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Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining

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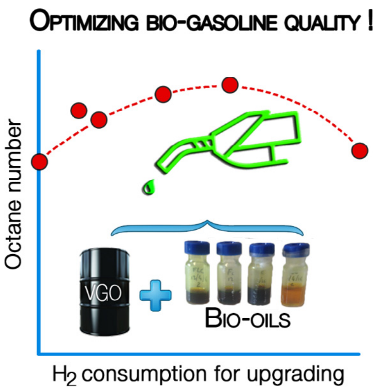
HIGHLIGHTS

- Pyrolysis oil was upgraded at different temperatures into partially deoxygenated oils.
- These partially deoxygenated oils were co-refined in a labscale cracking unit.
- There's an optimum in octane ratings of the produced liquids.
- Optimum upgrading corresponds to a H_2 consumption of 200 NL/kg_{PL}.

GRAPHICAL ABSTRACT



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ABSTRACT

Co-refining of biomass derived pyrolysis liquids (PL) in a Fluid Catalytic Cracking (FCC) unit with crude oil fractions is a promising route to produce second generation biofuels. To improve the yield and ensure co-processed fuel quality, a hydrotreating step can be deployed prior to co-processing. In this paper the conversion, yields and naphtha or gasoline composition are analyzed during a 10 wt.% PL/90 wt.% vacuum gasoil (VGO) co-processing step as a function of the PL hydrotreating severity, expressed in terms of hydrogen consumption.

The naphtha yield was not impacted by the hydrotreatment procedure and always slightly higher than that of pure VGO cracking. An optimum in the naphtha quality in terms of octane rating was found as a function of the PL upgrading severity. The optimum was achieved with mildly hydrotreated PL's, corresponding to a H_2 consumption of 202 NL/kg_{PL}. These mildly hydrotreated PL's led to similar coke formation during co-refining as pure VGO cracking. These results indicate that the upgrading of PL's should be restricted to a hydrogen consumption of less than 200 NL/kg_{PL}.

1. Introduction

The first generation of biofuels, like ethanol and biodiesel, have been successfully integrated into the pool of petroleum-based

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Nomenclature

DO	decanted oil	PL	pyrolysis liquid
FCC	Fluid Catalytic Cracking	PO	pyrolysis oil
HDO	HydroDeOxygenation	RO	refined oil
LCO	light cycle oil	RON	research octane number
LPG	Liquefied Petrol Gas	TAN	Total Acid Number
MAT	micro activity test	USY	ultra-stabilized Y zeolite
MON	motor octane number	VGO	vacuum gas oil
MRCT	micro carbon residue test		
PDO	partially deoxygenated oil		
PIONA	Paraffins, Isoparaffins, Olefins, Naphtenes, Aromatics		

fuels. However, they compete with food production and need to be replaced by second generation biofuels, which are produced from lignocellulosic feedstocks. A realistic and rather straightforward production route consists of co-refining biomass pyrolysis oil with crude oil fractions in conventional oil refineries [1–4]. Co-processing allows repurposing existing refinery infrastructure to produce blends of fossil and biofuels, providing a compliance solution controlled by the refiners [5]. Moreover, it avoids dedicated blending infrastructures without blendwall limits [5].

Co-refining of bio-oils in a Fluid Catalytic Cracking (FCC) unit, leads to changes in the product quality, such as a higher aromaticity and the presence of residual (phenolic) oxygenates as well as an increased coke content of the FCC catalysts [6–11]. To preserve naphtha yield and quality while avoiding excessive coke production, a pyrolysis liquid upgrading process can be deployed prior to the co-processing step [12,13]. These upgrading processes are based on a hydrotreatment step, aiming to reduce the number of oxygen functionalities in the pyrolysis liquid (to render a 'stabilized oil') or to substantially remove the oxygen to render a lean fuel ('deoxygenated oil'). In both cases the liquids are less prone for charring [14].

