Continuous co-processing of HTL bio-oil with renewable feed for drop-in biofuels production for sustainable refinery processes

Sharma, Kamaldeep; Castello, Daniele; Haider, Muhammad Salman; Pedersen, Thomas Helmer; Rosendahl, Lasse

Published in:
Fuel

DOI (link to publication from Publisher):
10.1016/j.fuel.2021.121579

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Sharma, K., Castello, D., Haider, M. S., Pedersen, T. H., & Rosendahl, L. (2021). Continuous co-processing of HTL bio-oil with renewable feed for drop-in biofuels production for sustainable refinery processes. *Fuel*, *306*, Article 121579. https://doi.org/10.1016/j.fuel.2021.121579

Fuel 306 (2021) 121579

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Continuous co-processing of HTL bio-oil with renewable feed for drop-in biofuels production for sustainable refinery processes

Kamaldeep Sharma, Daniele Castello, Muhammad Salman Haider, Thomas Helmer Pedersen, Lasse Aistrup Rosendahl *

Department of Energy Technology, Aalborg University, Denmark

A R T I C L E I N F O

Keywords:
Hydrothermal liquefaction
Biocrude
Renewable feed
Co-hydroprocessing
Drop-in biofuel

A B S T R A C T

This study demonstrates the co-hydrodeoxygenation of partially upgraded bio-oil (PUB) obtained from hydrothermal liquefaction of pinewood, with rapeseed oil (RO) to produce bio-derived drop-in fuel. Enhanced miscibility of PUB in RO showed the high potential of HTL bio-oil for co-processing with different refinery streams in existing refineries. Co-processing experiments were conducted in a continuous unit under different processing conditions and the obtained results were compared with the hydroprocessed oils produced from the pure RO. Temperature and weight hourly space velocity (WHSV) are found to be important parameters to achieve complete deoxygenation and controlling the properties of co-processed bio-oils. Product quality analysis of co-processed bio-oils obtained under optimized conditions showed no oxygen contents and micro carbon residue but high n-paraffins. Furthermore, boiling point distribution of co-processed bio-oils was measured by SimDis, which was found analogous to boiling range of biodiesel. Fuel characteristic properties such as flash point, pour and cloud points of co-processed bio-oils were also measured and found improved compared to the properties of hydroprocessed oil obtained from RO. Therefore, this study demonstrates that HTL bio-oil can be successfully co-processed with renewable feed and petroleum refinery streams in a continuous hydroprocessing unit without any modification to reduce the environmental impacts and overcome the cost, availability and sustainability issues of oleochemical based feedstocks.

1. Introduction

Biofuels as low carbon intensity and high energy density fuels are the only real option for all form of sustainable transportation fuels in the coming decades, thus offering flexible solutions for the key partners in biofuels trade. To date, biofuels on large-scale have been synthesized commercially by the hydrotreating of oleochemical based feedstocks such as animal fats, vegetable oils and used cooking oil [1,2]. The resulting hydrogenated esters and fatty acids (HEFA) fuels have been tested suitable with low technical risk for use in conventional jet and diesel engines and consequently certified by ASTM in 2011 [3]. However, the limited supply and high cost (USD 500–1200/t) of oleochemical feedstocks in comparison to lignocellulosic biomass waste (USD $75–$125/t) put significant questions on their availability for large-scale processing [4]. Furthermore, insufficient greenhouse gas (GHG) emission reduction and infrastructure incompatibility are the other challenges limiting the increased utility of these biofuels to meet the demand [5]. Therefore, regulations are required to take effect globally over the sustainability of feedstock and distinct GHG reduction targets in transportation and aviation sector, as well as the recognition of sustainable biofuels from biomass as an alternative to reduce emissions. Questions of feedstock sustainability will encourage the production of biofuels from lignocellulosic feedstocks, which are widely available and not in competition with food [6]. The applicability of lignocellulosic biomass as a favourable feedstock for next generation biofuels has been demonstrated by the successful integration of first generation bioethanol and biodiesel into existing infrastructure [7].

Hydrothermal liquefaction (HTL) involved in the production of high-density second generation biofuel intermediates with high-energy efficiency and less oxygen contents from wet waste biomass, have the affinity to provide a sustainable and low-cost energy supply while attaining the GHG reduction goal [8,9]. In comparison to other thermochemical conversion methods, low oxygen contents of HTL biocrude is asset in achieving a high miscibility with renewable feed as required for co-processing activities [10,11]. Previously, heterogeneous catalysts were used to improve the quality of HTL biocrude and suppressing the

---

* Corresponding author.

https://doi.org/10.1016/j.fuel.2021.121579
Received 14 April 2021; Received in revised form 2 July 2021; Accepted 26 July 2021

formation of non-compatible solid residue as by-product [12]. Despite of having different catalytic advancements in HTL, lignocellulosic HTL biocrudes are not yet available on commercial scale and are more complex to process directly in a refinery [13]. Alternatively, co-processing of lignocellulosic HTL bio-oil with refinery streams in an oil refinery could offer a chance to enhance biofuel production while maintaining fuel quality standards [14]. Furthermore, co-processing of lignocellulosic HTL bio-oil in existing refineries represents a near-term GHG mitigation approach by producing renewable and infrastructure-compatible drop-in biofuels with minimum capital expenditure [7]. Moreover, co-processing of HTL bio-oil produced from lignocellulosic feedstock with oleochemical feedstocks could be an efficient way to decrease the GHG emission of HEFA fuels, as well as to enhance the physicochemical properties of final fuels due to potential synergy between aromatic and paraffinic feedstocks. Additionally, co-processing of biocrude with oleochemical feedstocks may help to address the associated issues of feedstocks sustainability, cost and GHG emission by increasing the utilization of renewable fuels in refineries. To facilitate the co-processing process, basic understanding of behaviour of lignocellulosic biocrudes in complex refinery operations must be known. Therefore, there is a need to develop technologies that could address technical challenges in the actual implementation and operation of co-processing in order to improve process efficiency and product quality. Till date, FCC technique has been used for the co-processing of pyrolysis bio-oil with refinery streams but the issues like reduced diesel yield, feedstock contaminants, coke formation and catalyst deactivation account for a source of concern to the refiners from both technological and economic perspectives [15–17]. Furthermore, the operational costs of FCC units are high because of economic losses posed by deactivation of cracking catalyst ascribed to the deposition of metals, nitrogen and sulfur originated from feedstocks during FCC reaction [18].

There are limited reports describing the behaviour of bio-oil/vegetable oil blends when treated for hydrodeoxygenation (HDO). Alvarez-Majmutov et al. [19] carried out co-hydroprocessing of fractions (10 vol%) distilled from HTL biocrude with vacuum gas oil using commercial NiMo/Al_2O_3 catalyst in a continuous pilot unit. It was observed that the addition of distilled biocrude fractions more than 10 vol% in the hydroprocessor decreased the activity of catalyst. Recently, Garcia-Perez et al. [20] reported the co-processing of lignin rich oil extracted from pyrolysis bio-oil with canola oil using commercial CoMo/Al_2O_3 catalysts. However, 1-butanol was also added to stabilize resulting oil and to reduce the coke formation from 34.7 wt% to 6.65 wt%. To the best of our knowledge, there is no report regarding the direct use of HTL bio-oil for co-processing with renewable feed. Therefore, great technical challenges need to be addressed in the actual implementation and operation of co-processing of HTL bio-oil with renewable feed in order to improve process efficiency and product quality.

In this study, continuous co-HDO of blend, prepared by mixing 5 wt % HTL partially upgraded bio-oil (PUB) in 95 wt% rapeseed oil (RO), was performed successfully for 10.5 days (249.6 h) over sulfided NiMo/Al_2O_3 catalyst in a fixed bed catalytic reactor. Depending on processing conditions, a maximum of 26.7 g of H_2 is consumed per 1 kg of PUB-RO (5–95 wt%) blend processed to yield co-HDO oil. The stability of NiMo catalyst during continuous co-HDO operations was checked by repeating mass balances under standard conditions and a sustained activity of catalyst was observed. However, the initial screening of operating conditions was done through the batch co-HDO experiments of PUB-RO blends (5–95 wt% and 20–80 wt%) using micro batch reactors to identify the best conditions and study the effect of reaction severity on quality of processed oils. Furthermore, the fuel characteristic properties and elemental analyses of co-processed bio-oils revealed substantial improvement in physicochemical properties as compared to the properties of hydrogenated RO. Hence, the main objective of this study is to assess the co-HDO of HTL bio-oil and renewable feed to identify suitable co-processing conditions in standard fuel units, while meeting the requirements of GHG reduction and low-cost production of fuels with improved physicochemical properties. The present study reveals the mixing of low-cost HTL bio-oil into oleochemical feedstocks or refinery streams could be an effective drop-in point for HTL bio-oil in the existing infrastructure to reduce the cost and achieve GHG reduction targets.

