

Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units

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Hydrodeoxygenation (HDO) of pyrolysis oil fractions was studied to better understand the HDO of whole pyrolysis oil and to assess the possibility to use individual upgrading routes for these fractions. By mixing pyrolysis oil and water in a 2 : 1 weight ratio, two fractions were obtained: an oil fraction (OFWA) containing 32 wt% of the organics from the whole oil and an aqueous fraction water addition (AFWA) with the remaining organics. These fractions (and also the whole pyrolysis oil as the reference) were treated under HDO conditions at different temperatures (220, 270 and 310 °C), a constant total pressure of 190 bar, and using 5 wt% Ru/C catalyst. An oil product phase was obtained from all the feedstocks; even from AFWA, 29 wt% oil yield was obtained. Quality parameters (such as coking tendency and H/C) for the resulting HDO oils differed considerably, with the quality of the oil from AFWA being the highest. These HDO oils were evaluated by co-processing with an excess of fossil feeds in catalytic cracking and hydrodesulfurisation (HDS) lab-scale units. All co-processing experiments were successfully conducted without operational problems. Despite the quality differences of the (pure) HDO oils, the product yields upon catalytic cracking of their blends with Long Residue were similar. During co-processing of HDO oils and straight run gas oil in a HDS unit, competition between HDS and HDO reactions was observed without permanent catalyst deactivation. The resulting molecular weight distribution of the co-processed HDO/fossil oil was similar to when hydrotreating only fossil oil and independent of the origin of the HDO oil.

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[†] In memory of Michiel Groeneveld.

Introduction

Biofuels can help with the reduction of CO₂ emissions from fossil fuel usage as well as contribute to the security of energy supply. Unlike first generation biofuels (bio-diesel and bio-ethanol) advanced biofuels can be produced from a wide range of ligno-cellulosic biomass feedstocks, including waste, and their production does not necessarily compete with food or feed production.

Broader context

To meet the growing demand of energy, biomass can be used as a renewable and CO₂-neutral source. Moreover, biomass is expected to be an important source of renewable liquid transportation fuels and chemicals. Pyrolysis can be used as a pre-treatment step to convert the dry solid biomass into a liquid (pyrolysis oil) which has a higher energy density and is easier to handle than bulk biomass. However, pyrolysis oil (also known as bio-oil) still has limited end-user applications due to its low energy content (compared to fossil fuels) and instability.

This work considers the upgrading of pyrolysis oil fractions to produce oils that can be further co-processed in standard refinery units like FCC and HDS. In the underlying concept (www.biocoup.com), pyrolysis oil is produced where biomass is available and then transported to a central upgrading unit. This unit is located next or inside a standard petroleum refinery, enabling the use of existing facilities. Then, the upgraded oil is co-processed with fossil feed to obtain a product that can be readily incorporated in the refinery process chain. The ultimate product (mixture of fossil and biomass-derived organics) can be used as chemicals and fuels source, taking advantage of existing distribution networks.

One of the options to produce advanced bio-fuels is the co-processing of upgraded pyrolysis oil (also known as bio-oil) in standard refinery units.¹ Using this approach, pyrolysis oil can be obtained where the biomass is available and because of the energy densification that the pyrolysis process provides, transportation costs to existing (large scale) refineries could be reduced. The upgrading step would then be integrated in the refinery, using its utilities and product distribution network.

Hydrodeoxygenation (HDO) appears to be a promising upgrading step for the pyrolysis oil prior to its co-processing in refinery units.¹⁻⁴ A review by Elliot (2007) reviews the achievements regarding HDO of pyrolysis oil over 25 years.⁵ Recent results indicate that stabilisation of pyrolysis oil by low severity HDO might be sufficient to allow co-processing using refinery processes like FCC or hydroprocessing.^{1,6} This reduces overall hydrogen consumption during upgrading and is likely to improve overall economics of the production of bio-transportation fuels from pyrolysis oil. The complete removal of oxygen in the upgrading does not seem essential for subsequent co-processing.