An optimum might exist between hydrogen consumption and degree of deoxygenation of pyrolysis liquids on the one hand, and overall product yield/quality on the other hand. Pyrolysis liquids (without prior treatment) as such can successfully be co-fed in FCC, as already demonstrated by the Petrobras Company [15] as well as by other groups [5,16]. However, it proceeds at the expense of overall biomass-to-fuel carbon yield, while fully deoxygenated liquids might successfully be co-fed in the crude oil distillation as well, but require large amounts of hydrogen, rendering the process extremely costly [17–19].

Alternative processes have been tested such as the use of catalytic-pyrolysis-derived bio-oils [12,20,21], where it was found that still large amounts of oxygenates were present in the final products. Recently, Wang et al. have shown [21] that the addition of catalytic-pyrolysis-derived oil up to 10 wt.% gave nearly equivalent oxygenate content and also similar selectivity of gasoline, bottom oil, and coke compared to pure vacuum gasoil (VGO) catalytic cracking, suggesting the catalytic-pyrolysis-derived bio-oil was a suitable feedstock for FCC co-processing. However, the process of catalytic pyrolysis remains costly and complex, requiring a FCC like reactor to avoid fast catalyst plugging and deactivation [19]. A number of other studies on FCC co-processing using probe molecules or bio-oils model compounds have been published [22–25]. The general trends reported can be used to understand the more complex processes corresponding to real feedstocks.

This paper focuses on the impact co-processing has on standard FCC processing, depending on the degree and severity of the upgrading of added pyrolysis liquids. A series of bio-mass derived pyrolysis liquids, treated at different conditions to vary the overall hydrogen consumption, is used as a co-feedstock with a standard fossil oil based feed material in a standard MAT (microactivity test) unit for co-FCC testing using an industrial FCC catalyst. The amount of hydrogen consumed during the hydrotreatment step defines the severity of the prior hydrotreatment process. The obtained product distribution after co-FCC, especially the yields of naphtha, LCO (light cycle oil), slurry oil, dry gas, LPG (liquefied propane gas) and coke, is correlated with the severity of the treatment of pyrolysis liquids and changes in naphtha composition are presented, especially in terms of the octane rating.

2. Experimental

2.1. FCC catalyst

The FCC catalyst, an ultra-stabilized Y zeolite (USY) embedded in a macro-porous matrix, is provided by Grace GmbH & Co KG, and details are listed elsewhere [26]. Before use, the fresh FCC catalysts is deactivated following standardized protocols [27] applying a sequence of (i) metalation by a Mitchell impregnation (Ni and V naphthenates) to target levels of 250 ppm Ni + 1300 ppm V, (ii) a modified advanced cyclic propylene steaming (CPS3), (iii) a deactivation temperature of 816 °C and 40 redox cycles, (iv) a final reduction cycle.

2.2. Feedstock

The crude oil feed was a mixture of 74 wt.% hydrotreated vacuum gas oil (VGO) and 26 wt.% decanted oil (DO) recycle, used by REPSOL in commercial operation. For sake of simplicity, this blended crude oil feed will be referred to as VGO. The upgraded pyrolysis liquids were provided by BTG Biomass Technology Group BV and are obtained by pyrolysis of pine wood at 450–500 °C and a gas residence time of 1 s, as reported in [28]. This pyrolysis oil (PO) has been treated over a Ni-based catalyst (Picula™) at pressures of 200 bar and temperatures up to 250 °C [28]. After water removal, the partially deoxygenated oils (PDO) were further deoxygenated over the same Ni-based catalyst, leading to the samples labeled according the hydrotreatment temperature (see Table 1) and ultimately to a fully deoxygenated oil labeled as refined oil (RO) over a sulfided commercially available CoMo-based catalyst. Table 1 indicates the hydrogen consumption and the applied temperature for the different pyrolysis liquids upgrading steps.

2.3. MAT setup

A standard micro activity test unit (MAT) and protocol was applied to simulate the co-processing of pyrolysis liquid in an FCC unit. The MAT unit has been designed to perform up to four independent and consecutive fixed bed cracking tests following the specifications described by the standard method ASTM