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Bio-based refinery intermediate production via hydrodeoxygenation of fast pyrolysis bio-oil

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ABSTRACT

Pyrolysis bio-oil is unsuitable as transportation fuel due to its chemical composition and high oxygen (>30 wt%) and water (>20 wt%) content rendering the upgrading essential prior any downstream use. The current work investigates the upgrading of a flash pyrolysis bio-oil via mild hydrotreatment (HDT), targeting to a potential intermediate refinery feed. Various operating parameters of HDT were tested, including three temperatures (573, 603 and 633 K), two pressures (4 and 7 MPa) and two H_2/bio-oil ratios (506 and 843 NL/L). According to the results, during HDT of bio-oil, massive plugging by coke formed in the reactor. The unsaturated oxygenates in bio-oil are regarded as the predominant coke precursors since they can interact with the catalytic surface. From all the examined conditions, it was found that the longest catalyst life, (5 days on stream), was achieved at 7 MPa pressure, 843 NL/L H_2/bio-oil ratio and 603 K temperature. Furthermore, several properties of the initial bio-oil were improved, such as viscosity (156 → 4.9 cSt), carboxylic acids (78 → 0.2 mgKOH/g), density (1.024 → 0.9162 g/ml), and oxygen content (37 → 4 wt%). Conclusively, mild HDT constitutes a promising technological pathway for bio-oil upgrading towards a reliable intermediate refinery feed.

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1. Introduction

The production of renewable liquid transportation fuels attracts the international research and the market interest, in line with the ambitious 2020 and 2030 energy and climate targets set by the European Union (EU) policy, considering the increasing global demand for their fossil counterparts and the resulting environmental impacts. On this basis, the utilization of non-food/feed biomass is promoted, while the most promising bio-chemical and thermo-chemical value chains for biofuels production have been prioritized by the European Industrial Bioenergy Initiative (EIBI, 2019) [1] under the Strategic Energy Technology (SETIS, 2019) Plan [2], listing pyrolysis among them. Today, conventional biofuels such as FAME (Fatty Acid Methyl Esters) biodiesel are used as blending components with petroleum-based products to meet the current demands for conventional diesel fuel with 7 v/v % bio-content (EN 590 standards for ultra-low Sulphur diesel). However, there are some drawbacks from using FAME biodiesel as an alternative diesel-type fuel, such as, its lower energy content over conventional diesel, its high oxygen content, low stability etc. [3,4]. Because of the unfavorable properties of FAME, catalytic hydroprocessing of triglycerides for paraffinic fuels production has been widely explored. These new advanced paraffinic fuels are called HVOs (hydroprocessed vegetable oils) or green diesel (hydroprocessed used cooking oil) [5,6]. However, these advanced biofuels (HVOs or green diesel) are associated with higher retail prices and demand high investment costs, justifying only high throughput plants [7,8]. To minimize the enormous investment costs, co-hydroprocessing of heavy petroleum fractions with bio-based feedstocks is currently being explored, utilizing the underlying conversion capacity of the

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existing refineries. Various types of feedstocks have been studied for their co-processing effectiveness [7].

Among the organic fractions considered for co-processing feedstocks, bio-oil from fast pyrolysis of lignocellulosic biomass is investigated, aiming to increase the share of advanced biofuels in the diesel pool. Pyrolysis is a fundamental thermochemical technology, operating in an inert atmosphere and high temperatures (673–1073 K), cracking large biopolymers (20,000 to 400,000 a.m.u.) into smaller molecules (less than 200 a.m.u.) with relatively higher energy content [9,10]. The pyrolysis products are classified in liquid, solid and gaseous fractions. The maximization of the liquid fraction, bio-oil, is achieved via fast pyrolysis that applies high heating rates. By applying ablative fast pyrolysis (AFP), the energy-intensive grinding of the straw, which is essential in the case of fluidized-bed pyrolysis, could be avoided [11,12].

Pyrolysis bio-oil is very unstable due to its acidity, high oxygen content, high concentration of the thermally labile compounds, such as olefins and aldehydes/ketones, and high concentrations of heavy compounds. Therefore, bio-oil upgrading is necessary for bio-oil to be used in the transportation sector [13]. Toward this direction, hydrotreatment (HDT) and in particular hydrodeoxygenation (HDO) appears to be of great perspective to address this challenge [14–16]. In particular, bio-oil is treated at a temperature range (573–723 K) under high pressure hydrogen atmosphere ($\leq$13.8 MPa), using heterogeneous catalysts [17]. HDO results in bio-oil oxygen removal in the form of water through a series of C–C, C–O–C and C–OH bond cleavage, and hydrogenation reactions [18,19]. Deoxygenated bio-oil is an energy dense and non-corrosive product, with boiling point within diesel range, and oxygen content less than 2 wt% [20]. However, the high hydrogen partial pressure required, as well as the catalyst coking under high temperatures, are the main issues that have to be addressed for the sustainable improvement of the current technology. In particular, many bio-oil components become very reactive when heated up, tending to form coke, and thus leading to reactor fouling and product deterioration [21–24]. For this reason, an additional stabilization step has been suggested to suppress or prevent the coke formation leading to a stabilized mild hydrotreated bio-oil [25,26].

Mild HDT involves medium-severity hydrotreating conditions that allow the partial oxygen removal from the bio-oil and partial hydrogenation, rendering a stabilized bio-based intermediate that can be more efficiently handled upon downstream processing [17]. Mild HDT was employed as a first low temperature stabilization step of bio-oil, in which the carbonyl groups are hydrogenated into more stable alcohols [27]. The mild catalytic hydrotreatment of the bio-oil, according to Ref. [23], involves an operating window for temperatures ranging from 423 to 673 K and pressures over 5 MPa, other study [28] suggests that the first stabilization step should take place at a temperature range between 373 and 573 K while the second more severe hydrocracking step should be performed at a range of 623–673 K. The composition and properties of the mild HDT products strongly depend on the reaction conditions, while the catalysts employed are playing an important role in catalytic reactions [29–31]. In particular, the commercial CoMo and NiMo catalysts are commonly utilized at high temperatures above 623 K. However, the aforementioned catalysts might be still sufficiently active, providing active hydrogen, at lower temperatures and replacing noble metal catalysts. Nevertheless, the information regarding the application of these catalysts at low temperatures and the coke formation during bio-oil heating up is rather limited [21]. Furthermore, the major challenge in the bio-oil mild HDT is to maintain an operable reactor ΔP for an extended time thus the limitation of coke formation, which can also be affected by the reaction conditions [32,33].

The present study aims to investigate the potential of upgrading pyrolysis bio-oil from lignocellulosic biomass via mild HDT, targeting to intermediate products that have properties compatible with fossil-based intermediates, with the intention to be employed as refinery co-feeds for hybrid fuels production. To that purpose, the effect of various operating conditions on the process performance, as well as on the product quality was investigated. More specifically three reaction temperatures, two pressures and two H_2/bio-oil ratios were tested in a continuous-flow hydroprocessing pilot-plant of the Chemical Process and Energy Resources Institute (CPERI) of the Centre for Research and Technology Hellas (CERTH). Until now, most of the available literature data were limited only to model compounds, mostly batch reactors and targeting to final liquid biofuels (drop-in biofuels). With these novel results, the advantage of a typical fast pyrolysis bio-oil upgrading via mild hydrotreatment has been investigated, forming the basis for future targeted research on the exploitation of the bio-oil as a potential refinery intermediate stream.

