



Feature Article

Co-processing of lignocellulosic biocrude with petroleum gas oils

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ABSTRACT

A biocrude was obtained via the catalytic hydrothermal treatment of lignocellulosic biomass. This was further co-hydroprocessed with Straight Run Gas Oil (SRGO) under desulphurization conditions. Amounts of biocrude of up to 20 wt% could be co-processed, while maintaining a diesel stream density within the specifications contained in the road diesel regulation EN 590. The changes in the diesel properties associated with an increasing amount of biocrude were not a simple linear function of biocrude content. Rather, some positive correlations seem to exist between biocrude and SRGO at low biocrude contents, possibly due to intramolecular hydrogen transfer, yielding a diesel stream with a better quality than would be obtained from simply mixing hydrotreated pure streams in a 80% to 20% ratio.

1. Introduction

The demand for liquid transportation fuels is expected to remain very strong in the decades to come, as it is likely that the increase in ICE (internal combustion engine) efficiency and the development of electric propulsion will be balanced by nearly a doubling of the car fleet in the next 20 years [1]. To fulfill the associated demand for liquid fuel, while striving to decrease CO₂ emissions, an avenue is provided by the introduction of unconventional resources such as biomass-derived fuels. First generation biofuels from edible sugars or oils have limited environmental benefit and supply. Meanwhile, large amounts of lignocellulosic biomass in the form of wood, leftovers or dedicated energy crops are available, with an estimated 1 billion tonnes per year for the United States alone [2]. Although insufficient to replace all of the liquid fuel currently produced, it certainly has the potential to meet a part of the demand. Several routes for the transformation of lignocellulose into liquid fuels are being industrialized, while attempting to compete with petroleum-based fuels on an unsubsidized or narrowly subsidized basis. Lignocellulosic materials may be deconstructed into their components (cellulose, hemicellulose and lignin) by chemical or enzymatic treatment and the sugars fermented into alcohols. The main obstacles to low cost cellulosic alcohols remain the pretreatment cost, and the constrained yield of alcohol per ton of dry biomass due to the presence of impurities in the sugar stream and the inability to ferment lignin [3]. Hemicellulose can be converted into high quality diesel via the Sylvan process [4,5]. The whole lignocellulose may also be gasified, and the

syngas processed through Fisher-Tropsch systems to yield a high quality hydrocarbon stream. The process was demonstrated, but the process efficiency is about 50% and the associated capital costs remain very high [6]. Moreover, with smaller scale units, adapted to the biomass supply network, these costs increase even further. Another process that takes advantage of processing the whole biomass is fast pyrolysis. While the process is cheap and the amount of energy of the dry biomass retained in the liquid biocrude can be above 60%, said biocrude quality is too low for a straightforward application to transportation fuel. Upgrading through hydrotreatment has proved to be challenging due to the high oxygen content, and the process requires harsh operating conditions [7]. Catalytic pyrolysis has been explored attempting to improve bio-oil quality while reducing mass yield through in-situ deoxygenation [8,9]. Another simple technology that treats the whole of the lignocellulose is hydrothermal treatment. In an aqueous medium when water is brought near its critical point (330–380 °C, 200–300 bar), the lignocellulose breaks apart yielding a liquid and some gas (essentially CO₂ with only very minor amounts of H₂, CO and CH₄). Compared to pyrolysis oil, this liquid is of higher molecular weight and stable with a substantially lower oxygen content that makes upgrading much easier [10–12]. As a result, the energetic content of the oil phase from hydrothermal treatment was reported in the range of 30–35 MJ/kg for a wide range of organic feeds [13] as compared to the energetic content of pyrolysis oil, often in the range of 15–20 MJ/kg depending on the water content [14]. However, the biocrude also still needs to be refined further to meet transportation fuel requirements. As

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an oxygenated, hydrogen-deficient feed, the best upgrading process is through hydrotreatment. It would be an advantage to process these biocrudes within existing refineries, taking advantage of the huge oil processing and distribution infrastructure available already. It has to be also taken into account that a world-scale biomass operation may process up to one million ton of dry biomass per year. With a very conservative mass yield of 25 wt% of low oxygen biocrude this translates into approximately 4000 barrels per day of biocrude, that is between 10 and 20 wt% of the throughput of a large scale gas oil hydrotreater. It is then sound to test co-processing of biocrude with gas oil in mixtures up to 20 wt%. Higher blend ratios would benefit from separate processing under optimized operating conditions and catalyst. Previous attempts to hydrotreat biocrudes from hydrothermal treatment required low space velocities in order to achieve full deoxygenation [15,16]. Instead, we have explored the co-processing of biocrudes from hydrothermal treatment in gasoil hydrotreating units with limited amounts of biocrude under common refining conditions, using common refinery catalysts.

