



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 \sim 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 hydrotreatment 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 behavior 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].

The second possibility is related to the production of drop-in bio-fuels by blending HDT-Bio-oil of appropriate specifications with finished fuels. Specifically, bio-oil is converted to a near-finished fuel or blend. Blended component should meet all applicable standards for finished fuel. Therefore, in this case, multi-stage reaction schemes might be required to upgrade bio-oil. Developing tailored made upgrading processes suitable for bio-oil special characteristics would necessitate capital-intensive investment costs for the construction of a smaller scale, standalone unit [14,21,23].

Finally, the third technological pathway, which is the subject under study, concerns co-processing of HDT-Bio-oil with fossil-based intermediate(s) in underlying refinery process unit(s). Hydroprocessing is a widely applied technology in conventional refineries, commonly used to crack large molecules and/or to remove S, N and metals from petroleum derived feed stocks; thus processing several refinery intermediates [24]. Therefore, co-processing of HDT pyrolysis bio-oil in existing refinery facilities necessitates the identification of suitable refinery entry point(s) (of each of the resulting primary distillation and process-derived intermediates). In this case, the relative goal would be to succeed with minimum pretreatment requirements to convert the bio-oil into a form that a refinery can further process successfully [14,25–27]. The quality targets of the bio-oil are based on refinery process feedstocks' specifications, as defined by the petro-chemical industry that serve as product end-users. Toward this direction, important properties from the refiner's perspective involve [13]:

- (a) the boiling range distribution
- (b) the hydrocarbon types (Paraffins, Olefins, Naphthenes and Aromatics-PONA) and especially aromatic content and
- (c) heteroatom (sulphur, nitrogen, oxygen) content.

Therefore, based upon the bio-oil quality specifications, the potential entry points in the refinery were defined, revealing the optimal potential for directly co-feeding bio-oil in a compatible refinery process. The analysis was based on mapping several petroleum fractions' quality properties (i.e., boiling curve, gravity/density, overall elemental composition) within a conventional refinery, as schematically depicted in Fig. 1. The numbered streams were considered as possible entry points, comparing refinery intermediates' characteristics with bio-oil materials. In particular, the properties of the various refinery fractions, i.e. potential bio-oil "Entry Points" are juxtaposed in Table 1, which includes fuel properties that are either provided via related literature or via BP. It should be noted that the properties for streams 7, 10 and 12 are not a consideration in the present study. The study focuses on streams directed to hydrotreating units. Moreover, in Table 2 the properties of mild HDT-Bio-oil used for the purposes of this study are provided, focusing on those comparable to refinery intermediates' properties.

Furthermore, in order to effectively apply this blending strategy, Total Acid, Number (TAN) criteria should be also met by the mild hydrotreated bio-oil. The produced mixture of HDT-Bio-oil/fossil-based intermediate is expected to have reduced acidity, compared to HDT-Bio-oil, as a result of the dilution effect. However, HDT-Bio-oil TAN value should be lowered, in order to limit the acidity of a produced blend of specific HDT-Bio-oil/refinery intermediate ration to be less than 2 mg KOH per g oil [28].

The results of juxtaposition of HDT-Bio-oil and refinery intermediates' properties are presented in Table 3, indicating the compatibility and thus potential for co-processing. Based on the results (density, distillation data, and stoichiometric composition) the following refinery streams (numbered in Fig. 1) have been identified as potential candidates for co-processing with HDT-Bio-oil:

- *Straight Run Distillate Diesel (SRGO) equivalent to fossil intermediate No2*: SRGO is fractionated during crude oil atmospheric distillation and represents the main refinery stream addressed for diesel fuel production. The intermediate has quite low sulphur and aromatic

content and is subjected to hydrotreatment to improve its quality characteristics and meet diesel fuel specifications.

- *Atmospheric Gasoil (GASOIL) equivalent to fossil intermediate No3*: Atmospheric gas oil is a product of crude oil atmospheric distillation column. GASOIL serves as an FCC feedstock. This intermediate is usually subjected to hydrotreatment prior to the FCC process to reduce the quite high sulphur content.
- *Light cycle oil (FCC LCO) equivalent to fossil intermediate No9a*: Light cycle oil is a product of the FCC unit. FCC LCO presents increased sulphur and aromatic content. The high aromatic content and the resulting low cetane number render FCC LCO a low-quality diesel blend. Therefore, FCC LCO is subjected to hydrotreatment to reduce sulphur level to meet the appropriate specification and to saturate aromatics increasing its cetane number.
- *Heavy cycle oil (FCC HCO) equivalent to fossil intermediate No9b*: Heavy cycle oil is a product of the FCC unit. FCC LCO presents increased density and viscosity, while it contains high amounts of sulphur and aromatics.
- *Light vacuum gas oil (LVGO) equivalent to fossil intermediate No4*: Light vacuum gas oil is a product of the vacuum distillation column that processes atmospheric column's bottom stream. LVGO serves as an FCC feedstock. This intermediate is usually hydrotreated upstream an FCC unit in order to reduce the sulphur and nitrogen content.

3. Materials and experimental methods

Refinery intermediates and mild-hydrotreated 2nd generation biomass bio-oil samples were used for the purposes of the current miscibility study. Mild hydrotreated ablative pyrolysis oil (HDT-Bio-oil) was mixed to ~30 vol% with fossil-based refinery intermediates in order to evaluate the potential miscibility and moreover reactivity leading to agglomerates that can prohibit catalytic hydroconversion. Furthermore, analytical characterization of the samples has been carried out and results have been compared.

3.1. Raw material

Typical 2017 fossil-based refinery intermediates from a European BP refinery and upgraded bio-oil from University of Chemistry and Technology, Prague (UCTP) were delivered to Centre of Research and Technology, Hellas (CERTH), in order to study possible refinery entry points and specs for HDT-Bio-oil. The received HDT-Bio-oil and refinery intermediates were stored in a cool room (−6 °C) prior to experiments, to avoid degradation. Regarding bio-oil, the aqueous phase was separated prior to experimentation using a balloon separator.