2. Materials and methods

2.1. Feedstock and catalysts

The pyrolysis bio-oil utilized in the current study was the organic phase product of the ablative fast pyrolysis of lignocellulosic biomass and specifically of a mixture consisting of barley and wheat straw at 50 wt% each (Picture 1) [11,34]. The bio-oil was stored in a refrigerator to avoid aging. The bio-oil was mixed with a small quantity of DMDS (Dimethyl Disulphide) as it is necessary to maintain a certain sulphur level (up to 1000 wppm) in the hydrotreating feedstock when a sulphiding catalyst is employed. The properties of the bio-oil employed in the experiments are presented in Table 1. DMDS was selected as a hydrogen sulphide source, which can be in an industrial application partially replaced

Table 1
Properties of organic phase of the flash pyrolysis bio-oil.

Properties	Units	Value	Analysis Method
Density at 15 °C	g/ml	1.024	ASTM D-4052
Sulphur	wppm	1183	ASTM D-5453
Hydrogen	wt%	8.32	ASTM D-5291
Carbon	wt%	53.92	ASTM D-5291
Oxygen	wt%	37.64	Calculated by difference
H_2O (dissolved)	wt%	21.86	ASTM D-1744
MCR	wt%	15.7	ASTM D-4530
TAN	mgKOH/g	219	ASTM D-664
CAN	mgKOH/g	78.0	–
Carbonyls content	mmol C=O/g	2.2	Faix method
Phenolics content	mmol phenol/g	4.1	Folin-Ciocalteu method
Kin. viscosity	cSt	156	ISO 3104
Distillation curve			
mass % IBP	K	315	ASTM D-7169
mass %_5	K	415	
mass % _10	K	450	
mass %_30	K	499	
mass %_50	K	549	
mass %_70	K	629	
mass %_90	K	741	
mass %_95	K	788	
mass %_FBP	K	943	
Gasoline (cut point 489 K)	wt %	26	
Diesel (cut point 633 K)	wt %	44.65	
Residue	wt %	32.5	

by H_2S recovery from the off-gas from conventional hydrotreating processes [35]. According toTable 1, the bio-oil has high density (1.024 g/ml) and consists of large molecules, as confirmed by the elevated distillation curve. Finally, it has high oxygen content due to high content of water, carbonyls, phenols and carboxylic acids, leading to high Total Acid Number (TAN) 219 mgKOH/g. Based on these quality characteristics, an upgrading step is essential to transform this heavy feedstock with high carbonization residue to a higher added-value liquid, whereas the hydrotreatment should focus on the oxygen removal as well as on the cracking of the heavy molecules.

For this study, a custom made $NiMo/Al_2O_3$ catalyst developed by Ranido was used. The particle size of the catalyst was from 0.8 to 1.2 mm. In order to maintain a desired Liquid Hourly Space Velocity (LHSV), the catalyst was diluted with an inert material at a 5.6 v/v inert material/catalyst ratio to ensure that it would be effectively dispersed throughout the reactor for achieving good heat and mass transfer, while disabling feed channeling. Catalyst presulphiding was performed by a procedure defined by the catalyst manufacturer. As the catalyst was specially developed by Ranido for the purposes of the current research, no further details considering the composition and structure of the catalyst can be provided.

Finally, a TRL3 hydroprocessing pilot plant of CERTH was employed for all the experiments. The current plant is described in more detail in the authors' previous work [36,37].

2.2. Hydrotreatment experiments

The main premise of this study was to investigate the bio-oil upgrading potential via mild hydrotreatment, aiming to produce a refinery-compatible bio-based intermediate. To that aim, the effect of temperature (573, 603 and 633 K), pressure (4 and 7 MPa) and H_2/bio-oil ratio (506 and 843 NL/L) on process performance as well as on product quality was investigated. H_2/bio-oil ratio is one of the most important parameters that define the hydrotreating process as it presents the excess of hydrogen during the process. More specifically it describes the hydrogen feed flow in Normal Liter (i.e. at 1 atm and 293 K) per Liter of liquid flow (bio-oil). For the investigation of each set of temperature-pressure-H_2/bio-oil operating parameters, referred as "condition", all the other operating parameters remained constant. Each condition testing (experiment) was considered complete when the reactions reached steady state, usually after 2–3 days on stream (DOS), as determined by monitoring the product density and sulphur content. The total liquid product collected on the third DOS of each experiment was analyzed in more detail. The gas product collected on the third DOS (after steady state was achieved) was chromatographically analyzed on-line, as previously mentioned. For comparison purposes, condition 2 was considered as the control condition. Table 2 presents the operating window of all conditions tested during the current study.

Table 2
Operating experimental window of the hydrotreatment experiments.

Parameter	Units	Cond. 1	Cond. 2[a]	Cond. 3	Cond. 4	Cond. 5
Temperature	K	**573**	**603**	**633**	603	603
Pressure	MPa	7	7	7	**4**	7
LHSV	h^{-1}	1	1	1	1	1
Feed flow	ml/h	20	20	20	20	20
H_2/bio-oil	[b]NL/L	843	843	843	843	**506**

[a] Control condition.
[b] NL/L: Normal liter (i.e. at 1 atm and 293 K) per liter of liquid flow (bio-oil).

2.3. Analyses

For the evaluation of the feed and liquid products, samples were collected and analyzed in the CPERI/CERTH and UCTP analytical laboratory. Several analyses were performed in the products as well as in the corresponding feed samples. Specifically, the density was determined via ASTM D-4052 [38], while the distillation curve was estimated according to the Simulated Distillation ASTM D-7169 [39]. The concentrations of the sulphur in the feed and liquid products was determined by ASTM D-5453 [40]. Hydrogen and carbon content were determined via the ASTM D-5291 method [41]. Once total carbon, hydrogen and sulphur content (wt %) were determined, the oxygen concentration was calculated by difference assuming negligible concentration of all other elements in the product. It should be noted that due to the nature of bio-oil, the nitrogen analysis was impossible to be performed in the laboratory equipment. However, according to the literature [7], bio-oil in general is almost a nitrogen free feed and thus it was assumed that the nitrogen content is so small that it can be consider as nitrogen free feed. Moreover, standard procedures were applied for the determination of dissolved water concentration (WC, ASTM D-1744 [42]), total acid number (TAN, ASTM D-664 [43]) and kinematic viscosity (ISO 3104 [44]). Micro-conradson carbonization residue (MCR) was analyzed in agreement with ASTM D-4530. Total content of carbonyls was measured by Faix method after oxidation followed by reverse potentiometric titration, for more details see Ref. [38]. The amount of carboxylic acids (CAN) was determined by potentiometric titration, using tetrabutylammonium hydroxide as titrant, according to the method published elsewhere [45]. Total content of phenolics was analyzed by Folin-Ciocalteu method as described in detail by Rover and Brown (2013) [46]. Quantification of volatile compounds was carried out by GC-MS, more than 100 compounds were quantified directly and around 100 other compounds were quantified indirectly using the response factor of structurally most similar compound in the standard via the method described by Auersvald et al. (2019) [47]. Finally, the gaseous products were analyzed on-line via an Agilent 7890 series gas chromatograph analyzer, equipped with one flame ionization detector and two thermal conductivity detectors. The gaseous product concentration enabled the mass balances calculations and the H_2 balance calculations.