2. Materials and methods

2.1. Biocrude preparation and characterization

The biocrude was taken from a 10,000 slurry tonnes per year capacity demonstration unit in which Pine woodchips, after comminution, were processed hydrothermally in the presence of a catalyst in a tubular reactor, yielding a raw biocrude. The woodchips are prepared by grinding to a suitable particle size for slurry pumping, suspended in water and raised to the operating reaction temperature by a combination of electrical heating, heat exchangers and supercritical steam injection. The slurry is pumped into a vertically oriented, serpentine tubular reactor [17]. Operating conditions are close to the critical point of water, typically sub-critical in the 330–350 °C temperature range and 200–250 bar [18]. The residence time in the reactor is typically around 20–30 min for woody biomass. At this stage the processing stream is an oil-water emulsion and contains a small amount of solid material, mostly ash from the feedstock. In the next step the stream is partially cooled and then directly flashed at the output of the high-pressure hydrothermal reactor, separating the produced gas and providing a means of heat recovery. The biocrude is typically denser than water and insoluble in water, ensuring a rapid and efficient separation of oily products and water phase. The catalyst and a number of water-soluble organics are removed with the water phase. These include products such as small ketones, acids and phenols that may be recovered from the aqueous stream for further valorization. On a dry basis the oily phase recovered accounts for up to around 35 wt% of the dry biomass reacted. This now already dewatered oil is further distilled to remove metals and the heaviest part of the biocrude (15–30 wt%) and to avoid the formation of coke upon heating at 350 °C or more in subsequent upgrading processes.

Elemental Analysis of the biocrude obtained after flash separation and distillation showed an oxygen content of around 12%, a low nitrogen content of 0.2%, no detectable sulphur (< 0.1%) and a carbon to hydrogen molar ratio of 1.36. This biocrude is of much higher quality than thermal pyrolysis oil, where oxygen contents as high as 40% with H/C molar ratio close to 1.0 are commonly found. The biocrude oxygen content and C/H ratio are indeed not too far from those of the triglycerides present in plant oils or animal fats that are currently commercially hydrogenated. Simulated Distillation (SIMDIS) of this oily product was also performed. Although SIMDIS data of oxygen-containing streams cannot be compared directly with those of pure hydrocarbon streams, since the removal of oxygen will result in a shift to lower temperatures, it nevertheless gives an upper limit of the boiling point ranges in the sample. In our case this indicates that the biocrude would be similar to a petroleum-based diesel stream, with 20 wt% boiling above 360 °C.

Table 1
Hydrotreatment catalyst properties.

Catalyst	NiMo
BET (m ² /g)	200
Pore Volume (cm ³ /g)	0.41
NiO (wt%)	5
MoO ₃ (wt%)	22

2.2. Hydrotreating catalyst physicochemical properties

A commercial sample of a NiMo supported on alumina was used as the hydrotreating catalyst. Its general properties are summarized in Table 1. While this catalyst is optimized for Gas Oil (GO) hydrotreating and hydrodesulphuration, it is not particularly optimized for hydrodeoxygenation, but is thought to have enough activity for treating blends with low amounts of biocrude without modifying operating conditions for GO treatment.

As the boiling point of the biocrude heaviest components lies in the range of Vacuum Gas Oil (VGO), the catalyst was shaped into 0.2 to 0.8 mm particles to avoid diffusion limitation, as is commonly done for laboratory VGO hydrocracking [19]. Before the run, the catalyst was sulphided *in-situ* at 400 °C with a stream of 10% H₂S in H₂ (120 ml/min) for at least 12 h.

2.3. Hydrotreating set-up

A fixed bed was used for the processing of Straight Run Gas Oil (SRGO) and its various mixtures with Biocrude (BIO) and/or Light Cycle Oil (LCO) from Fluid Catalytic Cracking. The liquid mixture is fed from a heated, stirred tank (60 °C) through an HPLC pump into the reactor, where it contacts with the catalyst in the presence of hydrogen. Liquids are collected in a condenser at room temperature below the reactor, while the non-condensed gases are released through a Back Pressure Regulator (BPR) valve and can be analyzed online by a gas chromatograph. 4 g of catalyst were mixed with Silicon Carbide (CSi) to adjust the total bed volume to 8 ml (9 mm internal diameter, 130 mm length) in order to attain bed isothermicity and avoid coke plugging. CSi layers of around 1 cm thickness are also added above and below the catalytic bed to act as preheater and minimize heat losses from the bed. After sulphidation of the catalyst, the reactor was set to operating temperature and the system was pressurized with hydrogen. Once the pressure was stabilized, feed injection was started. Feed rate was 4 g/h (Weight Hourly Space velocity 1 h⁻¹) and the hydrogen flow rate was maintained at 100 Nml/min, which represents 13.3 wt% of the liquid feed. As hydro-desulphurisation (HDS) usually consumes less than 1 wt% and hydrodeoxygenation (HDO) of Biocrude is expected to consume between 3 and 6 wt% based on the oxygen content of the feed, this large excess will ensure that hydrogen partial pressure remain high at every point in the reactor. After the system settles down for a 2–4 h period, mass balances were performed at regular intervals.

2.4. Mass balance and product analysis

For each mass balance, the liquids recovered from the separator were weighed. At least one gas analysis was carried out during the period. Gas samples were taken downstream of the BPR valve. CO, CO₂ and C₁–C₆ gas concentrations were determined. Coke yield was disregarded for the mass balance for being very low (< 0.2 wt% of the liquid fed), as confirmed later by the analysis of coke on the catalyst. When Biocrude was present in the feed, an aqueous phase formed a well-defined layer at the bottoms of the liquids, and could be easily extracted by pipetting. Water content was determined by Karl-Fischer Titration, such as to be able to calculate overall water yield. The oily phase was found to be substantially free of water. This phase was

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