3.2. Mixtures preparation

The miscibility of the HDT-Bio-oil/refinery intermediates was examined by preparing a set of binary bio-oil/ refinery intermediates mixtures, using the five pre-selected refinery streams (Table 3) and 30 vol% bio-oil. In particular, as described in the previous section on the identification of refinery's candidate entry points and HDT-Bio-oil specs, the five fossil-based candidates that were used were SRGO, GASOIL, FCC LCO, FCC HCO, LVGO. Therefore, the following mixtures have been prepared: (a) HDT-Bio-oil + SRGO (30/70), (b) HDT-Bio-oil + GASOIL (30/70), (c) HDT-Bio-oil + FCC LCO (30/70), (d) HDT-Bio-oil + FCC HCO (30/70), (e) HDT-Bio-oil + LVGO (30/70). The miscibility tests were performed at room temperature (~25 °C). The mixtures were intensively shaken manually till complete mixing of the two liquid samples was achieved.

3.3. Analytical characterization of samples

According to the needs of the present study, the following portfolio

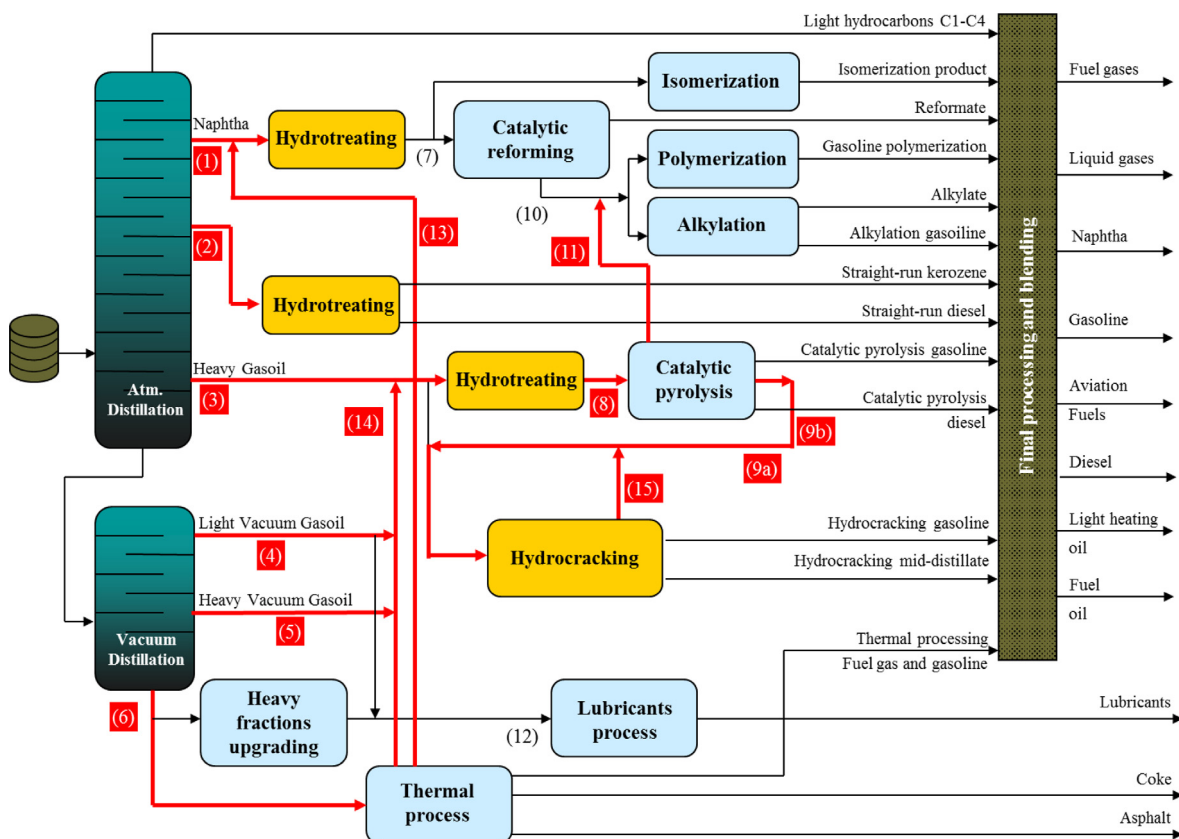


Fig. 1. Refinery diagram (Potential refinery entry points are numbered and highlighted in red colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of analytical methods was applied to the materials before and after the mixing tests. Sampling took place on the main volume of the product after mixing.

3.3.1. Analytical methods

The bulk density was measured via American Society for Testing and Materials method, ASTM D4052. The surface tension of the fuel samples was determined via ASTM D1331. Surface tension measurements were carried out at room temperature ($\sim 25^\circ\text{C}$). Kinematic viscosity was measured via ASTM D 445. The ultimate analysis was conducted based on ASTM D-5291 and ASTM D 4294. Refractive Index is determined based on ASTM D1218. Finally, distillation analysis was based on ASTM D 6352.

3.3.2. Microscope analysis

HDT-Bio-oil/refinery intermediates binary systems were investigated via light microscopy. In particular, the five mixtures of bio-oil/refinery intermediates were observed under Nikon ECLIPSE TE2000-S optical microscope in order to comparatively assess the homogeneity of the mixtures. Microscopy specimen was prepared by placing approximately 10 mg of sample between two standard microscopy glasses. The typical magnification level used for light microscopy images was 20, while the camera's magnification was 10 resulting in a total magnification of 200.

4. Results and discussion

4.1. Fuels characteristics

The characteristics of the samples, as received, are listed in Table 4. Furthermore, fuel properties of the selected HDT-Bio-oil/refinery intermediates mixtures are shown in Table 4, as well.

4.2. Phase behavior of HDT-Bio-oil/refinery intermediate binary mixtures

Miscibility of two streams can be measured as the homogeneity of the mixture. Since bio-oil is a micro emulsion [15] and the dark colour can mask the phase separation lines, good miscibility of the bio-oil/refinery intermediates mixtures was considered when a microscopic image similar to that of bio-oil was obtained. The approach is in consistency with previous research work on bio-oils' mixtures phase behavior [16].