3. Results and discussion

3.1. Catalyst efficiency

The aim of experiments denoted as Cond. 1, 2 and 3 was to investigate the effect of temperature while keeping all the other parameters constant (Table 2). Cond. 2 was used as the control condition, which was also employed for the experiments aiming to explore the effect of H_2 pressure (Cond. 4) and H_2/bio-oil ratio (Cond. 5). The product collected during the third DOS of each condition was analyzed in detail, as it was considered a representative sample of that particular condition. The liquid product of each condition consisted of an organic dark liquid top layer and a water phase bottom layer that were separated via sedimentation (see Picture 2). The water phase was formed via the decarboxylation and dehydration reactions [48], which is a typical side-product of biomass catalytic hydrodeoxygenation. Both organic- and water-phase products have a significantly different appearance over the initial bio-oil (color, odor, viscosity), while the organic phase was considered as the main product and was further analyzed.

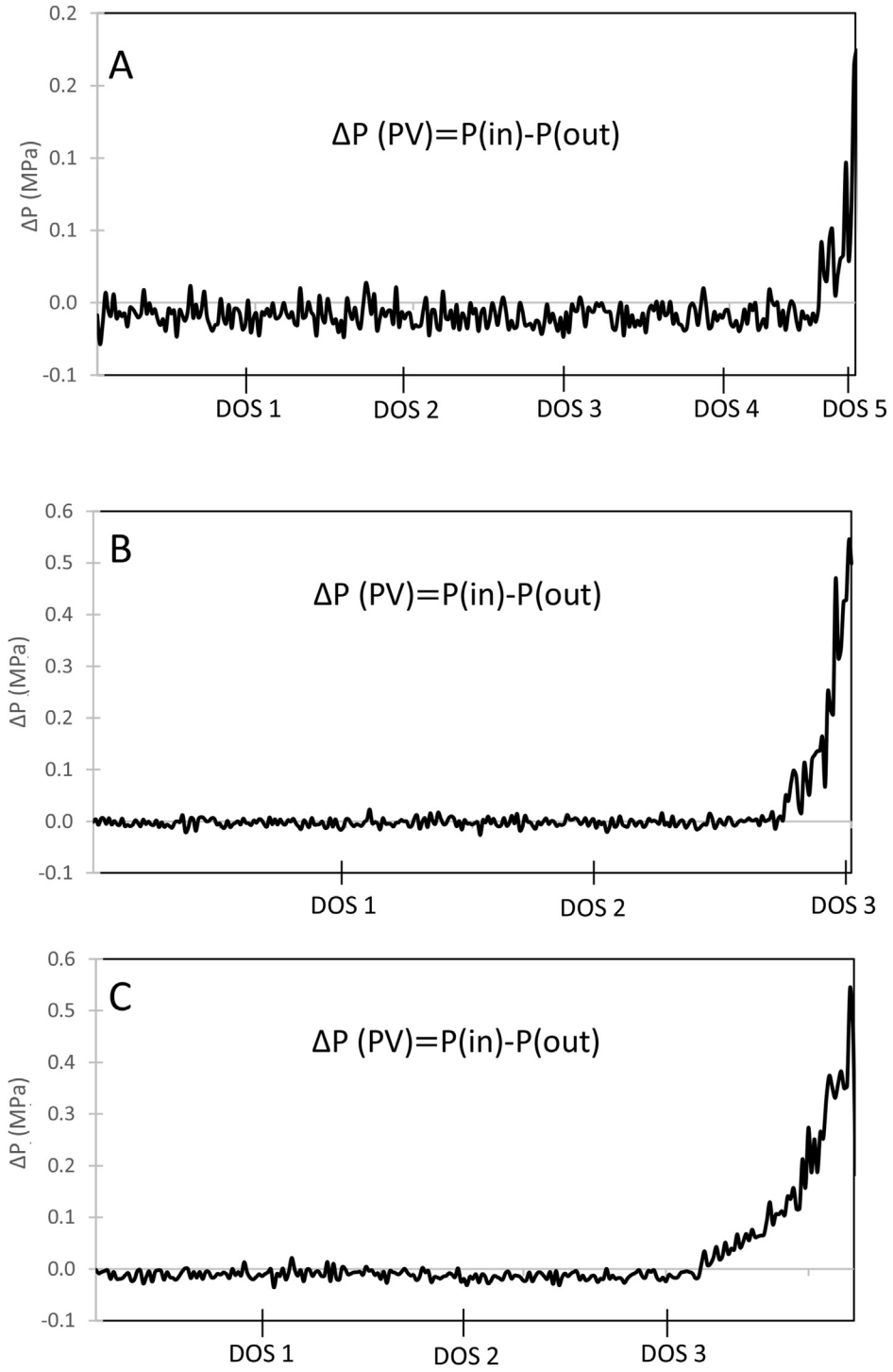


Fig. 1. ΔP creation during bio-oil upgrading in A) condition 1, B) condition 4 and C) condition 5.

Each of the experimental conditions 1, 2 and 3 lasted five DOS, before ΔP occurred in the reactor. Pyrolysis oil has a tendency for coke formation during mild hydrotreating conditions, because it contains highly reactive species such as guaiacol and alkoxyphenols [49]. The catalyst clogging and deactivation was daily monitored via the reactor ΔP and the total liquid product sulphur content respectively. The propagation of ΔP vs time during testing for condition 1 is indicatively presented in Fig. 1A, showing a sudden ΔP build-up up to 0.17 MPa after 5 DOS (119 h) due to coke formation. It should be noted the analysis of the reactor content showed massive plugging by coke formed from the unstable bio-oil, and catalyst decomposition into dust. The unsaturated oxygenates in bio-oil, especially phenols and furans, are regarded as the predominant coke precursors since they can strongly interact with the catalytic surface [50]. In addition, minerals are attributed to catalyst poisoning, the condensation of ketones, sugars and aldehydes are

attributed to re-polymerization and formation of tar-like products, which can not only block the surface but also can result in plugging of continuous operation upgrading units [51,52]. The ΔP plots of conditions 2 and 3 were similar to condition 1 and for brevity reasons they are not presented in the study.

Condition 4 aimed to investigate the effect of pressure while keeping all the other parameters constant, as presented in Table 2. The pressure of 4 MPa was investigated at the middle reaction temperature of 603 K and compared with the control condition 2 (7 MPa). The procedure followed for the condition 4 was similar to the conditions 1–3, whereas the collected organic phase product during the third day was analyzed in detail as the representative product. During the third DOS (67 h) significant increase of ΔP by 0.56 MPa was observed forcing to the termination of the experiment (Fig. 1B). The catalyst deactivation and the destruction of active centers were reflected by the increasing content of heteroatoms in liquid products with time on stream. The faster creation of ΔP (two DOS earlier) compared to control condition 2, shows the importance of higher pressures in the process for prolonging the experiment.