2. Experimental section

2.1. Materials

Dimethyldisulfide (DMDS) used for the sulfidation/sulfidation of hydrotreating catalyst was purchased from Sigma-Aldrich Co. Ltd. RO of food grade was used for co-hydrodeoxygenation experiments. Distilled water was used for analytical measurements. HTL biocrude for co-processing activities was produced from pinewood under supercritical conditions at continuous Bench Scale 1 facility with 1/3 barrel/day production capacity at Aalborg University, Denmark [21]. The conversion efficiency from biomass to bio-oil was 80% on energy basis and 40% on dry mass basis.

2.2. Characterization techniques

Elemental composition of co-processed products and feed was measured by Perkin Elmer, 2400 Series II CHNS/O elemental analyzer (ASTM D5291) using acetanilide as standard. The oxygen contents were calculated by difference. Water contents in feed was measured by Karl Fischer titration using a TitroLine 7500 KF instrument. Qualitative analysis of oils was performed on a GC–MS instrument (Thermo Scientific, Trace 1300 and ISQ QD). The gaseous products were analyzed by GC-2010 gas chromatograph equipped with GC-BID detector and Supelco 1006 PLOT column. Hydrogen consumption was determined by measuring unreacted H_2 concentration in gaseous product. HHV of samples were measured using an IKA C2000 oxygen combustion calorimeter (ASTM D2015). The distillation curves of co-processed oils were determined by SimDis using gas chromatograph GC-2010 (Shimadzu Inc., Japan) equipped with flame ionization detector (FID) and Zebron ZB-1XT column (ASTM D7169). Density of oils was measured at room temperature (22.5 °C) using DMA 500 density meter (Anton Paar). Cloud and pour point of co-processed bio-oils were measured using OptiMPP instrument (ASTM D2500 and ASTM D7346). Flash point of oils was measured using Herzog optiflash instrument (ASTM D3828). Furthermore, MCR analysis using an Alcor's MCRT-160 instrument (ASTM D4530) determined the thermal stability of co-processed bio-oils.

2.3. Co-HDO set-up and experiments

Activation of the hydrotreating catalyst. Commercial $CoMoO_4/Al_2O_3$ and $NiMoO_4/Al_2O_3$ catalysts were provided by Johnson Matthey™, used for the partial upgrading of HTL biocrude and continuous co-HDO of HTL biocrude with RO, respectively. The activation of both the catalysts was done in a continuous hydrotreater. In a typical procedure, the reactor was loaded with three subsequent layers of SiC (18 cm height), catalyst (CoMo or NiMo) (42 cm height) and SiC (26 cm height). To attain isothermal conditions and improve flow distribution, the catalyst was diluted with SiC as inert particles. The catalyst was sulfided using spiked VGO containing 0.1 wt% (2.5 wt% S) of DMDS. After that, the filled reactor was flushed with hydrogen for 30 min (30 NL/h). The hydrogen flow was kept at 30 NL/h and temperature was ramped to 120 °C with 10 °C/min, consecutively. Spiked VGO was fed to the reactor with a LHSV of 0.3 h^{-1}, while temperature was raised at a rate of 6 °C/h until 350 °C and pressure was gradually increased up to 10 MPa. After reaching the desired conditions, these were maintained for at least 10 h before starting the experimental run. The whole activation procedure lasted around 40 h. To keep activity of catalyst, blend was spiked to 1000-ppm sulfur with DMDS.

Batch co-HDO set-up and tests. Co-HDO was carried out in 25 mL stainless steel reactors (Fig. 1B). The top part of the reactor was

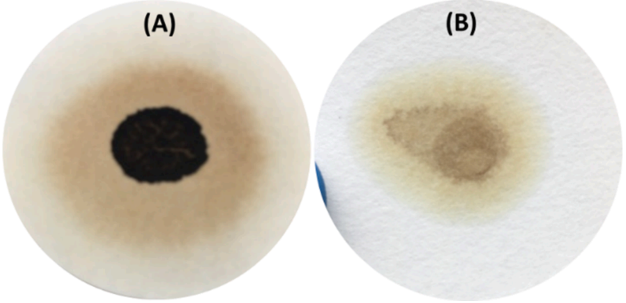

Fig. 1. Spot tests for visual detection of miscibility of raw HTL biocrude and 5 wt% PUB in RO.

connected to pressure transducer (Wika A-10) for pressure measurement during the reaction. The reactor was closed by a ball valve from the top to allow injection and sampling of gases (Fig. S1B) [22]. Reactors were loaded with 4 g of PUB-RO mixture (5–95 wt%) and 2 g of presulfided $NiMo/Al_2O_3$ with catalyst-to-oil ratio of 0.5. Then, the reactors purged with N_2 and pressurized with H_2 to desired initial pressure, which were then inserted in a fluidized sand bath SBL-2D (Techne, UK) heated at different temperatures (Fig. S1A). After reaction, reactors were opened and liquid products were filtered to separate the catalyst. The weight of oil, water and gases were noted to determine mass balances. To ensure the reproducibility of the results, each test run was performed in duplicates by using two identical reactors.

The operational parameters during batch experiments were designed accordingly to simulate a continuous co-HDO operation. To check the effect of bio-oil composition on the properties of co-processed bio-oils, blends containing both 5 and 20 wt% of PUB in RO were chosen for the co-HDO experiments. The effects of parameters like temperature, pressure, and reaction time were explored. The temperature was varied from 250 to 350 °C and H_2 pressure changed from 4 to 8 MPa with retention time of 4 and 2 h (Table S1) The catalyst to oil ratio in each experiment was 0.5. After co-HDO experiments, the upgraded liquid oil, gases and water phase were separated from mixture and the carbon balance in term of total weight percentage of carbon atoms in oils, gases and coke was calculated from feed input and total catalyst. However, the carbon present in the water phase was not included in mass balance.

Continuous co-HDO set-up and tests. A continuous hydrotreater configured as a fixed bed catalytic reactor was used for the co-HDO of PUB-RO blend. The whole setup contains three main parts: a syringe pump, a fixed bed catalytic reactor and two pressurized collection vessels (Figs. S1C and S2). The dual syringe pump connects the feed tank to the down-flow packed bed catalytic reactor with length of 86 cm and internal diameter of 1.5 cm.

During co-HDO operations, the reactor was heated to desired temperature with the individual temperature control heater output powers. A single multipoint thermocouple with ten different points is fitted inside the reactor to characterize the temperature profile during co-HDO experiments. H_2 was pressurized into the reactor through high-pressure lines and mass flow controller from a gas cylinder. The gas flow rate was measured with a wet gas flow meter for the mass balance. As shown in Fig. S1C, two reactors are connected to one small and one large sized high-pressure collection vessels with capacity around 1 L and 1 gallon, respectively. The uncondensed gases containing hydrogen, H_2S, CO, CO_2 and hydrocarbons are sampled, analysed and vented.

Continuous campaign was planned to study the effect of reaction severity on co-HDO of PUB-RO blend and evaluating technical feasibility of HTL bio-oil integration in refineries. The initial process parameters for continuous co-HDO campaign were 300 °C temperature, 8 MPa of H_2 pressure and 0.75 h^{-1} WHSV. To evaluate the effect of parametric variations on the quality of co-processed bio-oils, a set of experiments were planned with different pressures, 6, 8 and 10 MPa; temperatures, 300, 325 and 350 °C, and WHSV, 0.3, 0.75, 1.5 and 2.0 h^{-1}. The available H_2/oil ratio was fixed to 1000 NL/L for each experimental test. Under these reaction conditions, 13 samples were collected, achieving an average mass balance closure of 98 ± 5%. Continuous campaign was operated for 249.6 h (10.5 days) and approximately 5 kg of blend was processed. The water and gas yields were calculated at each mass balance and co-processed bio-oils were analysed to determine their fuel characteristic properties such as density, cloud point, pour point, flash point, MCR, boiling point distribution and HHV. Coke formation inside the reactor was checked after completion of co-HDO experiments. The catalyst activity over time was also monitored during co-HDO experiments by repeating the experiments under same conditions. For comparison, HDO of pure RO was also conducted under similar conditions and eight samples were collected (Table S4).

2.4. *Partial upgrading and miscibility/compatibility of HTL bio-oil with RO:*

Raw HTL biocrude is not miscible/compatible with the refinery streams [23]. In order to make a compatible homogeneous blend, HTL biocrude was partially upgraded over sulfided $CoMo/Al_2O_3$ catalyst. The mild hydrotreating of HTL biocrude was carried out in a continuous unit described in Section 2.3 to produce a partially upgraded HTL bio-oil (PUB) suitable for co-processing. HTL biocrude was processed between 280 and 320 °C temperature, 8–10 MPa pressure and 0.5 h^{-1} WHSV to determine process sensitivities. Following these hydrotreating tests, the optimum hydroprocessing conditions of 320 °C temperature, 10 MPa pressure and 0.5 h^{-1} WHSV were used in extended hydrotreating runs to produce sufficient amount of PUB for co-HDO experiments.

Next, the miscibility/compatibility of PUB was checked in RO to achieve a homogeneous blend for co-processing. Different proportions of PUB ranges from 2 to 20 wt% were mixed in RO, which were then stirred for a few hours and left overnight. Miscibility of blends was checked by spot test.

