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Study on phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates: A step toward bio-oil refinery integration

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ABSTRACT

To defossilize the current liquid energy backbone a sustainable renewable substitute for fossil crude oil is required. The long–term aim is to increase the co-feed of renewables beyond the current level. However, technical constrains and certain properties limit the conventional biogenic co-feed level to less than 10%.

The potential of identifying refinery compatible entry points to directly co-feed bio-based refinery intermediates and further co-process in existing petroleum crude oil refineries is investigated in the current study. The studied pyrolysis bio-oil has been upgraded via mild hydrotreatment (HDT) in order to fulfil specifications and become a "drop-in" biofuel in compatible refinery "location". The properties of HDT-Bio-oil as well as fossil-based refinery intermediates were compared and five fossil-based refinery intermediates have been concluded as potential candidates for co-processing. The miscibility of the aforementioned renewable and conventional fuels has been investigated. Among all refinery streams, Fluid Catalytic Cracking Light Cycle Oil (FCC LCO) and secondly Light Vacuum Gas Oil (LVGO) have been concluded to be the most promising candidates for co-processing, resembling HDT-Bio-oil's properties.

1. Introduction

The development of cost-competitive, diverse and sustainable liquid biofuels for today's transportation infrastructure has attracted the international research, market and governmental interest, with a number of policies and strategic environmental actions promoting their production as a means of sustainable development [1,2]. Specifically, the European Union (EU) target, as outlined in the Renewable Energy Directive (RED), is to increase the share of renewable energy in the transport sector up to 10% by 2020 [3]. The upcoming directive, RED II, is expected to set a higher level in the share of renewables by 2030 [4]. Toward this direction, to meet the objectives, new strategic EU policies have been developed supporting the replacement of linear economic models of today with circular and regenerative. However, the way toward circular economy and further bio-economy would necessitate first to link and integrate with different sectors, including the bio-based industrial sector (e.g. agriculture, bioenergy, bio-fuels) and the non-bio-based industrial sector (e.g. fossil-based refining). Developing symbiotic synergies between these different industrial partners may assist accelerating the transition to a competitive, resource efficient and low carbon economy by 2050.

Under this frame, several either bio-chemical or thermo-chemical technologies are being considered for producing biofuels. However, according to the European Industrial Bioenergy Initiative (EIBI) [5], launched under the Strategic Energy Technology (SET) Plan, fast pyrolysis is among the most promising [6]. Therefore, research focuses on developing and further validating strategies and innovative technological pathways that will overcome techno-economic limitations associated with the valorisation of pyrolysis bio-oil, as an alternative and renewable transport fuel. In this respect, bio-oil refinery integration appears to be of great perspective. However, certain challenges are related to the realization of this conceptual approach, in that these materials should be tailored to be chemically similar to existing refinery streams and therefore infrastructure-compatible.

Abbreviations: ASTM, American Society for Testing and Materials; CDU, Central Distillation Unit; CERTH, Centre of Research and Technology, Hellas; EIBI, European Industrial Bioenergy Initiative; EU, European Union; FCC, Fluid Catalytic Cracking; FCC HCO, Fluid Catalytic Cracking Heavy Cycle Oil; FCC LCO, Fluid Catalytic Cracking Light Cycle Oil; GASOIL, Atmospheric Gasoil; HDO, Hydrodeoxygenation; HDT, Hydrotreatment; HHV, Higher Heating Value; HPLC, High Performance Liquid Chromatography; HVGO, Heavy Vacuum Gas Oil; IBP, Initial Boiling point; Kin. Viscosity, Kinematic Viscosity; LVGO, Light Vacuum Gas Oil; NABC, National Advanced Biofuels Consortium; RED, Renewable Energy Directive; PONA, Paraffins, Olefins, Naphthenes and Aromatics; RI, Refractive Index; SET, Strategic Energy Technology; SRGO, Straight Run Distillate Diesel; TAN, Total Acid Number; UCTP, University of Chemistry and Technology, Prague; VGO, Vacuum Gas Oil

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Pyrolysis bio-oil has undesirable physical properties and limited storage stability [7]. In particular, bio-oil is a mixture of oxygenated compounds formed during the decomposition of lignin, hemicellulose, cellulose and water (produced during the process and from the inherent moisture content of the biomass). The heteroatom distribution in pyrolysis bio-oil differs from the characteristic of petroleum refinery fuels and therefore affects co-processing. The oxygen content is typically 45–50 wt%, the water content 15–30 wt% and the higher heating value of pyrolysis oil, HHV ~17 MJ/kg, relatively low compared to fossil fuels (HHV 45 MJ/kg) [8,9]. In addition, pyrolysis bio-oil is highly immiscible with non-polar liquid hydrocarbons due to its high polarity and hydrophilic nature [10]. All these properties render the direct co-processing of pyrolysis oil itself in standard refinery units at least problematic. However, bio-oil could be considered an alternative energy source with respect to environmental concerns, while it may assist fulfilling the bio-content regulatory requirements in transport fuels and strengthen energy diversity and security. In this perspective, also other bio-based feedstocks are used, as vegetable oils and residual lipids [11,12]. Nevertheless, conventional pyrolysis bio-oil requires upgrading aiming to reduce oxygen and water content and thus acidity, increasing its compatibility with fossil-based intermediates and thus enabling co-processing without the need for major refinery modifications. Several pyrolysis process modifications are currently being studied to obtain bio-oils of improved quality, such as catalytic pyrolysis. Pre-upgraded pyrolysis bio-oil via mild-HDT could be a potential refinery co-processing feedstock [13,14]. In particular, mild hydrotreated bio-oil is partially deoxygenated and the properties are tuned into a form that a refinery can process successfully.