At condition 5 the effect of a lower H_2/bio-oil ratio (506 NL/L) was examined. In that case, the ΔP of 0.54 MPa was occurred during the middle of fourth DOS (84 h) (Fig. 1C). Compared to the control condition 2 where the only difference was the higher H_2/bio-oil ratio (843 NL/L), condition 5 lasted by one and half DOS shorter. These current results illustrate the importance of the high hydrogen flows during the bio-oil's HDT. In general, from the above analysis, it was observed that the higher reaction pressures and H_2/bio-oil ratios are preferable in terms of catalyst life expectancy.

3.2. Product evaluation

Bio-oil is a complex mixture of mostly oxygenated compounds with different functional groups, such as carboxylic acids, aldehydes, furfurals, alcohols, carbohydrates, and ketones including high amounts of water [51], with a volumetric energy density between 5 and 20 times higher than the original biomass [53]. In addition, various lignin derivative compounds i.e. phenol and guaiacol are present, limiting its direct application as fossil fuel replacement. Moreover, this oil has high viscosity, it is insoluble in commercial hydrocarbons, corrosive and thermally unstable (Table 3). To that aim a first mild-HDT step is essential prior to its use as a fuel. The main hydrotreatment target is the oxygen removal from initial bio-oil via hydrodeoxygenation (HDO) reactions as water that was spontaneously separated from low polar organic phase as an aqueous phase [54]. As the aqueous phase consists of water, no further analysis was performed in the aqueous phase. The properties of the organic liquid products from the third day of each condition are depicted in Table 3. The yields of aqueous phase for conditions 1–3 were between 38 and 40 v/v % which shows that there is no strong dependence on the reaction temperature. However, the yields of aqueous phase for cond. 4 was 37 v/v% showing that lower pressure leads to lower deoxygenation as confirmed by the results for oxygen content that was almost two times higher at 4 MPa than at 7 MPa. As far as cond. 5 is concerned, the results show that the density, the aqueous phase as well as the sulphur content of the product are higher compared to cond. 2. This shows that the deoxygenation reactions are competitive to desulphurization and cracking reactions. According to Mortensen et al. [55], the presence of H_2S to keep the catalysts in the sulfide state leads to incorporation of sulphur in the organic product as long as the deoxygenations take place. Once the oxygen content is low the remaining sulphur is removed since the applied NiMo catalysts are well-known desulphurization catalysts. Thus, the hydrogen is consumed mostly for deoxygenation reactions instead of cracking and desulphurization reactions. In addition, according to Table 3, the oxygen content is slightly higher for cond. 5 compared to cond. 2. However, the difference is not significant and is a result of measurements accuracy. From the above findings, it is observed that at lower H_2/bio-oil ratio the hydrogen is not enough to cover the needs of all hydrotreating reactions, thus higher H_2/bio-oil ratio is preferable. In general, considering all conditions, the oxygen removal was so deep that over 90 wt% of the oxygen was removed from the bio-oil and thus the product at 633 K contained less than 2 wt% of oxygen.

The instability of bio-oil from one side is related to the overall oxygen content and from the other side is a function of the reactivity and the diversity of the oxygenated group types that are compatible reaction partners for molecular weight increasing C–O or C–C bond forming reactions. Therefore, the effectiveness of the stabilization step is naturally tied to the ability of mixture to incorporate hydrogen to saturate reactive double bonds [56]. H/C ratio is a measure of hydrogen incorporation into the bio-oil and is depicted in Fig. 2. In these cases, the H/C ratio was decreased by 11–17% via mild-HDT. The decreased of H/C ratio is due to the much higher carbon content (55–61%) of the products (see Tables 1 and 3). As a result, although the hydrogen content increased by 30–40%, the H/C ratio decreased. Fig. 2 also presents the variation of O/C content ratio which is related to the instability of the bio-oil. According to the findings, a reduction of the oxygen content for the upgraded products is easily observed compared to the initial bio-oil (Table 3 and Fig. 2). These results confirmed the successful

Table 3
Properties of the upgraded bio-oils via mild HDO.

Properties	Units	Cond.1	Cond.2	Cond. 3	Cond.4	Cond.5	Method
Aqueous (2nd) phase	v/v%	40.4	40.5	38.6	37.1	45.6	–
Density	g/ml	0.9702	0.9202	0.9162	0.9675	0.9488	ASTM D-4052
Sulphur	wppm	469.2	341.4	792.4	571.4	686.9	ASTM D-5453
Hydrogen	wt%	11.03	11.68	11.41	10.88	11.31	ASTM D-5291
Carbon	wt%	84.02	85.79	86.81	84.97	85.63	ASTM D-5291
Oxygen	wt%	4.90	2.49	1.70	4.09	2.99	Calculated by difference
Oxygen detectable by GC-MS	%	27	24	49	52	50	–
H_2O dissolved	wt%	0.090	0.025	0.001	0.072	0.099	ASTM D-1744
Kin. Viscosity	cSt	61.98	8.99	4.94	28.26	14.60	ISO 3104
MCR	wt%	3.3	2.6	1.6	4.1	3.2	ASTM D-4530
CAN	mgKOH/g	2.5	1.1	0.2	1.1	0.8	–
Carbonyls content	mmol C=O/g	LOD	LOD	LOD	LOD	LOD	Faix method
Phenolics content	mmol phenol/g	2.7	1.6	1.5	3.0	2.4	Folin-Ciocalteu method

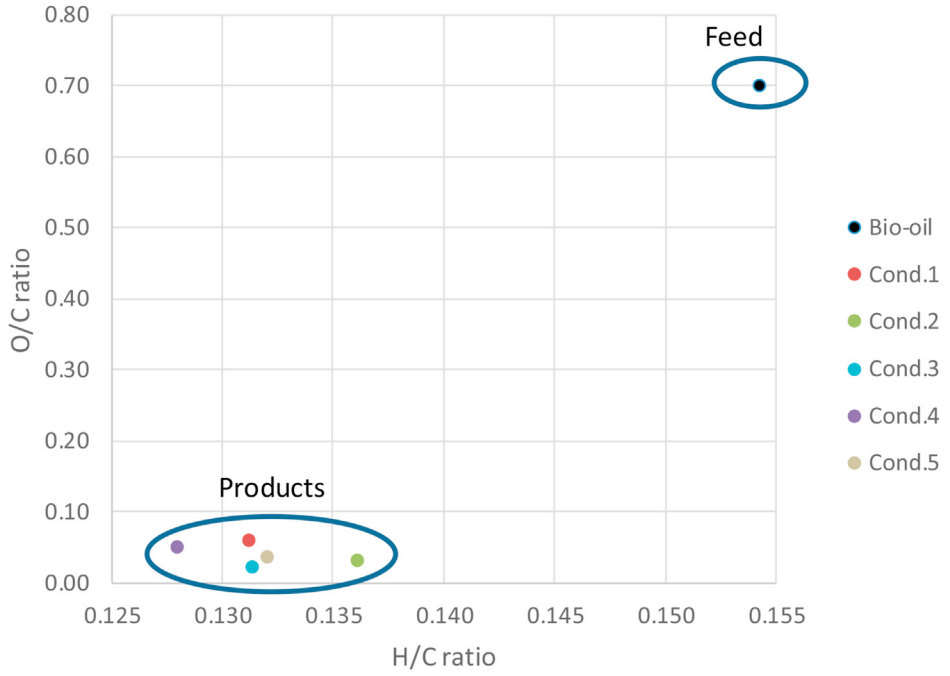


Fig. 2. O/C ratio vs H/C mass ratio for the upgrading products of each condition compared to initial bio-oil.