3. Results and discussion

3.1. *Miscibility of HTL biocrude and PUB in RO*

Before co-processing experiments, the miscibility of raw HTL biocrude produced from pinewood was measured in RO to achieve a miscible blend. Typically, 5 wt% of HTL biocrude was added in 95 wt% of RO. The resulting mixture was mixed thoroughly with a vortex mixer and left undisturbed Spot test performed for the visual detection of miscibility of resulting mixture, showed substantial amount of precipitates, which indicated that HTL biocrude is not miscible in the RO (Fig. 1A). As a result, it was deduced that raw HTL biocrude cannot be co-processed in its current form and should be upgraded first to reduce oxygen contents for enhancing miscibility.

HTL biocrude was partially upgraded in a fixed-bed continuous hydrotreater over sulfided $CoMo/Al_2O_3$ catalyst by processing at 320 °C temperature, 10 MPa H_2 pressure and 0.5 h^{-1} WHSV to achieve complete miscibility/compatibility in RO. Elemental analysis confirmed that oxygen content of HTL biocrude decreased from 10.75 wt% to 3.21 wt% and H/C ratio increased from 1.26 to 1.49 after mild upgrading at 320 °C. Furthermore, MCR analysis showed that carbonaceous residue in HTL biocrude significantly decreased from 25.4 to 10.6 wt%, which is attributed to the conversion of non-volatile components to volatile compounds by removal of reactive oxygen functionalities (Table 1). Next, the miscibility/compatibility of PUB was checked in RO as mentioned above. Interestingly, no precipitates were observed during spot test, indicated substantial amount of miscibility of blend (Fig. 1B). Fig. 2 shows the blends with different proportions of PUB (2–20 wt%) and RO (80–98 wt%). Due to the dark black color of the blends, the mixtures with more than 20 wt% of PUB in RO were hard to discriminate, therefore; the visual inspection of the obtained mixtures containing large amount of PUB (greater than20 wt%) could not be performed.

Table 1
Elemental and MCR analyses of biocrude, RO, PUB and PUB-RO blends.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	O[a] (wt.%)	H/C	MCR (wt.%)
Raw biocrude	80.00 ± 0.0	8.40 ± 0.2	0.85 ± 0.1	10.75 ± 0.5	1.26	25.35
PUB	85.52 ± 0.38	10.61 ± 0.02	0.67 ± 0.04	3.21 ± 0.40	1.49	10.59
RO	77.45 ± 0.18	11.85 ± 0.08	0.20 ± 0.48	10.5 ± 0.23	1.92	0.31
PUB-RO (5–95 wt %)	78.48 ± 0.19	11.14 ± 0.19	0.24 ± 0.19	10.14 ± 0.02	1.88	1.04
PUB-RO (20–80 wt %)	79.41 ± 0.26	11.06 ± 0.01	0.49 ± 0.2	9.04 ± 0.47	1.75	3.49

[a] Oxygen contents were calculated by difference.

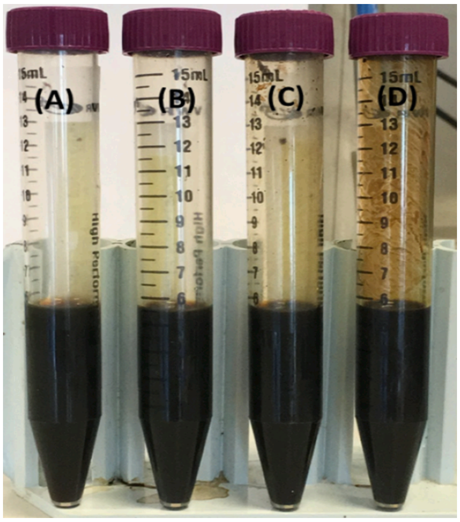

Fig. 2. Visual appearance of miscible blends of PUB and RO (A) PUB-RO (2–98 wt%) (B) PUB-RO (5–95 wt%) (C) PUB-RO (10–90 wt%) (D) PUB-RO (20–80 wt%).

The oxygen contents of PUB-RO (20–80 wt%) and PUB-RO (5–95 wt%) blends showed aggregate values of oxygen contents of individual component i.e. RO (10.5 wt%) and PUB (3.21 wt%) (Table 1).

3.2. Batch co-processing of PUB in RO

To evaluate the effect of reaction severity on quality of co-processed bio-oils and to determine suitable co-processing conditions for continuous co-HDO experiments, batch co-HDO runs of blends of PUB and RO were carried out at operating conditions ranging from mild to severe. Furthermore, the effect of HTL bio-oil amount on properties of co-processed bio-oils was also checked by selecting blends containing 5 and 20 wt% of PUB in RO (95 and 80 wt%) as feed for co-HDO. Elemental composition and MCR of blends (5–95 wt% and 20–80 wt%) were determined and compared with that of pure RO. Comparatively, the oxygen and MCR contents in both blends are proportional to the quantity of PUB added into the blends (Table 1). In batch experiments, co-HDO of blend of PUB and RO (20–80 wt%) was performed with varied temperature (250–350 °C), H_2 pressure (4–8 MPa) and retention time (2–4 h). Based on this experimental scheme, the standard operating conditions for continuous co-HDO operations were evaluated. The resulting bio-oils obtained at 350 °C temperature and different pressures are the stable liquid oils while the one obtained at 250 °C temperature shows a semi-solid state (Fig. 3). The results shows that the temperature plays a key role in the enhancement of physical and chemical properties of the bio-oils.

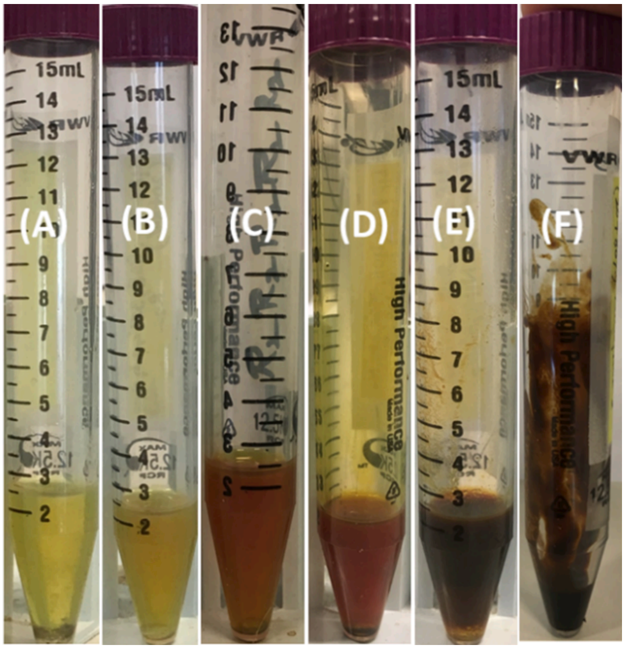

Fig. 3. Co-processed bio-oils at (A) PUB-RO 350-8-4 (B) PUB-RO 350-8-2 (C) PUB-RO 350-6-4 (D) PUB-RO 350-4-4 (E) PUB-RO 300-8-4 and (F) PUB-RO 250-8-4.

Among all obtained co-processed bio-oils, the highest bio-oil yield of 72.71 wt% was observed at 350 °C-8 MPa-4 h (PUB-RO350-8–4) conditions, which is almost comparable to yield of bio-oil produced at 350 °C-8 MPa-2 h (Table 2). The bio-oil yield decreased gradually from 72.71 to 66.45 wt% with decreasing H_2 pressure from 8 to 4 MPa, however, this decreasing trend was severe while decreasing temperature from 350 to 250 °C as shown in Table 2. It was observed that the lower availability of H_2 resulted in coke formation when operated at low pressure and temperature (Table 3).

3.2.1. Analyses of co-HDO bio-oils from batch tests

Elemental analysis of co-processed bio-oils produced at 350 °C and different initial H_2 pressure (4–8 MPa) did not show any oxygen content but high H/C ratio of approximately 2, comparable to the H/C ratio of diesel (Table 2) [3]. The low to considerable amount of oxygen contents in the bio-oils were observed on decreasing temperature from 350 to 250 °C. However, the decrease of retention time from 4 to 2 h showed no significant effect on elemental composition of bio-oil. This study shows that the temperature is an important parameter in the co-processing experiments to control the properties of bio-oils. The total carbon recovery was determined by measuring carbon balances in bio-oil, gases and solids (Table 3). Furthermore, the main composition of the hydrocarbon gases (i.e. methane (CH_4), ethane (C_2H_6) and propane (C_3H_8)) and their relative proportions were also provided in Table 3. The higher carbon loss in bio-oil was observed on changing temperature instead of changing the pressure. At low temperature (250–300 °C) and low H_2 pressure (4–6 MPa); the coke formation was high which shows these conditions are not sufficient to stabilize the starting bio-oil. However, the carbon loss to gases is minimal.

Table 3 shows that the carbon loss associated with decarboxylation (–CO_2) and decarbonylation (–CO) is favored at high temperature and low H_2 pressure. Therefore, co-HDO of blends of HTL bio-oil and RO at a higher temperature (350 °C) and H_2 pressure (8 MPa) was found to be crucial to prevent coking as well as decarboxylation and decarbonylation reactions.