In Fig. 2, the samples, as placed in microscopy glass, are illustrated. It is evident, even with naked eyes, that the mixture HDT-Bio-oil + LCO presents the best miscibility. Microscope analysis results (at a total magnification level of 200) are presented in Fig. 3. The miscibility of bio-oil with the 5 different refinery streams was comparatively assessed. The different samples were microscopically "scanned" in order to observe the phase appearance over different locations. Three sets of analysis under optical microscope took place, to evaluate the homogeneity over different sample locations. The results have shown the challenges in blending bio-oil with refinery intermediates. When putting the samples under the microscope cover glass, low viscosity samples spread around more than the viscous ones. Consequently, the layer thickness of viscous samples was higher than the one of low viscosity samples. Then, the colour intensity in the microscopy images reflected both sample colour and liquid layer thickness.

Bio-oil has a net-work structure [15]. In absence of additives (e.g. methanol), bio-oil molecules tend to attract to each other rather than disperse in petroleum fraction structure. The strong intermolecular forces make it difficult to disperse unless appropriate amount of compound(s) with comparable intermolecular force could be engaged [29]. Although it is possible for some components of bio-oil to be individually soluble with a petroleum fraction, such accessibility might be low due to a network structure formed by some heavy compounds (e.g.,

Table 1
Fossil-based refinery intermediates' properties^a.

	Stream in Refinery Diagram	(1)	(2)	(3)	(4)	(5)	(6)	(8)	(9a)	(9b)	(11)	(13)	(14)	(15)
Properties														
Density		0.69–0.74	0.82–0.85	0.79–0.86	0.89–0.91	0.92		0.89	0.86–0.93	0.98–1.01		0.76–0.77	0.85–0.88	0.82–0.86
Kin. Viscosity			1.50–9.95	10.30–21.00	> 20.50	54.29	58.46		< 7	140.6				
Refractive Index (RI)			1.4633	1.4377–1.4781	1.478	1.4927	1.496		1.5026–1.5169				1.4774–1.4814	
Conradson carbon				0.14	0.11		0.05							
Sulfur		0.21–0.62	0.30–0.70	1.25–1.45	1.31–2.75	1.30	1.00–6.00	0.14	1.25–3.50	1.72	0.05–0.15	0.05–1.10	0.49–3.20	0.001–0.01
Nitrogen			200	473.57	1441	1386.4	300–500						240–482	4–10
H ₂ Content			12.37	12.25–13.00	12.60			13.83						14.57
Carbon			87.60	85.37	0.09									85.11
Distillation Data														
IBP			166.0	152.0–211.0	198.0				152.0–200.0				130.0–168.0	253.0–272.0
10 vol%		60.0–80.0	234.0	287.6–367.0	361.0	403.6		366.0	225.0				190.0	371.0–380.0
20 vol%						424.0			243.2					
50 vol%		88.0–116.0	276.0	372.2–449.0	432.0	467.4		463.0	275.0				240.0	419.0–423.0
80 vol%						527.5			231.6					
90 vol%		113.0–175.0	310.0	421.0–528.0	445.0–494.0	561.6	565.0 +	541.0	331.0–360.0				326.0–360.0	465.0–473.0
Water			0.002	0.019	60.0				72.0–87.2				41.0	5.2 (1.35)
Aromatics distribution														
Refs.			[34]	[35]	[19,36]	[37]			[34,38]				[39]	[40,41]

^a Based on BP data and literature

Table 2
Properties of HDT-Bio-oil used in the current study.

HDT-Bio-oil (Current study)			
Density (20 °C)	kg/m ³	ASTM D4052	991
Kin. viscosity (40 °C)	cSt	D 445	45.39
	C	wt%	75.01
	H	wt%	ASTM 9.64
	N	wt%	D-5291 0.99
	O ^b	wt%	13.40
	S	wt%	ASTM D 4294 0.96
	Water	wt%	ASTM D95 3.72
Ref. Index		ASTM D1218	1.5175
	IBP	%	37.6
	10	%	173.8
	20	%	214.6
	50	%	320.2
	90	%	590.2

^b Calculated by difference (100- wt% C - wt% H - wt% N - wt% S, dry basis).

oligomers) in bio-oil [15,30]. On the other hand, additives such as methanol or amphiphilic compounds could help the dispersion of bio-oil.

Based on the aforementioned findings, the following remarks have been concluded: First, bio-oil and refinery intermediates are in general not miscible, as it has been also extensively reported in open literature [10,31]. Second, for the binary system of bio-oil/refinery intermediates, some components of bio-oil appeared to be soluble in petroleum fractions. Third, blends of some petroleum fractions with bio-oil present improved miscibility compared to each other. As in this study no additives were used to improve the miscibility, Fig. 3 presents following descended order for miscibility: LCO > LVGO > HCO > SRGO > GASOIL. In particular,

1. HDT-Bio-oil in all sets of analyses appears to have the same appearance. Dissolved water, waxy, heavy compounds and probably solid particles are observed.
2. HDT-Bio-oil + SRGO (30/70) sample is not homogenous. Different phases are observed and dark coloured agglomerates.
3. HDT-Bio-oil + GASOIL (30/70) sample is not homogenous. Different phases are clearly observed in 50 µm scale and dark coloured agglomerates.
4. HDT-Bio-oil + LCO (30/70) sample is homogenous. Waxy, heavy compounds that exist in HDT-Bio-oil have been transferred to the mixture. The images are comparable to those of HDT-Bio-oil.
5. HDT-Bio-oil + HCO (30/70) sample appears to have quite good homogeneity. Bio-oil compounds that are not soluble in HCO tend to agglomerate forming large particles.
6. HDT-Bio-oil + LVGO appears to have quite good miscibility with LVGO. Different phases are attributed to dissolved water and hydrophobic, non-polar compounds.

4.3. Fuel properties evaluation

Fuel properties evaluation has been conducted to: (a) indicate the physicochemical relativity between the liquids that will form the mixtures; HDT-Bio-oil and refinery intermediates, and (b) show the effect of HDT-Bio-oil addition to the refinery stream, in the underlying process.