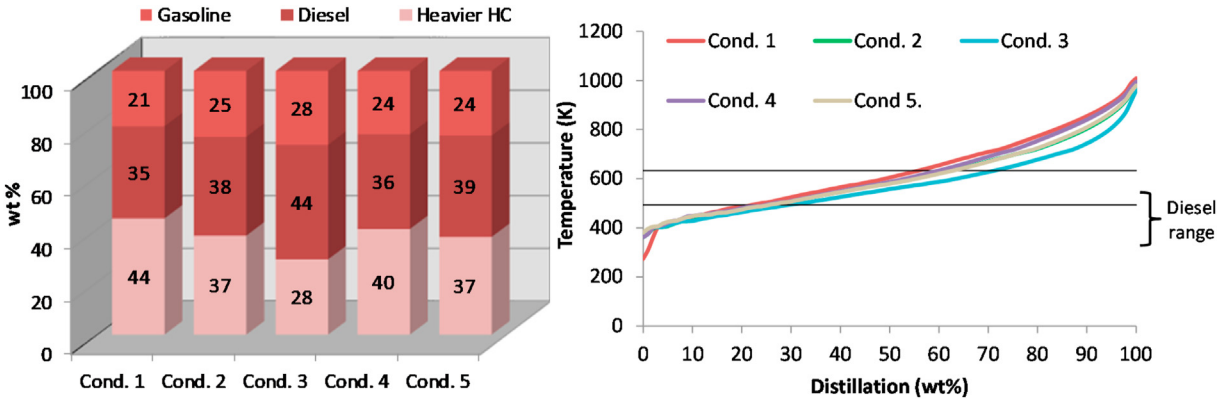


Fig. 3. Distillation curves of the upgraded bio-oils via mild HDO (conditions 1–5).

upgrading of the initial bio-oil to more stable hydrocarbon products.

The influence of various operating conditions on wt% yield for gasoline, diesel and heavier HC is presented in Fig. 3. Regarding the gasoline and diesel cut-points, it should be noted that they refer to the ones employed in practice during fractionation of the organic liquid product in order to separate the two fractions, and they can overlap as they are set to collect the molecules that might be drawn away due to the momentum of the fractionation column. In the analysis of gasoline and diesel yields, two actual cut-points are considered which are used to evaluate the potential of gasoline and diesel production yields. Cut point for gasoline is at 489 K, for diesel is at 633 K and for heavier HC is the remaining product. According to the findings, higher reaction temperatures (Cond 1. → Cond. 3) favor cracking reactions. The cracking reaction led to the increase in content of diesel and gasoline range fractions from 56 to 72 wt% comparing conditions 1 and 3 (Fig. 3). The increase of cracking reaction also led to the decrease of density and kinematic viscosity (Table 3). From the distillation curves of the products it can be seen that the lower reaction pressure (Cond. 4) resulted in heavier molecules compared to the control condition 2 (Fig. 3). This was cause due to low extent of pyrolytic lignin cracking reactions, which confirms the highest carbonization residue at Cond. 4, almost by 60% higher than at condition 2. Although, the Cond. 5 product's viscosity is almost two times higher (14.60 cSt) than the one of the control Cond. 2 (8.99 cSt), the distillation curves have very close shape. The carbonization residue at Cond. 5 was only by 20% higher than at Cond. 2. From the above analysis, it is easily observed the upgrading of initial bio-oil to a higher quality liquid product which can be used as a refinery intermediate with favorable properties.

3.3. GC-MS analysis of organic liquid products

Among different functional groups in bio-oil, aldehydes were the easiest to be hydrogenated to produce alcohols. As is shown in Fig. 4A, all aldehydes identified in raw bio-oil disappeared from the

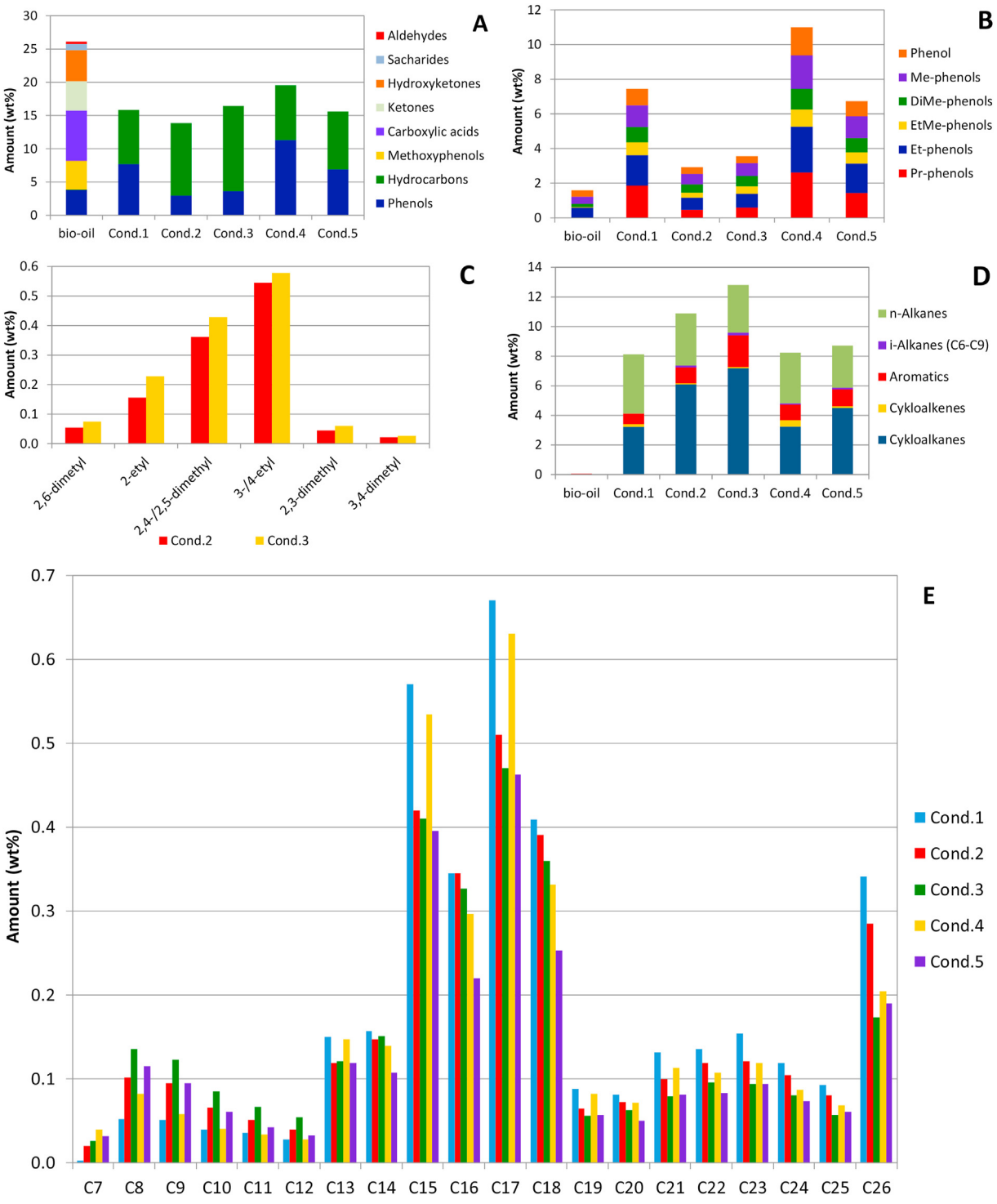


Fig. 4. Results from GC-MS quantitative analysis showing the amount of volatile compounds or their groups: (A) Primary groups, (B) Phenols based on the alkyl substitution, (C) Phenols with C2 alkyl substitution, (D) Hydrocarbon groups, (E) n-Alkanes.

liquid products after hydrotreatment.