Mittelbach et. al. proposed the use of SimDis as an efficient and effective method to classify diesel containing fuels regarding boiling

Table 2
Yields, elemental analysis and HHV of the RO, PUB and co-processed bio-oils obtained from PUB-RO (20–80 wt%) blend at different operating conditions.

Sample	Bio-oil yield (wt.%)	Elemental analysis [wt.%]				H/C	O/C	HHV [MJ/kg][b]
		C	H	N	O[a]			
PUB-RO350-8-4	72.71	85.15 ± 0.46	14.73 ± 0.02	0.12 ± 0.04	0 ± 0.52	2.08	0	47.08
PUB-RO350-8-2	71.44	85.25 ± 0.71	14.64 ± 0.12	0.11 ± 0.00	0 ± 0.83	2.06	0	46.97
PUB-RO350-6-4	68.00	85.45 ± 0.36	14.41 ± 0.06	0.14 ± 0.00	0 ± 0.43	2.02	0	46.81
PUB-RO350-4-4	66.45	85.56 ± 1.42	14.26 ± 0.27	0.19 ± 0.01	0 ± 1.70	2,00	0	46.67
PUB-RO300-8-4	67.24	85.5 ± 0.1	14.38 ± 0.03	0.09 ± 0.07	0.03 ± 0.19	2.02	0.0003	46.79
PUB-RO250-8-4	66.00	79.51 ± 0.24	12.58 ± 0.11	0.19 ± 0.02	7.72 ± 0.37	1.90	0.07	41.78

[a] Calculated by difference.
[b] Calculated by the Channiwala equation.

Table 3
Carbon balance of the performed batch experiments. Carbon yields are expressed in wt.% with respect to carbon in the feed. Coke was assumed to be composed of pure C.

Experiments	Oil (wt. C %)	Gases (wt. C%)				Coke (wt. C %)	Total (wt. C %)
		$CO-CO_2$	Hydrocarbons				
			CH_4	C_2H_6	C_3H_8		
PUB-RO350-8-4	77.97	0.94	0.19	0.16	0.77	7.5	87.53
PUB-RO350-8-2	76.69	0.83	0.12	0.13	0.65	9.47	87.89
PUB-RO350-6-4	73.17	1.28	0.10	0.18	0.80	11.46	86.99
PUB-RO350-4-4	71.60	2.54	0.21	0.42	1.68	12.26	88.71
PUB-RO300-8-4	72.40	0.45	0.02	0.04	0.49	15.99	89.39
PUB-RO250-8-4	66.08	0.04	0	0	0.14	15.00	81.26

characteristics and quality [24]. SimDis analysis revealed that bio-oil produced at 250 °C temperature exhibit high boiling range with lower value of recovery, while all other co-processed oils show around 90–95 wt% of recovery up to 280–320 °C temperature, which is the typical boiling range of green diesels [25]. SimDis analysis of pure RO was also carried out for the comparison purpose (Fig. 4). SimDis curves of pure RO showed a significant shift towards higher boiling points, which is attributed to the presence of oxygen containing compounds. However, it must be also pointed out that the increased boiling point due to oxygen contents is attributed to the attractions between the permanent dipoles of molecules with similar polarity. SimDis results correlate well with the elemental composition of co-processed bio-oils.

To evaluate the effect of amount of HTL bio-oil on the composition of co-processed oils, co-HDO of blend containing 5 wt% of PUB in RO (95 wt%) was also carried out under similar conditions. Experimental scheme implemented for batch co-HDO of PUB-RO blend (5–95 wt%) is shown in Table S3. The resulting bio-oils showed a single phase with visual appearance close to that obtained in previous run (Fig. S4). Elemental analysis of co-processed bio-oils showed no oxygen contents, whereas the carbon and hydrogen contents are almost similar except nitrogen, which is increased slightly in comparison to previous results. However, the H/C ratios are comparatively higher for all bio-oils, which indicates their better quality than the previous products. The distillation curves of resulting bio-oils followed same trend in the recovery values and boiling points distribution as observed for co-processed bio-oil from PUB-RO (20–80 wt%) blend (Table S3). These studies shows that the properties and composition of co-processed bio-oils remains almost unaltered on changing the amount of HTL bio-oil from 20 to 5 wt% in the blend.

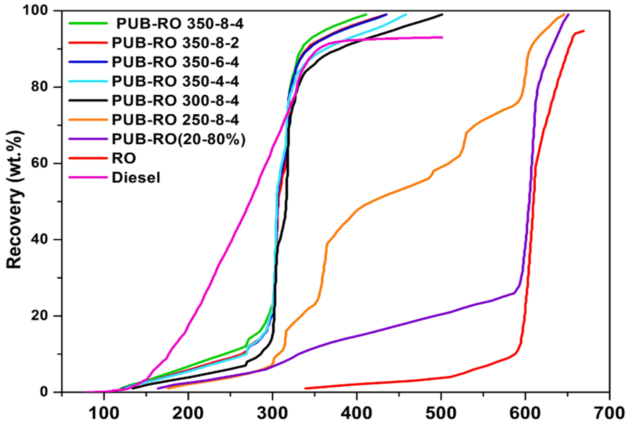

Fig. 4. SimDis pattern of co-processed bio-oils produced from PUB-RO (20–80 wt%) blend.

3.3. *Continuous co-processing of PUB in RO*

Continuous co-HDO of PUB-RO (5–95 wt%) blend were also conducted in a fixed bed continuous hydrotreater in the presence of sulfided NiMo/Al_2O_3 catalyst. The experimental plan followed to contemplate the implications of scaling-up batch experiments into a continuous operation is shown in Table 4. The resulting co-processed oils were analysed and their yields including gases and water formed, elemental composition and properties were compared with hydroprocessed RO (Table S5). The PUB-RO (5–95 wt%) blend was prepared by simple mixing of appropriate amounts of PUB and RO to feed in the continuous hydrotreater (Fig. 5).

The implemented parameters for co-processing were temperature, pressure, WHSV and H_2:oil for each mass balance under steady state conditions. However, the H_2:oil ratio was kept constant to 1000 NL/L for all planned experiments. Previously, the effect of two different H_2:oil ratios of 900 and 1300 on the quality of hydrotreated bio-oil was evaluated [26]. However, no significant effect of H_2:oil ratio on oil quality was observed. The continuous campaign was operated constantly for 249.6 h (10.5 days) and approximately 5 kg of co-processed bio-oil was produced. Total 13 samples (MB1-MB13) were collected over varied process parameters include temperature (300–350 °C), H_2 pressure (6–10 MPa) and WHSV (0.3–2 h^{-1}) as mentioned in Table 4 (Fig. 6). The mass balance calculation including oil, aqueous phase and gas yields were measured for each sample. The catalytic performance of sulfided NiMo catalyst was monitored continuously after a regular interval by repeating mass balances under same conditions. Fortunately, the same catalytic performance throughout the complete co-HDO campaign was observed from the comparison of results. The coke formation was negligible since traces of black solid inside the reactor was found after completion of co-HDO experiments.

The effect of process parameters on co-HDO of PUB-RO (5–95 wt%) blend was analysed from the comparison of properties of resulting co-processed bio-oils (Table 5). The yield of produced water through the HDO process is related to the extent of oxygen contents in the blend,

Table 4
The experimental protocol followed for co-HDO of PUB-RO (5–95 wt%) blend in the presence of sulfided NiMo/Al_2O_3.

Step	Duration (h^{-1})	Temperature (°C)	Pressure (MPa)	WHSV (h^{-1})	H_2 Consumption (g/kg)	Oil yield (%)	Gas yield (%)	Aqueous yield (%)	Total yield (%)
1	9.2	300	8	0.75	6.1	89.3	4,1	0,0	93,4
2	2.3	300	8	1.5	*	106.5	2.3	0.0	108.8
3	1.6	300	8	2.0	0.08	97.3	2.4	0.0	99.8
4	4.6	325	8	0.75	15.19	88.3	5.5	7.0	100.8
5	2.3	350	8	2.0	8.59	92.1	4.5	5.6	102.2
6	8.4	350	8	0.3	18.47	87.9	3.8	8.6	100.3
7	2.8	350	8	1.5	9.64	86.5	4.8	6.8	98,1
8	8.5	325	8	0.3	7.55	86.1	5.0	10.5	101.6
9	3.8	350	8	0.75	15.24	85.7	5.0	8.1	98.8
10	3.5	350	10	0.75	19.46	85.6	4.7	9.8	100.2
11	2.2	350	6	0.75	18.93	85.2	6.1	9.8	101.1
12	1.6	325	8	1.5	26.70	90.7	3.1	1.2	95.0
13	8.2	300	8	0.3	17.73	85.3	3.8	9.9	99.0

*Faulty gas flow controller with uncertain hydrogen feed.