Table 3
Combination matrix - Juxtaposed properties of HDT-Bio-oil and refinery intermediates (Potential co-processing pairs for further investigation are marked).

Co-processing candidates	Fossil-based Intermediates															
	1	2	3	4	5	6	7	8	9a	9b	10	11	12	13	14	15
HDT-Bio-oil		X	X	X					X	X						

4.3.1. Density

The density of the fuels (kg/m³), and in particular, density measurements of HDT-Bio-oil, refinery intermediates and their 30/70 blends, and the relative difference between the densities of HDT-Bio-oil and the selected refinery intermediates (%) are presented in Fig. 4. The density of the fuel blends ranges between 865 and 1064 kg/m³; they are close to or slightly different than those of refinery intermediates but differ from the corresponding bio-oil values. Regarding the relative difference between the densities of HDT-Bio-oil and the selected petroleum fractions (%), the following descending order in values is reported: FCC HCO < FCC LCO < LVGO < GASOIL < SRGO. Differences in densities between HDT-Bio-oil and refinery intermediates partially explain poor miscibility [18].

4.3.2. Viscosity

Viscosity is a measure of the resistance of a liquid to flow [32]. The viscosity of HDT-Bio-oil and refinery's intermediates (cSt), and the absolute relative difference in viscosity between HDT-Bio-oil and refinery's intermediates, as per the values of viscosity of refinery intermediates is presented in Fig. 5.

Viscosity measurements on blends have not been conducted. The viscosity of HDT-Bio-oil is significantly different from the viscosities of the refinery's intermediates. The viscosity of the blends are actually expected to represent an average of the viscous and much less viscous fuel liquid [18]. However, great differences between the values of viscosities of the blending components have as a result poor miscibility. Therefore, during the performance of the relative analytical characterization method for viscosity, anomalous shear forces are developed that result in false viscosity measurements, artifacts of the specific measurement process [18]. Regarding the relative difference between the viscosities of HDT-Bio-oil and the selected petroleum fractions (%), SRGO present the greatest differences, while FCC LCO, FCC HCO and LVGO present the smallest differences, as per the corresponding refinery's intermediates values.

4.3.3. Surface tension

The surface tension of fuels (dynes/cm) and relative difference between the surface tension of HDT-Bio-oil and the selected refinery intermediates (%) are presented in Fig. 6. Homogeneity of mixtures is related with similarities in physicochemical properties that reflect the type of intermolecular forces (adhesive and cohesive forces). Increased surface tension is correlated with oxygen containing compounds. Surface-tension for mixtures of liquids has been reported as difficult to predict. It has been noticed in many cases that fractional components of a mixture affect surface tension without correlating well with the amount of that component [33].

The measured surface tension of the fuel blends is ranged between 27.4 and 33.2 dynes/cm, respectively; values are close to or slightly different than those of refinery intermediates but differ from the corresponding bio-oil values. Regarding the relative difference between the surface tension of HDT-Bio-oil and the selected petroleum fractions (%), the following descending order in values is reported: FCC LCO < LVGO < FCC HCO < GASOIL < SRGO.

4.3.4. Distillation

The boiling range distributions for HDT-Bio-oil and the five refinery intermediates are presented in Fig. 7. Comparing distillation data, as Fig. 7 depicts, HDT-Bio-oil, at low temperatures (< 350 °C), simulates

Table 4
Properties of HDT-Bio-oil, petroleum intermediates (as received) and their mixtures.

			HDT-Bio-oil	SRGO	GASOIL	FCC-LCO	FCC-HCO	LVGO	HDT-Bio-oil + SRGO	HDT-Bio-oil + GASOIL	HDT-Bio-oil + LCO	HDT-Bio-oil + HCO	HDT-Bio-oil + LVGO
Surface tension	dynes/cm	ASTM D1331	31.3	27.2	29.8	30.5	33.7	30.1	27.4	29.3	30.1	33.2	29.9
Density (15 °C)	kg/m ³	ASTM D4052	1011.3	850.4	886.1	929.2	1077.5	855	865.1	895.0	957.1	1064.2	911.6
Kin. viscosity (40 °C)	cSt	D 445	45.4	1.5	20.5	6.9	140.6	22.0					
C	wt%		75.01	87.20 ^a	86.37 ^a	88.41 ^a	89.46	85.48	82.63	82.14	84.41	85.34	82.02
H	wt%	ASTM	9.64	12.37 ^a	12.50 ^a	9.10 ^a	7.95	12.68	12.84	12.53	9.32	8.25	11.64
N	wt%	D-5291	0.99	0.02 ^a	0.05 ^a	0.05 ^a	0.26	0.14	0.28	0.24	0.29	0.37	0.42
O ^b	wt%		13.40	0.01	0.73	0.19	0.02	0.02	3.44	4.18	3.96	4.17	4.47
S	wt%	ASTM D 4294	0.96	0.40 ^a	0.35	2.25 ^a	2.31	1.68	0.81	0.91	2.02	1.87	1.45
Water	wt%	ASTM D95	3.72										
RI		ASTM D1218	1.5175	1.4696	1.4902	1.5457	1.568	1.4968	1.4752	1.4921	1.5418	1.5893	1.4976
IBP	wt%		37.6	182.7	246.3	183.0	226.0	204.6					
5	wt%		137	222.8	305.4	209.0	328.0	286.0					
10	wt%		173.8	237.8	328.3	216.4	339.7	319.8					
20	wt%		214.6	255.2	353.8	225.0	357.0	362.6					
Distillation Data	30	wt%	245.8	269.0	369.6	233.3	372.9	392.6					
	40	wt%	280.2	279.2	382.1	241.4	388.0	416.0					
	50	wt%	320.2	288.7	393.1	250.5	403.3	435.2					
	60	wt%	376.2	299.5	404.1	261.1	420.7	452.4					
	70	wt%	437.4	310.9	415.5	273.4	442.6	469.6					
	80	wt%	509.2	322.2	428.3	287.2	472.3	488.8					
	90	wt%	590.2	338.5	445.8	304.7	519.2	514.0					
	95	wt%	640.8	351.7	461.3	317.5	568.4	533.0					
	100	wt%	736.8	362.8	503.4	328.1	688.7	574.8					

^a Estimations based on BP data and literature.