Based on GC-MS analysis, we can conclude that at all conditions all volatile oxygenates besides phenols were removed from the bio-oil, see Fig. 4A. Although we would expect the decrease of volatile phenols with increase of the reaction temperature the amount of volatile phenols at condition 3 was higher than at condition 2. This increase was caused by higher extend of pyrolytic lignin decomposition, leading to such high amount of volatile phenols that was not possible to deoxygenate at used LHSV. The increase in the extent of pyrolytic lignin decomposition was confirmed by the decrease in carbonization residue compared to condition 1 by 20% and 50% (Table 3) for condition 2 and 3, respectively. We could also observe this phenomenon on the increase of the ratio of oxygenates detected by GC-MS up to almost 50% for condition 3 (Table 3).

Although, we could expect the increase mainly in content of propyl phenols as the main structural motif of pyrolytic lignin, the increase at condition 3 was observed for all phenols almost equally showing no dependence on type of alkyl substitution (Fig. 4B). The steric hindrance of phenol hydroxyl group by alkyl chain was not confirmed (Fig. 4C). The amount of hydrocarbons increased with increase of reaction temperature, and thus, the extent of deoxygenation (Fig. 4D). As expected, the content of olefins decreased with increase of reaction temperature (Fig. 4D). As propylmonocyclic compounds belong to the most common structures, propylcyclohexene was the most abundant olefin (Fig. A1). Although, free double bounds are very reactive in hydrotreatment, almost 0.1 wt% of cycloalkenes was still observed at condition 3 (633 K and 7 MPa). It was caused by their simultaneous creation from phenolic compounds as intermediate products, and for their hydrogenation was not fast enough due to the high LHSV. The same results regarding to olefins were observed by Auersvald et al. (2019) [47]. The condition 1 (573 K and 7 MPa) was the only one when no isomerization was observed (Fig. 4D). The increase of reaction temperature increased not only the extent of pyrolytic lignin decomposition but also the cracking and isomeration reactions best observable on n-alkanes (Fig. 4E).

Table 4
Gas product analysis.

	Units	Cond.1	Cond. 2	Cond. 3	Cond. 4	Cond.5
Hydrogen	g/h	0.691	0.607	0.335	0.708	0.183
Methane	g/h	0.610	0.545	0.365	0.530	0.553
Ethane	g/h	0.375	0.393	0.272	0.422	0.315
Propane	g/h	0.187	0.197	0.135	0.231	0.158
i-Butane	g/h	0.008	0.010	0.007	0.012	0.006
n-Butane	g/h	0.072	0.079	0.051	0.106	0.056
i-Pentane	g/h	0.008	0.011	0.007	0.013	0.006
n-Pentane	g/h	0.024	0.030	0.017	0.041	0.020
C6+	g/h	0.046	0.042	0.028	0.074	0.032
Carbon dioxide	g/h	0.953	0.735	0.496	0.955	1.016
Carbon monoxide	g/h	0.017	0.011	0.011	0.040	0.005
Oxygen	g/h	0.031	0.002	0.005	0.008	0.002
Nitrogen	g/h	0.108	0.015	0.024	0.040	0.010
Hydrogen sulphide	g/h	0.011	0.011	0.006	0.013	0.008

According to water and oxygen content results, it is obvious that the HDO of most reactive compounds in the bio-oil was successfully completed. This was confirmed by GC-MS, phenols were determined as the only oxygenates in the samples. The reduction of CAN in the products from all conditions (≤2.5 mgKOH/g) showed the significant removal of acids. Very close results of CAN for conditions 2, 4 and 5 mark low effect of hydrogen lack on acids removal. Compare to that, the phenol content was significantly influence by the lack of hydrogen observing higher content at all phenol groups (Fig. 4B). Lower deoxygenation of phenols resulted in lower content of hydrocarbons with significantly higher content of olefins due to the lack of hydrogen for its saturation (Fig. 4D, Fig. A1).

Titration and UV-VIS methods allowed us to analyze the whole sample, not only volatile fractions as GC-MS. However, as well as by GC-MS, no carbonyls were detected by Faix method (Table 3). This means that if there were some carbonyls definitely in much less amount than 0.01 mmol/g, but it seems that all carbonyls were removed. Although no carboxylic acids were detected by GC-MS, some carboxylic acids were still observed by titration method. At condition 3, only 0.2 mgKOH/g of carboxylic acids compounds left in the sample (Table 3). Phenols were the only volatile oxygenates detected. By Folin-Ciocalteu method, the total content of phenols in the whole sample was determined. The decrease of total phenol content was observed with increasing of reaction temperature, however the temperature above 603 K (the increase to 633 K) decrease the phenol content only minimally (by 6%) (Table 3).

In general, bio-oil is a complex mixture of compounds such as aldehydes, saccharides, ketones, acids etc. These functionalities are thermally unstable and thus a first mild-HDT step is necessary to convert these compounds to their corresponding alcohols and make the initial bio-oil more stable consisting from phenols and hydrocarbons. This stabilization step does not completely deoxygenate the bio-oil. However, it improves the quality of the resulting bio-liquid, allowing it to be easier to handle and store for further upgrading and applications in existing crude oil refinery as an intermediate stream. According to the results of the current analysis, mild-HDT has successfully upgraded the initial bio-oil to hydrocarbons and phenols increasing the quality of the final organic product.

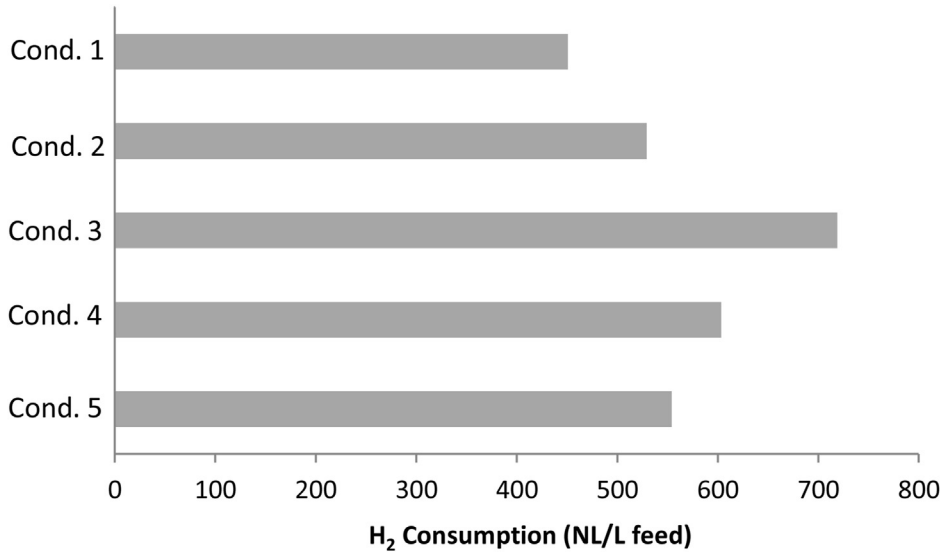


Fig. 5. Hydrogen consumption during HDO of bio-oil ((Normal Liter (i.e. at 1 atm and 293 K) per Liter of liquid flow (bio-oil)).