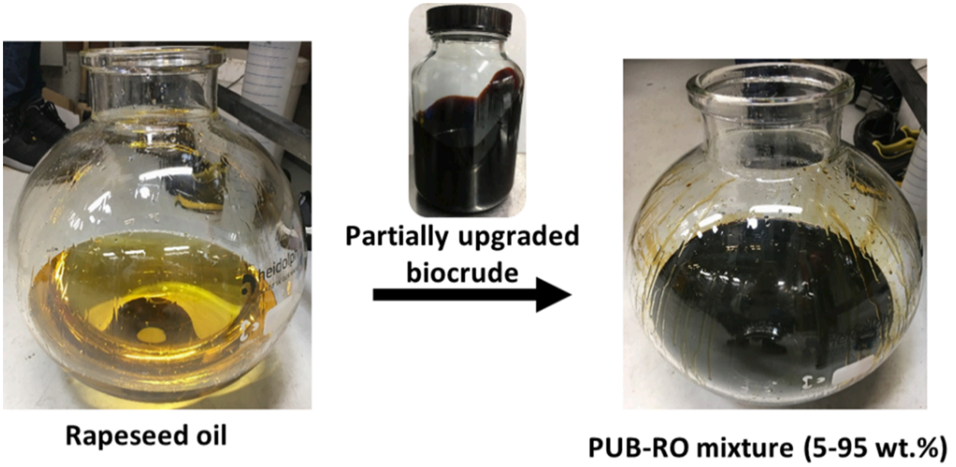

Fig. 5. Preparation of PUB-RO (5–95 wt%) blend as starting feed for the continuous co-HDO campaign on a fixed bed reactor.

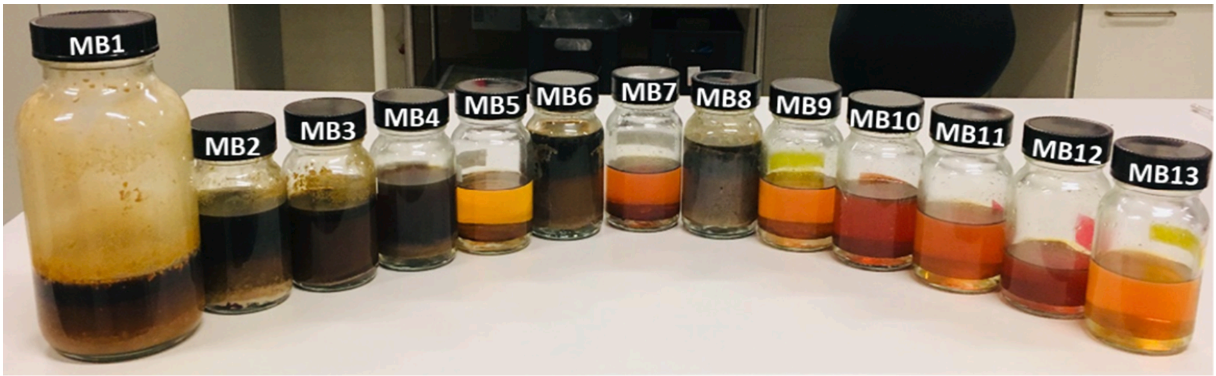

Fig. 6. Co-processed bio-oils (MB1-MB13, left to right) obtained during the continuous co-HDO of the PUB-RO (5–95 wt%) blend.

indicating that the oxygen was completely removed from the feed, as evident from elemental analysis (Table 5). The water yield was increased from 0% at 300 °C to 8.1% at 350 °C, confirming the high degree of HDO at higher temperatures. The yield of co-processed bio-oils was decreased from 89.3 to 86.7 wt% with increasing temperature from 300 to 350 °C. Higher bio-oil yield at lower temperature maybe due to lesser cracking and lesser formation of gaseous hydrocarbons (i.e. C_2H_6 and C_3H_8) in comparison to bio-oil produced at higher temperature (Fig. 8A) [27]. Furthermore, the absence of produced water and higher amount of produced CO and CO_2 indicates the decarbonylation and decarboxylation are the main pathways for the removal of oxygen from blend at 300 °C. The co-processed bio-oils produced at 300 and 325 °C showed semi-solid state, which could be due to the presence of more saturated hydrocarbons owing to the partial hydrogenation of RO at low temperature (MB1 and MB4 in Table 4 and Fig. 6) [28].

As shown in (Fig. 7), the H_2 consumption at different temperatures and WHSV during the co-HDO of PUB-RO (5–95 wt%) blend was monitored. The H_2 consumption was increased gradually on increasing temperature and was highest at 350 °C, indicating again a high degree of HDO of PUB-RO blend at the same temperature. However, the trend of H_2 consumed for reaction was irregular at different WHSV, which showed sharp increase first on increasing WHSV and then decreased

Table 5
Effect of temperature (at 8 MPa, 0.75 h^{-1} WHSV), pressure (at 350 °C, 0.75 h^{-1} WHSV), and WHSV (at 350 °C, 8 MPa,) on the properties of co-processed bio-oils obtained from PUB-RO (5–95 wt%) blend.

Bio-oil properties	Temperature (°C)			Pressure (MPa)			WHSV (h^{-1})			
	300	325	350	6	8	10	0.3	0.75	1.5	2.0
Oil yield (%)	89.3	88.3	86.7	85.2	86.7	85.6	87.9	86.7	86.5	92.1
Gas yield (%)	4.1	5.5	5.4	6.1	5.4	4.7	4.5	5.4	4.8	4.5
Water yield (%)	0.0	7.0	8.1	9.8	8.1	9.8	8.6	8.1	6.8	5.6
C (wt.%)	84.56 ± 0.02	83.99 ± 0.14	84.16 ± 0.01	83.83 ± 0.27	84.16 ± 0.01	83.81 ± 0.00	84.23 ± 0.07	84.16 ± 0.01	84.64 ± 0.15	84.43 ± 0.05
H (wt.%)	15.22 ± 0.01	15.52 ± 0.06	15.60 ± 0.02	15.44 ± 0.03	15.60 ± 0.02	15.52 ± 0.02	15.59 ± 0.02	15.60 ± 0.02	15.31 ± 0,07	15.27 ± 0.00
N (wt.%)	0.22 ± 0.00	0.48 ± 0.20	0.24 ± 0.03	0.73 ± 0.24	0.24 ± 0.03	0.67 ± 0.02	0.18 ± 0.04	0.24 ± 0.03	0.05 ± 0.08	0.30 ± 0.05
O[a] (wt.%)	0.00 ± 0.03	0.00 ± 0.40	0.00 ± 0.06	0.00 ± 0.53	0.00 ± 0.06	0.00 ± 0.04	0.00 ± 0.13	0.00 ± 0.06	0.00 ± 0.30	0.00 ± 0.10
H/C	2.17	2.22	2.23	2.20	2.23	2.22	2.22	2.23	2.18	2.17
O/C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HHV (MJ/Kg)	44.9	46.3	46.6	46.7	46.6	46.7	46.6	46.6	45.9	44.9
Cloud point (°C)	24.7	25.5	24.2	24.7	24.2	24.8	23.9	24.2	25.8	24.7
Pour point (°C)	21.5	22.4	21.3	21.4	21.3	21.9	20.6	21.3	22.7	21.2
Flash point (°C)	140.0	134.5	114.0	122.5	114.0	120.5	122.5	114.0	140.5	134.5
Density (g/ml) @22.5 °C	0.8365	0.8074	0.7797	0.7867	0.7797	0.7884	0.7902	0.7797	0.7949	0.8062
MCR (wt.%)	0.38	0.27	0.00	0.02	0.00	0.00	0.00	0.00	0.42	0.40
n-paraffins[b] (%)	94.52	94.83	92.36	93.07	92.36	92.92	88.26	92.36	–	93.95
i-paraffins[b] (%)	1.04	1.10	1.34	1.49	1.34	2.02	2.86	1.34	–	1.17

[a] Calculated by difference.
[b] Determined from GC–MS analysis.

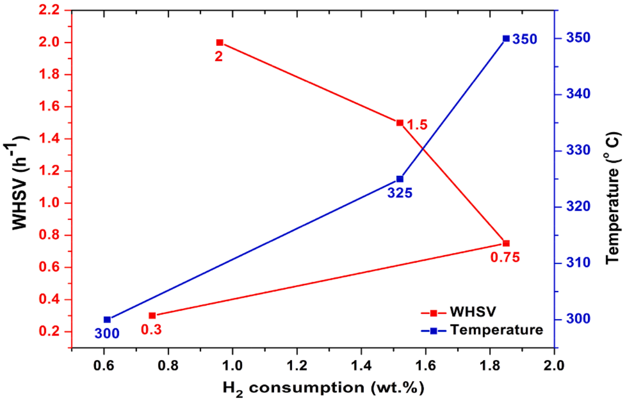

Fig. 7. H_2 Consumption during co-HDO experiments at different temperatures and WHSV.

gradually. Maximum H_2 consumption was observed at 0.75 h^{-1} WHSV.