^b Calculated by difference.

mostly FCC LCO and SRGO, while at high temperatures (> 450 °C) simulates FCC HCO and LVGO.

4.3.5. Heteroatom distribution

Concerning the heteroatom distribution (wt% oxygen, nitrogen, sulphur content) in the 30/70 mixtures of HDT-Bio-oil/refinery intermediates, the corresponding theoretical values for ideal (totally miscible) mixtures have been calculated. The calculated values of fuel mixtures are obtained via direct addition, considering each relative value of individual fuel compound and the percentage of each individual compound in the fuel blend mixture. The differences between the calculated values and the corresponding measured values, are attributed to poor miscibility, while the relative differences between the aforementioned values were considered as indicators of the degree of miscibility. The relative differences between the theoretical calculated values and the measured ones via ultimate analyses (Table 4), are presented in Fig. 8. It is concluded that HDT-Bio-oil blends with FCC LCO and LVGO present smallest differences.

4.3.6. Refractive index

The relative change in refractive index values between refinery's intermediates and their mixtures with HDT-Bio-oil is presented in Fig. 9. Table 4 presents the measured values of refractive index for

HDT-Bio-oil, refinery intermediates and their corresponding 30/70 mixtures. Specifically, the refractive index is a measure of aromaticity and unsaturation for a given liquid and it is used as a means of process control. Furthermore, since RI reflects the degree of unsaturation, its value is associated with hydrogen consumption during hydrotreatment. Therefore, RI is measured to indicate the effect of feedstock variation on the downstream refinery process (hydrotreatment). Comparing the mixtures, the following have been concluded: HDT-Bio-oil + SRGO (30/70), HDT-Bio-oil + GASOIL (30/70), HDT-Bio-oil + FCC HCO (30/70) and HDT-Bio-oil + LVGO (30/70) mixtures presented increase in refractive index values in comparison with the corresponding values for refinery intermediates. In particular, HDT-Bio-oil + LVGO (30/70) has shown the smallest% increase in refractive index value relative to LVGO, while it should be noted that HDT-Bio-oil + FCC LCO (30/70) has shown decrease in refractive index value relative to FCC LCO among all mixtures.

4.4. Comparative assessment

The current study investigates the phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates in order to identify the appropriate refinery entry points and showcase the potential integration of bio-oils in the conventional refinery. In particular,

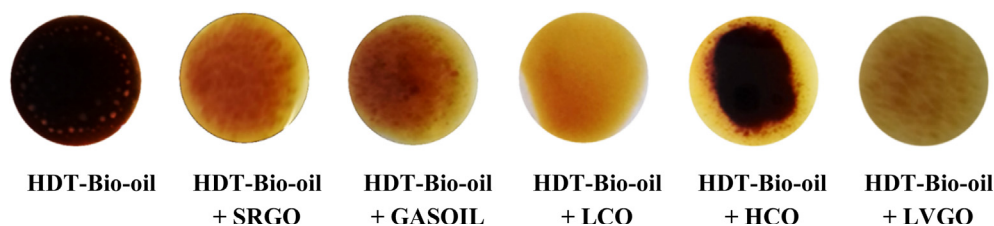


Fig. 2. Samples of bio-oil and their mixtures with petroleum intermediates, as placed on microscopy glasses.

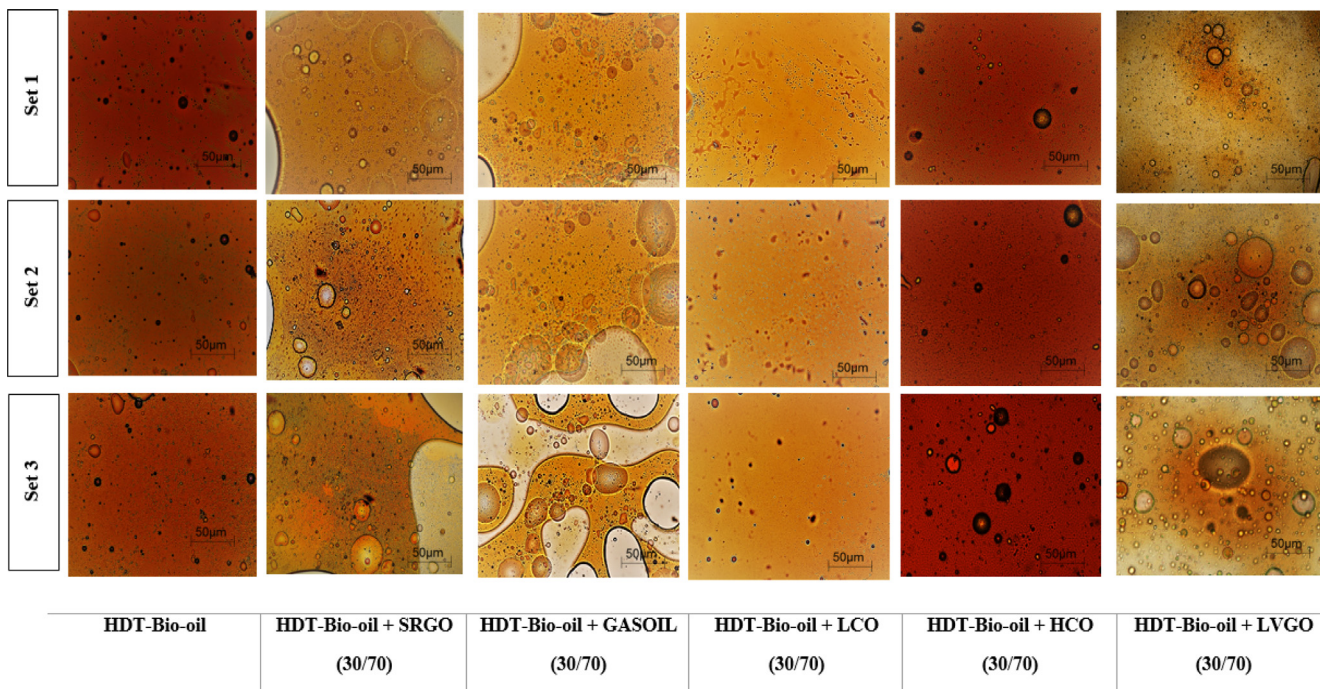


Fig. 3. Microscope analysis images of HDT-Bio-oil, selected petroleum fractions and their (30/70) mixture, respectively (magnification level for light microscopy images: 20; camera's magnification: 10).

