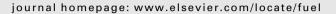
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Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production



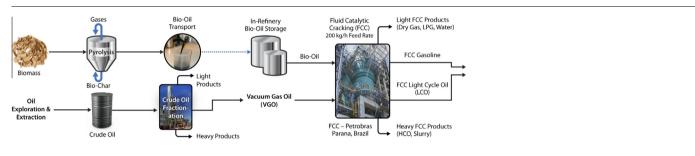
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G R A P H I C A L A B S T R A C T



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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⁻¹ 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 coprocessed 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 ¹⁴C isotopic analysis, showing that renewable carbon is not only being converted into coke, CO, and CO₂, 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 biooil 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 biooil [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) coprocessing in a continuous reactor FCC pilot unit, more coke and less gasoline were observed along with production of CO and CO₂. 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⁻¹ 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 biooil 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 \cdot h⁻¹ flow rate with vacuum gas oil and 5 or

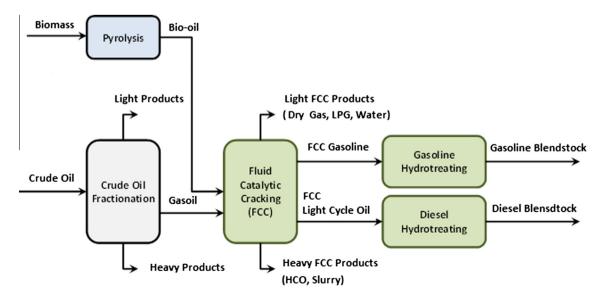


Fig. 1. Refining scheme. Bio-oil is directly co-fed into the FCC unit with VGO. Naphtha (gasoline range cut) and LCO (diesel range cut) are hydrotreated to remove sulfur and comply with fuels specifications.

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