The distribution of different gaseous products like CO, CO_2, CH_4, C_2H_5, and C_3H_8 produced during co-processing of PUB-RO blend under various process parameters was also plotted in Fig. 8. The carbon loss associated with decarbonylation and decarboxylation processes at high temperature was minimal and the observed trend showed first increase and then decrease of both CO and CO_2 gases on increasing the temperature from 300 to 350 °C. Furthermore, the gaseous hydrocarbon compounds (CH_4, C_2H_5, and C_3H_8) production after the co-HDO increased continuously on increasing the temperature. Evaluation of results revealed that at 300 °C, the most of oxygen was removed through decarbonylation and decarboxylation pathways. However, at 325 °C, the oxygen removed through HDO accounts for around 62 % of total oxygen removed, and the remaining removed through decarboxylation/decarbonylation reactions. In contrast, around 76% of total oxygen in PUB-RO feedstock was eliminated by HDO at 350 °C and the contribution of decarbonylation and decarboxylation reactions for oxygen removal was approximately 24% (Table 5). These findings were further confirmed from the yield of produced water at 350 °C, which was higher than that produced at 300 and 325 °C. Furthermore, the slight increase in CH_4 concentration and decrease of CO and CO_2 concentration suggested the favoring of CO_2 methanation when the co-HDO temperature was increased from 325 to 350 °C (Fig. 8A) [29]. The CO_2 methanation is followed by the reverse water gas shift reaction (WGS), producing CO in the presence of H_2.

However, the small increment for hydrocarbons such as C_2H_6 and C_3H_8 was also observed on increasing temperature from 300 to 350 °C.

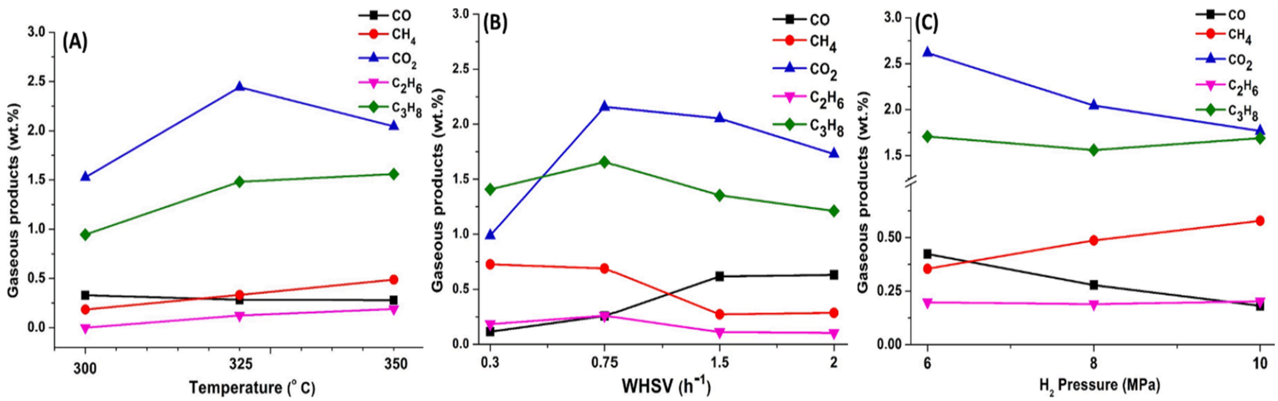

Fig. 8. Distribution of gaseous products at different co-HDO conditions.

Comparatively, the yield of hydroprocessed bio-oils from pure RO at 350 °C was almost similar to those of the blend, which was increased significantly with temperature (Table S5). Unlike the yield trend of co-processed bio-oils, the bio-oils obtained from pure RO showed gradually increased in yield on increasing temperature from 300 to 350 °C, which is probably due to oligomerization of intermediate olefinic products of triglycerides decomposition [30]. The observed trend in total gas yield with temperature during hydroprocessing of RO was in the same order as observed during co-processing of PUB-RO blend. Unlike co-processing of PUB-RO blend, the yield of produced water during the hydroprocessing of pure RO was increased first on increasing temperature from 300 to 325 °C and then decreased when the temperature was further increased to 350 °C. This indicates that HDO of pure RO is favored at lower temperature (325 °C), while high temperature may cause destructive hydrogenation and lead to the decarbonylation and decarboxylation pathways for oxygen removal.

After evaluating temperature influence, the effect of H_2 pressure on yield and properties of co-processed bio-oils was also studied. The degree of HDO depends on the solubility of H_2 gas in bioliquid, which is controlled by the partial pressure of hydrogen. A few consecutive experiments at three different initial H_2 pressures of 6, 8 and 10 MPa were carried out by keeping temperature and WHSV constant to 350 °C and 0.75 h^{-1}, respectively. The observed yield of liquid, solid and gaseous products along with the properties of co-processed bio-oils are presented in Table 5. The yield of produced water was increased from 8.1 to 9.8 wt % and gaseous products yield decreased from 5.4 to 4.7 wt% on increasing H_2 pressure from 8 to 10 MPa while the bio-oils yield showed a slight decreasing trend. The increase of pressure increases the available H_2 over the hydrotreating catalyst under operating conditions, facilitating the HDO via the hydrogenation of oxygen containing derivative present in biocrude [24] Conversely, the yields of gaseous products were decreased whereas yield of produced water remained unvaried on decreasing initial H_2 pressure from 8 to 6 MPa. Comparatively, at higher pressure, the composition of gaseous products showed enhanced CO methanation followed by reverse WGS reaction as confirmed from sharp decrease of both CO and CO_2 and increase of CH_4 (Fig. 8C). Whereas the other gaseous hydrocarbons (C_2–C_3) remained unaffected on changing the pressure. The yield of hydroprocessed bio-oils obtained from pure RO was increased first from 84.5 to 86.2 wt% on increasing H_2 pressure from 6 to 8 MPa, respectively and then decreased to 84.4 wt% on further increasing pressure to 10 MPa. However, water yield obtained during hydroprocessing of RO at different pressure followed reverse trend. The highest water yield of 9.6 wt% was produced at lowest H_2 pressure of 6 MPa, which was almost comparable to the water produced at 10 MPa. These results again confirm that H_2 pressure has no significant influence on the HDO of pure RO as revealed in case of co-HDO of PUB-RO blend.

Co-HDO of the PUB-RO (5–95 wt%) blend at four different WHSV of 0.3, 0.75, 1.5, and 2.0 h^{-1} was also studied. The effect of WHSV on the relative orders of different products yield and properties are shown in Table 5. On increasing the WHSV from 0.3 to 1.5 h^{-1}, the bio-oil yield first decreased from 87.9 to 86.5 wt% and then, increased to 92.1 wt% on further increasing WHSV to 2.0 h^{-1}. The increase of bio-oil yield at high WHSV is attributed to the lesser yield of gaseous product and produced water. The observed yield of produced water was found inversely proportional to the WHSV. Water yield decreased linearly from 8.6 to 5.6 wt% with an increase in WHSV from 0.3 to 2.0 h^{-1}, indicating that HDO is the less favored at high WHSV. Hydrogen consumed during the HDO to remove oxygen from PUB-RO blend was maximum at 0.75 h^{-1} WHSV (Fig. 7). However, the observed water yield during the hydroprocessing of pure RO at different WHSV followed irregular trend. The maximum yield of produced water of 10.3 wt% was observed at WHSV of 0.3 h^{-1}. However, no regular trend in gas yield at different WHSV was observed. Furthermore, the increase of WHSV led to a lower production of gaseous hydrocarbons such as CH_4, C_2H_6 and C_3H_8, whereas the production of CO and CO_2 gases was increased sharply and then, slightly decreased with increase of WHSV (Fig. 8B). This shows that HDO of PUB-RO blend is favored at lower WHSV whereas decarbonylation and decarboxylation are main pathways for the removal of oxygen at higher WHSV.

3.3.1. Analyses of co-HDO bio-oils from continuous operations

Elemental composition of co-processed bio-oils did not show any significant change on changing the HDO temperature and no oxygen contents were observed in bio-oils after co-processing at different parametric conditions. Oxygen contents were obtained by difference from carbon, hydrogen and nitrogen contents, thus the experimental errors due to these determinations were included in oxygen contents. The fuel characteristics of produced co-processed bio-oils were evaluated by measuring properties like density, cloud point, pour point, flash point, MCR and HHV. The cold flow properties like cloud and pour point of co-processed bio-oils were decreased slightly from 24.7 °C to 24.2 °C and 21.5 °C to 21.3 °C, respectively, with increasing temperature from 300 to 350 °C. Comparatively, the cold flow properties of the biodiesels derived from vegetable oils have been reported considerably higher than the conventional diesels [31]. However, properties of bio-oils depend on several factors such as processing conditions, type and composition of feedstocks, which could be a reason for these variations. Whereas the values of some properties like flash point, density and MCR decreased significantly from 140.0 to 114.0 (°C), 0.8365 to 0.7797 (g/ml) and 0.38 to 0.00 (wt.%), respectively, on increasing the co-processing temperature from 300 to 350 °C. The lower value of these properties at 350 °C represents the improved quality of resulting co-processed bio-oil. It is notable that the MCR of the PUB-RO blend (1.04 wt%) was decreased to zero, indicates the complete removal of oxygen containing functionalities and saturation of hydrocarbons. However, the HHV was increased a bit at 350 °C with respect to the bio-oils obtained at 300 and 325 °C.