Picture 1. Ablative flash pyrolysis bio-oil from lignocellulosic biomass.

3.4. Gaseous products composition

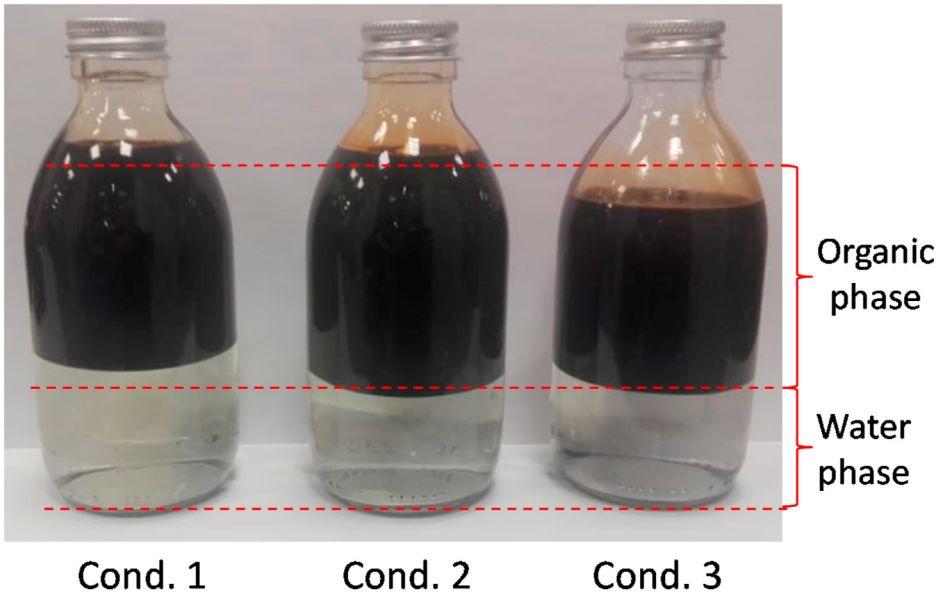
Generally, there are several reactions that take place during the bio-oil's mild HDT, for instance multiple reactions occurred, including hydrogenation, hydrogenolysis, decarboxylation, decarbonylation, hydrocracking and unwanted polymerization leading to the formation of coke. Clearly, through all of these reactions, gases (CO, CO_2, CH_4, ethylene, ethane, propylene and propane), water, and solids (heavy polymer and coke) were produced. More specifically, the CO_2 and CO were produced via decarboxylation [57] and decarbonylation reactions [58], respectively. Furthermore, methane originated from phenolics demethoxylation/demethylation and formic acid reduction. Ethane and propane are expected to be the products of acids, alcohols, ketones and aldehydes deoxygenation/hydrogenation and also as products from dealkylation reactions [35]. The gaseous product analysis of all the experimental conditions is juxtaposed in Table 4.

Oxygen removal through CO_2 and CO formation occurs at the expense of lowered carbon yield. According to Refs. [59,60], removing the oxygen content as CO_2 and CO, is not preferable as this negatively impacts the yields of the upgraded product as an area that can positively reduce the cost of producing liquid transportation fuel. As a result, removing oxygen as water is the preferred route. From the gas analysis (Table 4) can be seen that CO_2 formation was favored by lower H_2/bio-oil ratios (condition 5), while CO was favored by lower reaction pressures (condition 4). Similarly, methane formation was augmented in hydrotreatment conditions with low temperature (condition 1). From the gas product analysis, it is shown that a significant amount of carbon was lost to the gas phase forming primarily methane (12–20 wt% of the total gas) and CO_2 (21–37 wt% of the total gas). From the above findings, it was observed that higher pressure and H_2/bio-oil ratio are preferred.

3.5. Hydrogen consumption

Catalytic hydrotreatment in general consumes high amounts of hydrogen and thus it is very important to optimize hydrogen consumption in order to improve the operating cost of the overall process. For this reason, it is essential to estimate the H_2 consumption of mild-HDT upgrading of bio-oil. Hydrogen consumption was determined via the hydrogen mass balance of the process according to the following equations (1) and (2):

$$H_{2_{balance}} = \frac{H_{2_{Gas\ product}} + H_{2_{Liquid\ organic\ product}} + H_{2_{Liquid\ aqueous\ product}}}{H_{2_{Gas\ feed}} + H_{2_{Liquid\ feed}}} \quad (1)$$



Picture 2. Upgraded bio-oils from conditions 1, 2 and 3.

$$H_{2_{Consumption}} = H_{2_{Gas\ feed}} - \frac{H_{2_{Gas\ product}}}{H_{2_{Balance}}} \quad (2)$$

The hydrogen mass balance takes into consideration the stoichiometric hydrogen content of all feeds and products, i.e. the hydrogen feed flow-rate, the hydrogen content of the bio-oil feed and organic liquid product (obtained from the hydrogen elemental analysis via the LECO instrument), the stoichiometric hydrogen from the aqueous phase product and the hydrogen of the gas product calculated via the gas product flow-rate (from the wet test meter) and its hydrogen content from the GC-analyzer. Based on all these data, the hydrogen consumption is calculated in gr/h and standard liter of hydrogen per liter of feed, which is given in the manuscript.

The results of all conditions are depicted in Fig. 5. According to the findings, hydrogen consumption increased at higher reaction temperatures due to higher extent of HDO and cracking reactions as it was discussed in previous sections. Furthermore, higher reaction pressures and H_2/bio-oil ratio resulted in higher hydrogen consumption. This was due to higher extent of deoxygenation reactions confirmed by the lower oxygen and water content of the products of condition 2 compared to 4 and 5.

3.6. Overall process evaluation

Bio-oil is a highly oxygenated mixture of organic compounds, including carboxylic acids, aldehydes, ketones, ethers and phenolics thereby posing stability problems. This instability tends to produce an intractable solid upon heating during most refining processes including distillation or direct upgrading via hydrotreating. Therefore, a first upgrading step of a typical bio-oil via mild-hydrotreatment was investigated. The purpose of this mild-HDT step is to convert the aldehydes, ketones, and sugars to their corresponding alcohols and make the initial bio-oil more stable. The liquid product consisted of an organic dark liquid and a water phase that were separated via sedimentation, considering the organic phase as the high value liquid product. In general, bio-oil is a complex mixture of compounds and the resulting upgraded liquid still is a complex mixture. The results have shown that, the initial complex bio-oil was successfully converted to hydrocarbons and phenols. The properties of the upgraded bio-oil were improved as the initial viscosity, CAN and density reduced in a high manner. In particular, the upgraded organic phase is an excellent ignition quality intermediate feed consisting of diesel and gasoline range hydrocarbons that could be integrated in middle distillate hydrotreatment of a typical refinery for co-hydroprocessing with petroleum-based streams. The efficient removal of oxygen and water content from initial bio-oil via the proposed mild-HDT process render this technology as a very promising way to upgrade and promote the use of bio-oil for hybrid fuel production.