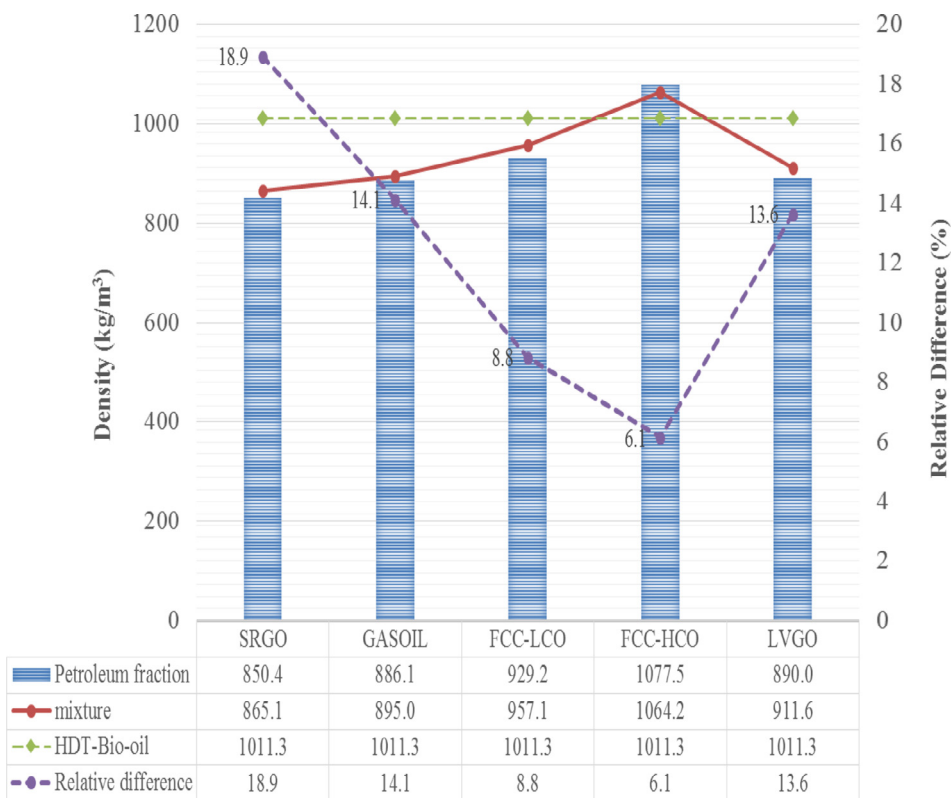


Fig. 4. Density of fuels (kg/m³) and relative difference between the densities of HDT-Bio-oil and the selected petroleum fractions (%).

the technological pathway under study concerns refinery integration of mild hydrotreated pyrolysis bio-oil.

On the basis of the experiments that were carried out in this study, the results suggest possible refinery streams, as candidates for downstream co-hydroprocessing with HDT-Bio-oil. SRGO, GASOIL, FCC LCO, FCC HCO and LVGO, which correspond to refinery streams No2, No3,

No9a, No9b and No4, respectively, as presented in Fig. 1, have been concluded as potential refinery entry points for the pre-upgraded bio-oil. A comparative assessment of possible refinery process locations for insertion of the HDT-Bio-oils is presented in Table 5.

The study focuses on feedstock investigations to show the potential technical bottlenecks for the hydrotreatment operation using the

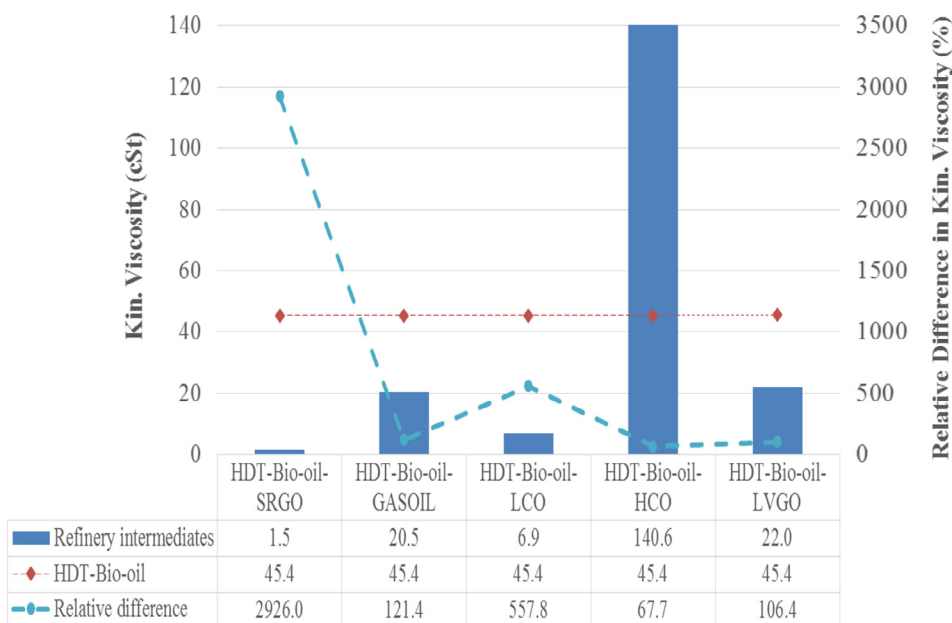


Fig. 5. Viscosity of HDT-Bio-oil and refinery intermediates (cSt) and relative difference between the viscosity of HDT-Bio-oil and the selected petroleum fractions, as per the values of viscosity of refinery’s intermediates (%).

