water (10–35 wt.%). Its high oxygen content decreases its heating value, and its high polarity impedes its miscibility with hydrocarbon fuels. Moreover, it exhibits high acidity and corrosiveness. Thus, bio-oil must be viewed as an intermediate product in the thermochemical biomass route that must be upgraded to be transformed into a transportation fuel.

The direct feeding of bio-oil in a fluid catalytic cracking (FCC) unit has been considered infeasible. Attempts to directly upgrade bio-oil have reported significant amounts of char, coke and water as the main products [7–10]. Bio-oil immiscibility with hydrocarbons has also been singled out as an impediment to its direct introduction in the FCC process [11].

Some authors suggest a previous stabilisation HDO (hydrodeoxygenation) step for the bio-oils prior to feeding them into the FCC [12–16]. Although technically feasible, this route offers obvious disadvantages because HDO requires large amounts of hydrogen at elevated pressures. Moreover, other aspects should be taken into consideration to analyse its techno-economic viability, such as the presence of alkaline metals and water in the bio-oil that could damage the catalyst and reduce HDO reactor run length between turnarounds. It is important to note that these studies were carried out at laboratory scales.

Other proposed routes involve the use of catalysts, replacing the silica sand in the pyrolysis unit to produce bio-oils with a better quality

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and lower oxygen content [17–19]. The resulting catalytic pyrolysis oil, also referred to as CPO, could be more easily hydrodeoxygenated, demanding less hydrogen at lower pressures. As an alternative to this approach, the CPO could be co-fed into an FCC unit [20].

However, some studies suggest that tests carried out on laboratory-scale FCC units would not necessarily reflect the heavy feed behaviour in larger or commercial scale units, especially with respect to the coke formation tendency. The results obtained in a circulating FCC pilot riser are frequently superior to those observed at small-scale units [21]. Therefore, the use of larger scales would offer additional advantages including a better understanding of the heavy feed behaviour of bio-oil. A Petrobras demonstration unit in São Mateus do Sul has been used intensively by Petrobras for many years to develop its FCC technology. One of the most important advantages is the different levels of feed injection. Feed nozzles are positioned at four different heights in the reactor. Therefore, bio-oil and the regular FCC stream can be introduced separately in the riser. In preliminary tests, raw bio-oil was co-processed along with a Brazilian vacuum gas oil (VGO) in the demonstration scale unit. Impacts on coke yield were drastically minimised, even when 20% bio-oil was used. Moreover, the impacts on coke with 10% bio-oil, the same level used in the pilot riser unit, were negligible, and none of the problems faced at the pilot scale, such as feed nozzle or feed line plugging, were observed at the demonstration scale [22].

The objective of this paper is to assess the potential of co-feeding the entire mass of bio-oil without any pre-treatment and standard gasoil in an FCC unit. For this purpose, a demonstration-scale riser reactor catalytic cracking unit, running at a conventional reaction temperature and other operating FCC conditions, was used. The influence on conversion, product yields and gasoline quality using a commercial FCC equilibrated catalyst was investigated. The amount of renewable carbon in the liquid product was measured by examining the amount of isotopic ^{14}C. The quality of the bio-gasoline obtained was also studied.

2. Experimental

2.1. Materials

The catalyst used in this study was a commercial FCC equilibrium catalyst supplied by FCC S.A. (Santa Cruz, Brazil) and collected in an industrial FCC unit located in one of the Petrobras refineries. Table 1 shows the physicochemical characteristics of the catalyst.

A fast pyrolysis liquid (bio-oil) from pine woodchips was acquired from BTG Biomass Technology Group B.V. (Enschede, Netherlands) and was used as the feedstock in the experiments [23]. A stable and single homogenous phase was formed. The bio-oil characterisation is reported on in Table 2.

A typical Brazilian vacuum gasoil (VGO) commercially processed in Petrobras FCC units was used to complement the feed rate (Table 3). It is worth noting that the usual feedstocks used in Brazil are heavier than those used in the USA or Europe.

Table 1
Properties of the FCC catalyst.

Physical properties	
Surface area (m^2/g)	148.0
Mesopore area (m^2/g)	47.9
Micropore volume (m^2/g)	0.046
Chemical analysis	
Al_2O_3 (wt.%)	45.4
Na_2O (wt.%)	0.4
RE_2O_3 (wt.%)	2.0
V (mg/kg)	1254
Ni (mg/kg)	2092

Table 2
Properties of the bio-oil.

Density (g/cm^3, 20 °C)	1.2154
Sulfur (ppm)	233
Flash point (°C)	>80
Pour point (°C)	9
Lower heating value (MJ/kg)	19.80
Higher heating value (MJ/kg)	21.46
Elemental analysis (wt.%)	
Carbon	42.35
Hydrogen	6.50
Oxygen (by difference)	51.15
Acidity (mg/KOH g)	70.32
Ashes (wt.%)	0.017
Metals (mg/kg)	
Na	2.2
K	8.1
Mg	2.4
Ca	2.4
Al	34
Si	10
Fe	66
Zn	14
Mn	1.8
V	<1
Ni	0.8
Cr	0.7
Solids (wt.%)	0.006
Water (wt.%)	25.5
Viscosity at 60 °C (mm^2/s)	48.4

2.2. Setup

Tests were conducted in a demonstration-scale fluid catalytic cracking unit equipped with a pseudo-adiabatic riser reactor and a continuous catalyst regenerator, operating under steady state conditions (Fig. 1). The catalyst inventory is 450 kg. The total feed rate was controlled at 150 kg/h. The catalyst circulation rate may be adjusted by changing the feed pre-heater temperature to achieve the set reactor outlet temperature (reaction temperature).

Two different bio-oil/VGO weight ratios were used: 10/90 and 20/80. 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-m-high cylindrical tube. The bio-oil cannot be heated above 50 °C because its heating accelerates polymerisation reactions and coke formation, which obstruct the feed lines. Therefore the introduction of the bio-oil through a separate feed nozzle below the VGO feed line permits the heating of the VGO up to 220 °C or 280 °C, as carried out in regular FCC commercial operations. The heating of the fossil feed decreases its viscosity and improves the feed dispersion.

Table 3
Properties of the reference feed—VGO.

Density (g/cm^3, 20 °C)	0.9472
API gravity	17.3
Sulfur (wt.%)	0.46
Total nitrogen (mg/kg)	0.24
Basic nitrogen (mg/kg)	1187
Aniline point (°C)	81.9
Ramsbottom carbon residue (wt.%)	1.73
TBP-analyses (°C)	
IBP: 130.8	
10%: 350.0	
30%: 426.8	
50%: 477.0	
70%: 539.4	
90%: 642.6	
FBP: 741.0	