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Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study

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ABSTRACT

An experimental study on hydrotreatment of ligno-cellulosic hydrothermal liquefaction (HTL) bio-crude to achieve a bio-feed compatible for co-processing at a refinery was made to investigate the effect of operating temperature, pressure and hydrogen to oil ratio. Using a conventional $NiMo/Al_2O_3$ hydrotreating catalyst at 350 °C and 337 NL H_2/L bio-crude, a promising bio-feed with 0.3 wt.% O, a HHV of 43.9 MJ/kg, a density of 894 kg/m^3 and an FT-IR spectra very similar to Northern Sea fossil crude oil was obtained. This work suggests that a gradual and sustainable phase-in of bio-feed through co-processing at existing refineries can be facilitated by intermediate hydrotreating of the bio-crude from hydrothermal liquefaction.

1. Introduction

Global energy demand in the transportation sector is increasing due to emerging markets and global growth [1]. The energy supply is however limited by depleting petroleum resources and decreasing resource quality [2]. Fig. 1 emphasises how the input to refineries on a long term scale is of decreasing quality, due to increasing densities and sulphur contents. The sulphur content has almost doubled since 1985, while sulphur allowances in fuel products are becoming stricter with a recent EU directive reducing the allowed sulphur content in marine fuel from 3.5% to 0.5% by 2020 [3]. Furthermore, it is a fact that greenhouse gas (GHG) emissions rise with refining of heavier crudes [4]. Meanwhile, environmental concerns necessitate ambitious efforts in mitigating GHG emissions. To resolve the mismatch between increasing environmental concerns, a growing energy demand and depleting resources of declining quality, the global dependence on fossil resources within transportation must be replaced by partly electric engines and partly a renewable feedstock that encloses the CO_2 cycle [5]. Pyrolysis and hydrothermal liquefaction (HTL) are thermochemical processes capable of converting biomass into liquid energy carriers [6]. In particular, HTL enables a feedstock-flexible conversion of non-food biomass to a liquid bio-crude with a higher heating value (HHV) reported around 35–40 MJ/kg [7], but recently measured above 40 MJ/kg [8]. Part 1 of this publication presents a TBP distillation curve for a HTL bio-crude with a large middle distillate fraction and around 47 wt.% atmospheric residue (>375°). Additionally, HTL bio-crudes possess higher quality than pyrolysis bio-oils as intermediate for biofuel production [9], due to oxygen contents around 5–10 wt.%, lower contents of corrosive carboxylic acids, kinematic viscosities as low as 10–20 cSt and lower water content around 0–5 wt.% depending on the separation method [8]. Though, with the above mentioned characteristics, the HTL bio-crude is still an intermediate that needs further, but significantly less, upgrading to be classified as compatible with existing transportation infrastructure [10]. In 2014 an extensive technoeconomic and lifecycle assessment made for the U.S. Department of Energy modelled the large scale production cost of liquid fuels from wood by pyrolysis+hydrotreating and HTL+hydrotreating respectively. HTL was concluded both more energy efficient and cheaper compared to pyrolysis and the production cost of a completely deoxygenated HTL fuel was estimated to 0.53 $ per litre gasoline equivalent [9]. The study is considered the most updated of its kind and the conclusions emphasise HTL as a relevant technology for drop-in biofuel production. Fig. 2 illustrates the HTL path from biomass feedstock to direct drop-in biofuel or bio-crude compatible for co-processing at an existing refinery.

Co-processing bio-crude with petroleum crude oil at existing facilities is considered a potential method towards obtaining com-

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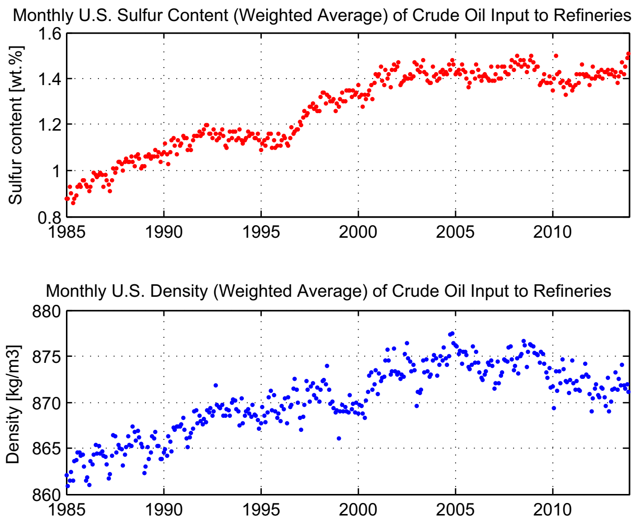

Fig. 1. Petroleum crude oil feeding U.S. refineries are generally becoming heavier and contain more sulphur [2].