considered mixtures. The aforementioned potential technical constrains could be related to diffusion of reactants and products and catalyst pore blockage due to immiscibility and reactivity effects leading to

agglomerates formation. 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

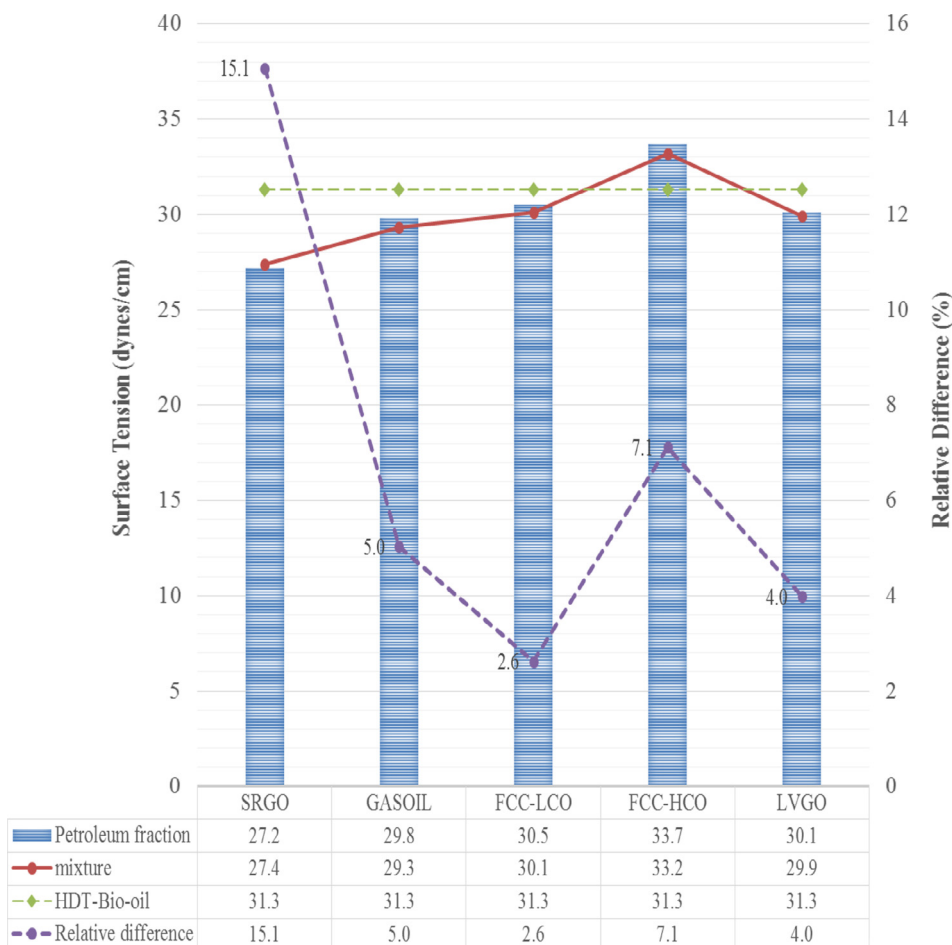


Fig. 6. Surface tension of fuels (dynes/cm) and relative difference between the surface tension of HDT-Bio-oil and the selected petroleum fractions (%).

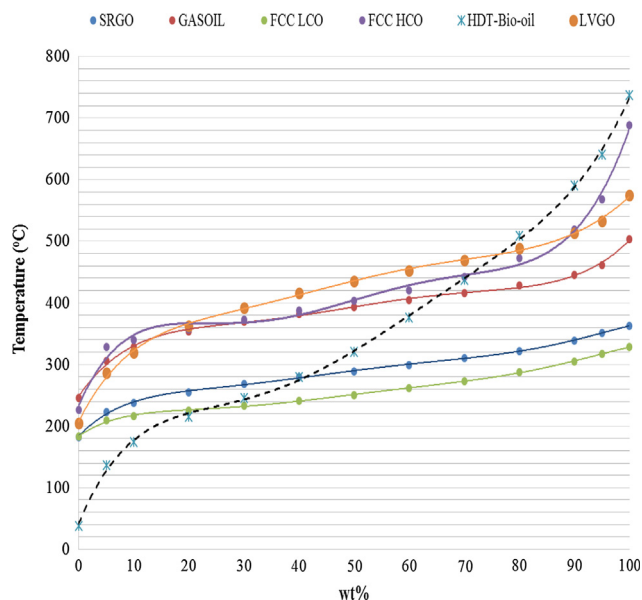


Fig. 7. Distillation curve of fuels (HDT-Bio-oil and selected petroleum fractions).

particularly targets to constitute a stepping stone towards further analyses and future directions for hydrotreatment of candidate mixtures at continuous, industrially relevant processes. In particular, 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 in industrially relevant environment. Although, the present miscibility assessment acts as pre-screening of candidate feedstocks for the targeted hydrogenation study that will follow-up, the study has potential other applications, taking into account refinery’s requirements to process only homogenous mixtures/feedstocks.

5. Conclusion

HDT-Bio-oil co-processing with refinery streams and validation that renders reliable late-stage research operation data, necessitated a miscibility study to identify compatibility of bio-based feedstocks with refinery’s intermediates. Toward this direction, the quality properties of typical refinery streams were used to define HDT-Bio-oil specifications for refinery integration. Based on the results (density, distillation data, and stoichiometric composition) the following refinery streams have been identified as potential candidates for co-processing with HDT-Bio-oil:

- Straight Run Distillate Diesel (SRGO)
- Atmospheric Gasoil (GASOIL)
- Light cycle oil (FCC LCO)
- Heavy cycle oil (FCC HCO)
- Light vacuum gas oil (LVGO)

Taking into account all the parameters of the previous comparative, multi-parameter analysis (phase behavior, density, surface tension, distillation data, refractive index), FCC LCO and LVGO have been concluded to be the most promising candidates for co-processing, resembling HDT-Bio-oil’s properties.