4. Conclusions

The main premise of this study was to explore the potential upgrading of a typical fast pyrolysis bio-oil via mild HDT towards the production of refinery intermediate products that could lead to renewable hybrid fuels via co-processing with petroleum fractions. To that purpose the effect of various operating conditions for HDT of bio-oil was explored in terms of catalyst life, process performance and product quality. According to the findings, the higher reaction temperatures favor HDO and cracking reactions reducing the viscosity and the boiling point of the organic liquid product. Furthermore, the higher reaction pressures and H_2/bio-oil ratios are preferable in terms of catalyst life expectancy. However, from the experimental results, it was found that in all examined cases, during HDT of bio-oil, massive plugging by coke formed in the reactor. The unsaturated oxygenates in bio-oil are regarded as the predominant coke precursors since they can strongly interact with the catalytic surface. From all the examined conditions, the longest catalyst life, (5 days on stream), was achieved at pressure of 7 MPa, H_2/bio-oil ratio of 843 NL/L and temperature of 603 K. In general, an upgraded organic liquid refinery intermediate feed was produced. Several properties of the initial bio-oil were improved via mild-HDT, such as viscosity that was reduced from 156 to 4.9 cSt, the amount of carboxylic acids (CAN) that was reduced from 78 to 0.2 mgKOH/g and density that was reduced from 1.024 to 0.9162 g/ml. In addition, the oxygen content was reduced from ~37 to ~4 wt%. Phenols were the only oxygenates present. The dissolved water of the initial bio-oil was totally removed as a second water phase due to significant decreasing of organic phase polarity. Conclusively, a mild-HDT step is essential for bio-oil in order to be upgraded to intermediate refinery streams towards hybrid transportation fuels production. This study put the basis for future research on miscibility tests of the upgrading bio-oil with petroleum-based streams for co-processing in order to produce hybrid transportation fuels. The current work is a first part of a European Union's Horizon 2020 research and innovation program under grant agreement No 727463 for the project "BIOMATES", more operating parameters including lower hydrotreating temperatures will be investigated in the future as a second part of the "BIOMATES".

CRediT authorship contribution statement

Athanasios Dimitriadis: Investigation, Writing - original draft, Hydroprocessing testing data, writing-original draft preparation. **Loukia P. Chrysikou:** Formal analysis, Analysis-gaseous product composition, Investigation-liquid product quality. **George Meletidis:** Data curation, Hydroprocessing testing data. **George Terzis:** Data curation, Hydroprocessing testing data. **Miloš Auersvald:** Data curation, Formal analysis, GC-MS analysis of liquid products, Writing - original draft, preparation/editing. **David Kubička:** Data curation, Writing - review & editing, GC-MS analysis validation, writing-reviewing. **Stella Bezergianni:** Methodology, Writing - review & editing, upgrading bio-oil via hydroprocessing, Validation-hydroprocessing testing results and outcomes, writing-reviewings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

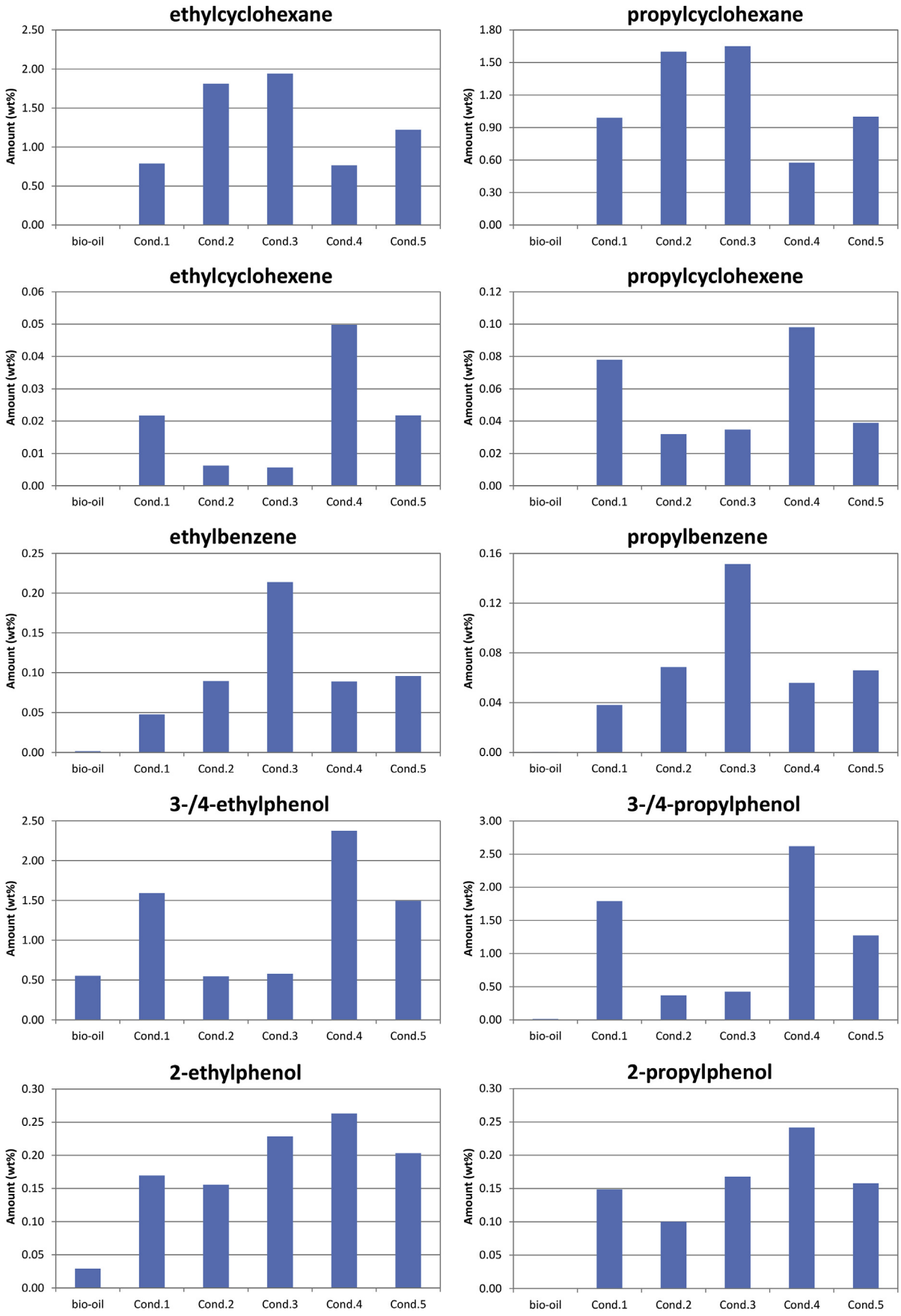


Fig. A1. Ethyl and propyl monocyclic compounds.

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