petitive production prices of drop-in biofuels [11,4,12]. A currently accepted dogma that biofuels must be delivered as finished, transport grade fuels, is associated with costly drawbacks. Firstly, a potential bio-refinery that produces final fuel products from bio-crude only, requires complex and thus expensive processing units that can handle a varying bio-crude composition in order to produce on-specification products. This is due to the heterogeneous nature of biomass that the bio-crude will be made from [12,13]. Secondly, market penetration will become difficult by competing rather than cooperating with the petroleum industry. By co-processing the bio-crude at conventional refineries the point of market introduction is moved upstream, which make it an attractive market proposition compared to producing transport grade finished fuels. This paper will focus on the required upgrading path for HTL biocrude to be refinery co-processing compatible. Specifically, a parametric study on the influence of temperature, pressure and hydrogen availability is made to show that upgrading HTL bio-crude to a fossil substitute with unlimited drop-in abilities seem to be a promising addition to the overall conversion of biomass to refinery bio-feed.

Fig. 3 illustrates the concept of co-processing petroleum and bio-crude oil. For illustrative purposes, the drop-in location is chosen prior to the distillation column in this specific example, but may be located differently as discussed later. Given that the bio-crude has unlimited drop-in abilities, unlike bio-ethanol and bio-diesel, the drop-in percentage may be increased gradually along with an increase in the production capacity of the bio-crude. A gradual increase of the drop-in percentage enables a smooth phase-in, where feasibility of co-processing and availability of both bio- and petroleum crude oil can be balanced.

1.1. Refinery's perspective on co-processing

Bio-crude forms an alternative source of feedstock for the refinery. A feedstock that matches a demand for renewable fuel products that is likely to grow with global focus on sustainable energy resources [12]. Additionally, a feedstock that forms an alternative, when expenses related to processing crude oil increases due to a decrease in crude oil quality [12]. Finally, co-processing ensures full usage of capital intensive refinery capacity on a long term basis.

Bio-crudes that are possible alternatives for petroleum crude oil as refinery feedstock are sometimes included in the class of opportunity crudes [12]. Characteristics that make opportunity crudes differ from the benchmark petroleum crude include a TAN above 1 mg of KOH/g oil and a higher overall density (>900 kg/m^3) [12]. An opportunity crude is not necessarily renewable, but the characteristics match those of the HTL bio-crude studied in present study. Corrosion issues in refinery units are increased by processing a high TAN feedstock. Likewise, fouling, cetane reduction and product stability are risks that arise with the processing of an

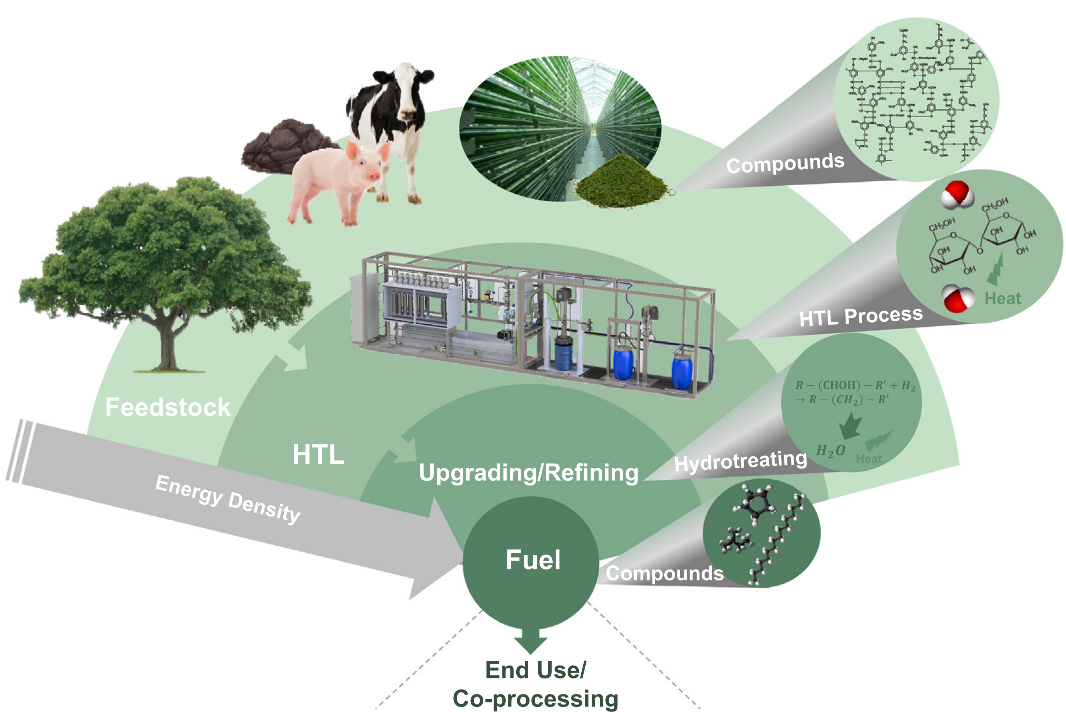

Fig. 2. HTL conversion of biomass to bio-crude, and subsequent upgrading/refining of the intermediate into drop-in biofuel [10].

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