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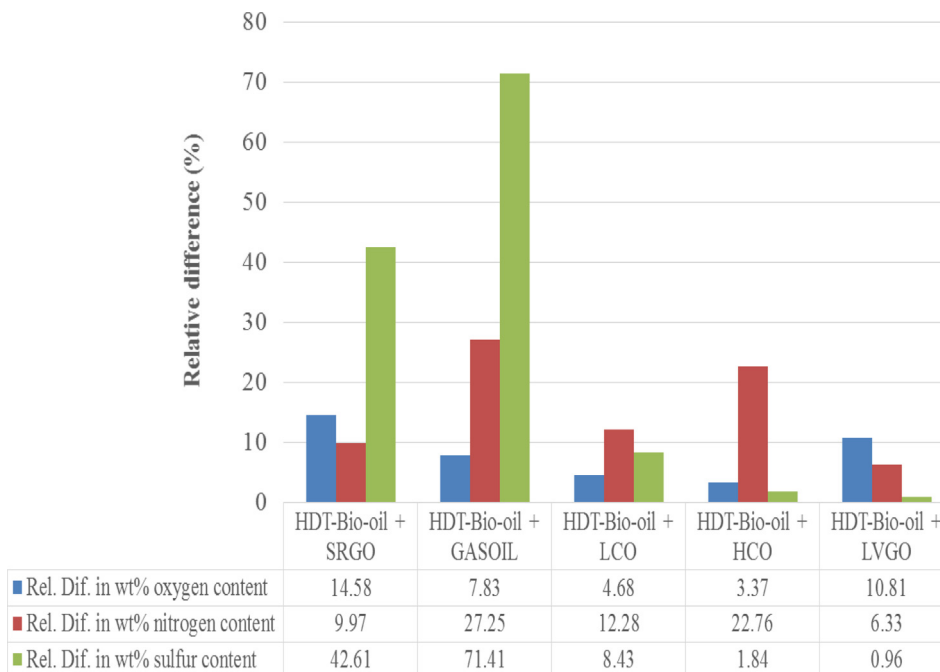


Fig. 8. Relative difference (%) in heteroatom content between measured values via ultimate analyses and calculated theoretical values for ideal (30/70) mixtures of HDT-Bio-oil/refinery intermediate.

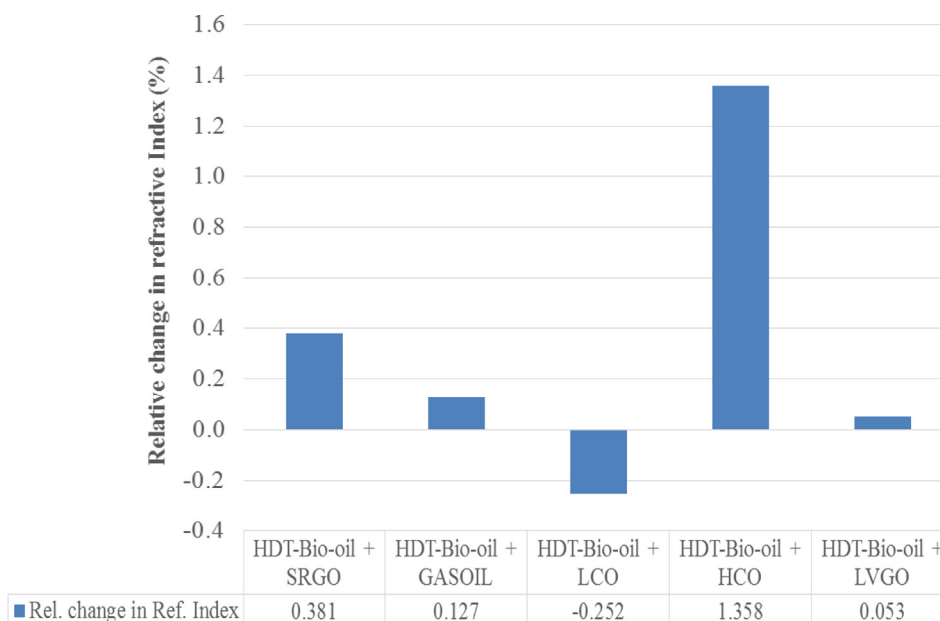


Fig. 9. Relative change in refractive index values between refinery's intermediates and their mixtures with 30 vol% HDT-Bio-oil (negative values represent% relative decrease).

Table 5
Refinery integration comparative assessment.

Candidate entry points	Process unit	Remarks
FCC LCO	Hydroprocessing	Good miscibility. The binary blend presents increased homogeneity. Experimental analyses of density, viscosity, elemental composition, RI and boiling point distribution reveal good matches for the binary blend. HDT-Bio-oil resembles the properties of FCC light cycle oil (LCO). Likely to follow the same processing path as FCC LCO
LVGO	Hydroprocessing	Quite good miscibility. Different phases attributed to dissolved water and mostly to hydrophobic, non-polar compounds. HDT-Bio-oil resembles the properties of LVGO. Density, viscosity, elemental composition, RI and boiling point distribution reveal quite good matches for the binary blend. Could follow the same processing path as FCC LVGO
FCC HCO	Hydroprocessing	Quite good miscibility. Agglomerates are formed that could cause catalyst blocking. HDT-Bio-oil resembles the properties of FCC heavy cycle oil (HCO). Quite good matches in density, viscosity, elemental composition, RI and boiling point distribution. Could follow the same processing path
SRGO	Hydroprocessing	Quite bad miscibility. Different phases are formed. Experimental analyses reveal comparatively greater differences in properties. Not such a good candidate
GASOIL	Hydroprocessing	Rather bad miscibility. Different phases and agglomerates are formed. Experimental analyses reveal comparatively greater differences in properties. Not a good candidate

Czech Republic, and Dr. Ulrich Pfisterer of BP Europa SE for providing the HDT-Bio-oil and refinery samples respectively.

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