Elemental composition of co-processed bio-oils produced at different pressures remained almost constant and did not change significantly. Despite the nominal increase in HHV value, the remaining characteristic properties such as cloud, pour, and density of co-processed bio-oils were constant on changing H_2 pressure. Among different applied H_2 pressures (6–10 MPa), the lowest flash point of 114 °C was recorded at 8 MPa. However, the degree of HDO was enhanced slightly as the yield of produced water increased by raising the pressure from 8 to 10 MPa but this change did not show any influence on properties of bio-oils. Above results, reveal that variation of H_2 pressure is less effective in controlling the bio-oils yield and quality in comparison to reaction temperature.

Also, WHSV did not show any effect on the elemental composition of co-processed bio-oils. The properties like HHV, cloud and pour point of bio-oils produced at 0.3 and 0.75 h^{-1} WHSV were almost comparable with each other but were improved slightly than the bio-oils produced at higher WHSV (1.5 and 2.0 h^{-1}). Nonetheless, the flash point and density of bio-oil produced at 0.75 h^{-1} WHSV were lowest than the bio-oils produced at higher WHSV. The probable reason behind this might be the less cracking, which is most probably due to lower retention time (higher WHSV). Furthermore, MCR of 0.42 and 0.40 wt% were observed in the co-processed bio-oils produced at higher WHSV of 1.5 and 2.0 h^{-1} whereas no MCR were observed at lower WHSV (0.3 and 0.75 h^{-1}). These observations revealed that 350 °C temperature, 8 MPa pressure and 0.75 h^{-1} WHSV are optimum operating conditions for the production of high quality bio-oils in standard fuel units.

Above-mentioned properties of hydrotreated RO were also measured. The fuel characteristic properties of hydroprocessed RO at 350 °C, 8 MPa and 0.75 h^{-1}, especially cloud point, pour point and flash point were found to be 25.8, 22.9 and 145.0 °C, respectively, which are higher than that of co-processed bio-oils obtained under same conditions (Table S5). However, the other properties such as HHV, density, MCR and elemental analysis of bio-oils produced by hydrotreating of pure RO were found comparable with that of co-processed bio-oils. These results indicate that the mixing of a low-cost feedstock to RO did not create significant problems and/or it leaded to improved fuel properties in comparison to hydroprocessed RO. Although the overall values of above mentioned fuel characteristic properties of co-processed bio-oils are higher than the conventional diesel, HTL bio-oil led a noticeable improvement in fuel characteristic properties especially in flash point and density as compared to the hydroprocessed RO. Therefore, co-processing of HTL biocrude/bio-oil from different biomasses with oleochemical feedstocks can be an alternative to the current expensive and unsustainable lipid based feedstocks for the production of low-cost and low carbon intensity biofuels with improved properties. Future studies must be done to test the co-processing of HTL bio-oil-renewable feed blends containing higher concentration of HTL bio-oil, which can significantly improve the quality and properties of existing hydro-processed fuels.

H/C ratio has been considered as a crucial parameter to measure the quality of hydrodeoxygenated bio-oils [9]. Chemical conversion of oxygen containing organic compounds present in PUB-RO blend to carbon and hydrogen rich products are presented using a Van Krevelen diagram. H/C and O/C ratios for co-processed bio-oils produced at different conditions and PUB-RO (5–95 wt%) blend are plotted in Fig. 9a, which clearly shows the effect of process parameters on the H/C ratio of bio-oils. Conversely, PUB-RO blend showed highest O/C and lowest H/C ratio, which were altered subsequently after the co-HDO at different conditions. However, O/C ratio was zero for all co-processed bio-oils but H/C ratio varied on changing the process parameters. Among various parameters, temperature severely affected the quality of the bio-oils. H/C ratio was increased sharply on increasing the temperature from 300 to 350 °C, which again confirmed the role of temperature in attaining high quality of bio-oils. The higher H/C ratio of co-processed bio-oils at high temperature indicates that the conversion process entails production of saturated hydrocarbons as well as reducing the length of paraffinic hydrocarbon chains, therefore generating lighter products [32]. Furthermore, the other parameters like H_2 pressure and WHSV also contributed towards the improvement of H/C ratio, hence, improved the bio-oils quality. The results again revealed the 350 °C temperature, 8 MPa pressure and 0.75 h^{-1} WHSV are the ideal conditions for the co-processing, as the H/C ratio was highest at these conditions.

The boiling point distributions of pure RO, PUB-RO blend and all co-processed bio-oils were measured upto 650 °C by SimDis and are shown in Fig. 9b. Hydrotreatment of vegetable oil demonstrates an attractive technique for the alternative liquid fuel production, particularly containing renewable diesel components [33]. The narrow boiling distribution around 300–350 °C of all co-processed bio-oils indicates that these oils can be regarded as a single fraction containing synthesized diesel as the main component. Due to the presence of oxygenates, the RO and PUB-RO showed only 10 and 25 wt%, respectively, recovery as distillable fractions even at very high boiling range of around 600 °C. However, the complete distillation recovery of bio-oils obtained at high H_2 pressure of 10 MPa was achieved. On increasing the co-HDO temperature from 300 to 350 °C, the recovery of the co-processed oil increased significantly from around 76 to 92 wt% at boiling range of diesel (300–350 °C). This enhanced recovery shows the increased amount of bio-oils available as a distillate fuels, hence indicates the overall improved quality of the bio-oils with increasing reaction temperature. Furthermore, the complete bio-oil recovery within same boiling range was observed with an increase in H_2 pressure from 8 to 10 MPa. However, the bio-oils co-processed at high WHSV and low temperature shows lower distillation recovery (wt.%) at the same boiling point and contain residual fractional cuts of higher boiling points. These results are in agreement with the observed higher H/C ratios of the bio-oils produced under same conditions. It has been reported that hydroprocessing at high temperature and H_2 pressure favors the production of high quality diesel hydrocarbons [34]. Therefore, operating at higher temperature and H_2 pressures is beneficial especially to produce bio-oils with improved quality equivalent to the conventional diesel fuel.

4. Conclusions

This study demonstrates the technical feasibility and potential of HTL bio-oil for co-processing with renewable feed in the existing refineries to produce hydrocarbon fuel. Additionally, the enhanced miscibility of partially upgraded HTL biocrude in different refinery streams could provide a future opportunity to integrate it into existing petroleum refineries and distribution infrastructure. Elemental analysis revealed that all co-processed bio-oils were completely deoxygenated. Among different operational parameters implemented during the co-processing of PUB-RO blend, temperature and WHSV were found more effective in controlling the yield and properties of co-processed bio-oils. Co-processed bio-oils obtained at high temperature (350 °C) and low WHSV (0.3 and 0.75 h^{-1}) showed improved HHV and cold flow properties in comparison to hydrotreated RO. Furthermore, a narrow boiling range and high recoveries of co-processed bio-oils obtained under above conditions were observed at boiling point of 350 °C analogous to that of diesel. Future studies must be dedicated to test co-processing of higher concentration of HTL bio-oil with refinery streams, which may not require any major operational modification. Subsequent exploration studies of co-processing of HTL bio-oil with petroleum refinery streams will present the economic feasibility and lifecycle analysis of present co-processing strategy.

CRediT authorship contribution statement

Kamaldeep Sharma: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Writing-original draft, Writing-review & editing. **Daniele Castello and Muhammad Salman Haider:**

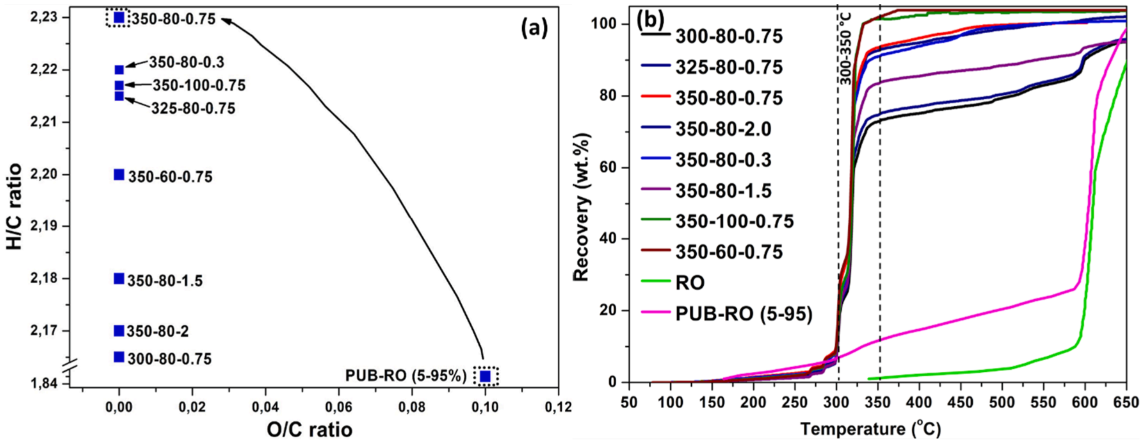

Fig. 9. (a) Van Krevelen plot (O/C vs. H/C) (b) SimDis boiling point distribution curves of the co-processed bio-oils at different reaction conditions.