In the present study the potential of identifying refinery compatible entry points to directly co-feed bio-based refinery intermediates, and further co-process in existing petroleum crude oil refineries is investigated. In the technological forum, cutting edge research studies address bio-oil co-processing with petroleum fractions highlighting the importance of detailed kinetic studies and product profiling [7,12–14]. Moreover, feedstock homogeneity is a key requirement for refineries. However, limited research works focus on the phase behavior and fuel properties of the considered binary blends. Relative conceptual approaches, found in the international scientific contribution, concern the multiphase phase structure and properties of bio-oils and its blends with alcohols and/or glycerol [15–17], while, co-solvents or emulsions are being proposed to increase solubility of pyrolysis oil [18]. Therefore, the current study aims to investigate the phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates in order to identify suitable refinery entry points and showcase the potential integration of bio-oils in the conventional refinery. In particular, 2nd generation biomass bio-oil produced via ablative fast pyrolysis and upgraded via mild catalytic hydrotreatement will be used. In order to identify possible petroleum refinery entry points (processing units) for introduction and integration of bio-oil, the following tasks have been conducted as part of the study's methodology:

A. Comparison of bulk fuel properties of HDT-Bio-oil with those of typical refinery streams.
B. Assessment of miscibility between HDT-Bio-oil and refinery intermediates.

The evaluation of phase bahavior and fuel properties, as indicators of compatibility between HDT-Bio-oil and refinery intermediates, has been conducted to: (a) indicate the physicochemical relativity between the liquids that will form the mixtures and (b) show the effect of HDT-Bio-oil addition to the refinery stream, in the underlying process. The study is part of "BioMates" Horizon2020 research and innovation EU project. The BioMates project aspires in combining innovative 2nd generation biomass conversion technologies for the cost-effective production of reliable bio-based intermediates that can be further upgraded in existing oil refineries as renewable and reliable co-feedstocks. The refinery intermediates, identified via this study as compatible with HDT-Bio-oil, will be further investigated via dedicated experimental testing on co-hydroprocessing. The study particularly targets to constitute a stepping stone towards further analyses and future directions for hydrotreatment of candidate mixtures at continuous, industrially relevant processes. Reaction pathways' investigations and in detail multi-parameter hydrotreatment testing will formulate the operating window (e.g. temperature, pressure, catalyst) and finalize the proposed strategy for successful operation. Therefore, the current miscibility study acts as a pre-screening of candidate feedstocks for the targeted hydrogenation study that will follow. However, the study has potential other applications, taking into account refinery's requirements to process only homogenous mixtures.

2. Refinery entry point candidates and bio-oil specifications

Bio-oil co-processing with petroleum fractions has attracted research and development interest [7,13,14]. However, a few research groups focus on the aforementioned binary blends feedstock investigations. Fogassy et al. have performed some miscibility tests of Vacuum Gas Oil (VGO) with hydrotreated pyrolysis bio-oil, which indicated that pyrolysis bio-oils having less than 20 wt% of oxygen content mix well with VGO, producing a homogeneous mixture [19]. All their tests were performed with VGO-hydrotreated pyrolysis bio-oils blends containing 20 wt% hydrotreated pyrolysis oil. De Miguel Mercader et al. have also performed some miscibility tests of hydrotreated pyrolysis bio-oils with Long Residue (Fluid Catalytic cracking, FCC, feedstock) [20]. Although the miscibility at room temperature was limited, especially for the bio-products obtained from milder hydrodeoxygenation (HDO) conditions, after mixing and heating to 75 °C the hydrotreated pyrolysis bio-oil was miscible with the petroleum fraction, which was also verified by utilizing the mixture in two consecutive experiments containing 20 wt% hydrotreated pyrolysis bio-oils. Moreover, regarding bio-oil refinery integration, the National Advanced Biofuels Consortium (NABC) has been running a project. Specifically, the NABC Refinery Integration team utilized analytical results to characterize the biomass-derived materials relative to typical petroleum refinery intermediates, blend stocks, and finished fuel blends. The objectives of the research group were to compare bulk properties of NABC products to those of refinery streams, and based on their comparison to identify probable entry points (processing units) for introduction and integration of NABC intermediates into the petroleum refinery. The latter analysis was based on bulk properties and mainly on boiling curves and gravities/densities [21].

Building on existing knowledge, the present study attempts to recommend suitable refinery fossil-based co-feeds in order to ingrate and co-process a bio-based feedstock and in particular, upgraded, partially deoxygenated bio-oil (HDT-Bio-oil). In this perspective, possibilities for bio-oil refinery integration could include:

A. Introduction into the Central Distillation Unit (CDU)
B. Blending with finished fuels
C. Integrating with refinery intermediates

The first option, which is actually ruled out, concerns the introduction of bio-oil in the CDU. The reactivity of bio-oil, due to the presence of oxygenated species, would lead to polymerization and molecular weight growth during distillation, especially since distillation operation takes place under heating [13,22]. Furthermore, the crude unit fractionates molecules. Therefore, blending a bio-based feedstock with crude oil, entering the CDU, would affect the downstream processes contaminating the refinery's streams, and moreover refinery's units that do not function for heteroatom removal. This bio-oil insertion pathway would primarily require extensive bio-oil upgrading via HDT to remove almost all of the oxygen present in the bio-oil [14,23].