Conceptualization, Data curation, Visualization, Writing - review & editing. **Thomas H. Pedersen & Lasse A. Rosendahl:** Supervision, Project administration, Resources, Writing - review & editing, Funding acquisition.

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.

Acknowledgments

This research acknowledges support from “4REFINERY” (Grant Agreement No. 727531) project, funded by the European Union’s Horizon 2020 research and innovation programs.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.121579.

References

[1] Pearlson M, Wollersheim C, Hileman J. A techno-economic review of hydroprocessed renewable esters and fatty acids for jet fuel production. Biofuels Bioprod Biorefin 2013;7:89–96. https://doi.org/10.1002/bbb.1378.

[2] Neste, Renewable Raw Materials. Neste (2018). [Online]. Available: https://www.neste.com/companies/products/renewable-fuels/renewable-raw-materials.

[3] Hongjian W, Wenzhi L, Xinyu C, Qing Y, Jiashuo L, Hanping C. Renewable bio-jet fuel production for aviation: A review. Fuel 2019;254:1155992.

[4] Karatzos S, McMillan JD, Saddler JN. The potential and challenges of drop-in biofuels. IEA (International Energy Agency) Bioenergy Task 2014;39:1–202.

[5] Karatzos S, Van Dyk JS, McMillan JD, Saddler J. Drop-in biofuel production via conventional (lipid/fatty acid) and advanced (biomass) routes. Part I. Biofuels, Bioprod Bioref 2017;11:344–62. https://doi.org/10.1002/bbb.

[6] Van Dyk S, Su J, McMillan JD, Saddler JN. ‘Drop-in’ biofuels: The key role that co-processing will play in its production. IEA (International Energy Agency) Bioenergy Task 2019;39:1–154.

[7] Lange J-P. Lignocellulose liquefaction to biocrude: A tutorial review. ChemSusChem 2018;11:997–1014. https://doi.org/10.1002/cssc.201702362.

[8] Gollakota ARK, Kishore N, Gu S. A review on hydrothermal liquefaction of biomass. Renew Sustain Energy Rev 2018;81:1378–92. https://doi.org/10.1016/j.rser.2017.05.178.

[9] Castello D, Pedersen TH, Rosendahl LA. Continuous hydrothermal liquefaction of biomass: a critical review. Energies 2018;11:3165. https://doi.org/10.3390/en11113165.

[10] Durak H, Genel Y. Hydrothermal conversion of biomass (Xanthium strumarium) to energetic materials and comparison with other thermochemical methods. J Supercrit Fluids 2018;140:290–301. https://doi.org/10.1016/j.supflu.2018.07.005.

[11] de Miguel Mercader F, Groeneveld MJ, Kersten SRA, Geantet C, Toussaint G, Way NWJ, et al. Hydrodeoxygenation of pyrolysis oil fractions: Process understanding and quality assessment through co-processing in refinery units. Energy Environ Sci 2011;4:985. https://doi.org/10.1039/c0ee00523a.

[12] Durak H, Genel S. Catalytic hydrothermal liquefaction of lactuca scariola with a heterogeneous catalyst: The investigation of temperature, reaction time and synergistic effect of catalysts. Bioresour Technol 2020;309:123375. https://doi.org/10.1016/j.biortech.2020.123375.

[13] van Dyk S, Su J, Mcmillan JD, Saddler JN. Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels Bioprod Bioref 2019;13:760–75. https://doi.org/10.1002/bbb.1974.

[14] Gueudré L, Chapon F, Mirodatos C, Schuurman Y, Venderbosch R, Jordan E, et al. Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining. Fuel 2017;192:60–70. https://doi.org/10.1016/j.fuel.2016.12.021.

[15] Al Jamri M, Li J, Smith R. Molecular Modeling of co-processing biomass fast pyrolysis oil in fluid catalytic cracking unit. Ind Eng Chem Res 2020;59:1989–2004. https://doi.org/10.1021/acs.iecr.9b05361.

[16] Wang G, Li Z-K, Liu Y-D, Gao J-S, Xu C-M, Lan X-Y, et al. FCC-catalyst coking: sources and estimation of their contribution during coker gas oil cracking process. Ind. Eng. Chem. Res. 2012;51:2247–56.

[17] Jiménez-García G, de Lasa H, Quintana-Solórzano R, Maya-Yescas R. Catalyst activity decay due to pore blockage during catalytic cracking of hydrocarbons. Fuel 2013;110:89–98. https://doi.org/10.1016/j.fuel.2012.10.082.

[18] Bai P, Etim UJ, Yan Z, Mintova S, Zhang Z, Zhong Z, et al. Fluid catalytic cracking technology: current status and recent discoveries on catalyst contamination. Catalysis Reviews 2019;61:333–405. https://doi.org/10.1080/01614940.2018.1549011.

[19] Xing T, Alvarez-Majmutov A, Gieleciak R, Chen J. Co-hydroprocessing HTL biocrude from waste biomass with bitumen-derived vacuum gas oil. Energy Fuels 2019;33:11135–44. https://doi.org/10.1021/acs.energyfuels.9b02711.

[20] Han Y, Pires APP, Garcia-Perez M. Co-hydrotreatment of the bio-oil lignin-rich fraction and vegetable oil. Energy Fuels 2020;34:516–29. https://doi.org/10.1021/acs.energyfuels.9b03344.

[21] Jensen CU, Rodriguez Guerrero JK, Karatzos S, Olofsson G, Iversen SB. Fundamentals of hydrofaction™: renewable crude oil from woody biomass. Biomass Conv Bioref 2017;7:495–509. https://doi.org/10.1007/s13399-017-0248-8.

[22] Jensen CU, Hoffmann J, Rosendahl LA. Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study. Fuel 2016;165:536–43. https://doi.org/10.1016/j.fuel.2015.08.047.

[23] Sharma K, Pedersen TH, Toor SS, Schuurman Y, Rosendahl LA. Detailed investigation of compatibility of hydrothermal liquefaction derived biocrude oil with fossil fuel for co-refining to drop-in biofuels through structural and compositional analysis. ACS Sustainable Chem Eng 2020;8:8111–23. https://doi.org/10.1021/acssuschemeng.9b06253.

[24] Bachler C, Schober S, Mittelbach M. Simulated Distillation for Biofuel Analysis. Energy Fuels 2010;24:2086–90. https://doi.org/10.1021/ef901295s.

[25] Dahiya A. Cutting-edge biofuel conversion technologies to integrate into petroleum-based infrastructure and integrated biorefineries. Bioenergy 2015:467–85. https://doi.org/10.1016/B978-0-12-407909-0.00028-6.

[26] Haghighat P, Montanez A, Aguilera GR, Rodriguez Guerrero JK, Karatzos S, Clarke MA, et al. Hydrotreating of hydrofaction™ biocrude in the presence of presulfided commercial catalysts. Sustainable Energy Fuels 2019;3:744–59. https://doi.org/10.1039/C8SE00439K.

[27] Zhao X, Wei L, Cheng S, Julson J, Anderson G, Muthukumarappan K, et al. Development of hydrocarbon biofuel from sunflower seed and sunflower meat oils over ZSM-5. J Renew Sustain Energy 2016;8:013109. https://doi.org/10.1063/1.4941911.

[28] Mills CE, Hall WL, Berry SEE. What are interesterified fats and should we be worried about them in our diet? Nutr Bull 2017;42:153–8. https://doi.org/10.1111/nbu.12264.

[29] Zhao A, Ying W, Zhang H, Hongfang M, Fang D. Ni/Al$_2$O$_3$ catalysts for syngas methanation: Effect of Mn promoter. J Nat Gas Chem 2012;21:170–7. https://doi.org/10.1016/S1003-9953(11)60350-2.

[30] Zarchin R, Rabaev M, Vidruk-Nehemya R, Landau MV, Herskowitz M. Hydroprocessing of soybean oil on nickel-phosphide supported catalysts. Fuel 2015;139:684–91. https://doi.org/10.1016/j.fuel.2014.09.053.

[31] Giakoumis EG. A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation. Renewable Energy 2013;50:858–78. https://doi.org/10.1016/j.renene.2012.07.040.

[32] Yue L, Li G, He G, Guo Y, Xu L, Fang W. Impacts of hydrogen to carbon ratio (H/C) on fundamental properties and supercritical cracking performance of hydrocarbon fuels. Chem Eng J 2016;283:1216–23. https://doi.org/10.1016/j.cej.2015.08.081.

[33] Horáček J, Akhmetzyanova U, Skuhrovcová L, Tišler Z, de Paz Carmona H. Alumina-supported MoNx, MoCx and MoPx catalysts for the hydrotreatment of rapeseed oil. Appl Catal B 2020;263:118328. https://doi.org/10.1016/j.apcatb.2019.118328.

[34] Douvartzides SL, Charisiou ND, Papageridis KN, Goula MA. Green diesel: biomass feedstocks, production technologies, catalytic research, fuel properties and performance in compression ignition internal combustion engines. Energies 2019;12:809. https://doi.org/10.3390/en12050809.