Pyrolysis oil can be separated into two fractions by the addition of water, from which a heavy organic rich fraction, and an aqueous fraction are obtained.⁷ Depending on the amount of water added, the properties of the resulting fractions differ significantly. For example, if an oil : water ratio of at least 1 : 10 is used when the pyrolysis oil is added drop-wise to intensively stirred ice-cooled water and then filtered, the resulting heavy fraction is a powder, called “pyrolytic lignin”.⁸ Typically, the remaining aqueous fraction contains many different components with the “sugar constituents” being a major part (60–70 wt% of the organics in this aqueous fraction).⁹ In this paper, the aqueous fraction obtained by water addition will be referred to as AFWA. The remaining fraction, when oily in appearance, will be referred to as OFWA (oil fraction water addition) and when powder-like, “pyrolytic lignin”.

Pyrolytic lignin has a lower oxygen content when compared to whole pyrolysis oil (22–30 wt% compared to 33–40 wt%, both on dry basis).⁸ For deep deoxygenation,^{2,10} this seems advantageous because it reduces the stoichiometric amount of hydrogen required to remove the oxygen as water. Piskorz *et al.*¹¹ processed OFWA (in their publication it is called “un-dried pyrolytic lignin”) under HDO conditions. A light organic phase was obtained with a yield between 60 and 65 wt% (based on dry feed) with a molar H/C ratio of 1.5 and an oxygen content of ~0.5 wt%. The hydrogen consumption was high with 813 NI kg⁻¹ of product. Oasmaa *et al.*¹² and Meier *et al.*¹³ conducted hydro-treatment experiments on Kraft and organocell lignins using conventional sulfided NiMo and CoMo catalysts. They found that it is possible to create an oil-like product from lignin and that the presence of catalyst and high hydrogen pressures reduces considerably the formation of coke. de Wild *et al.*¹⁴ used a Ru/C catalyst for the HDO of the liquid product obtained after pyrolysis of lignin to produce phenols. Using a batch autoclave with an end temperature of 359 °C and starting with 100 bar of H₂, they concluded that Ru/C was too active for their process because they mainly produced cycloalkanes, cyclohexanols and alkanes. UOP LCC⁴ patented a process in which OFWA (called pyrolytic lignin in the patent) is hydrotreated and thereafter hydrocracked resulting in the production of 30 wt% gasoline.

Although still relatively little is known about the exact reactions during HDO, the HDO stabilisation step seems to be required to reduce or inhibit rapid self-polymerisation of pyrolysis oil that can result in reactor plugging and high coke yields.¹⁵ In a previous study on high pressure thermal treatment (HPTT) of whole pyrolysis oil,¹⁶ this fast polymerisation was observed when processing the oil at high pressure (200 bar), temperatures between 200 and 350 °C and residence times as short as few minutes. Severe increase in the oil’s molecular weight and disappearance of sugar constituents, from the aqueous phase by-product towards the oil phase, indicated that polymerisation of these sugars contributed to the increase in molecular weight. In our previous study on the HDO of whole pyrolysis oil,¹ with an increasing temperature, also a transfer of water soluble (sugar based) components to the oil phase product was observed, increasing thereby the oil yield. However, in this case, no increase in molecular weight was observed.

This suggests that it should be possible to produce HDO oil from AFWA, and especially from the sugars in it, as long as a proper stabilisation step is applied to prevent excessive polymerisation. Gagnon and Kaliaguine¹⁷ reported that a hydrogenation pre-treatment of the vacuum pyrolysis oil at temperatures as low as 80 °C stabilised the mono- and oligosaccharides (typically present in AFWA) from the vacuum pyrolysis oil allowing further HDO without strong polymerisation. During the stabilisation step in HDO functional groups, such as aldehydes, ketones and C=C double bonds, are likely to be hydrogenated towards more stable groups, less prone to polymerisation.¹⁸ Based upon pre-fractionation of the pyrolysis oil into AFWA and OFWA, HDO of both fractions thus seems a possible process option.

HDO of AFWA can also give more insight into the contribution of the components typically present in this fraction to the yields and qualities of the different product phases (aqueous, oil and gas) upon HDO of the whole oil. Wildschut *et al.*¹⁹ conducted HDO experiments in an autoclave using glucose and cellobiose as model compounds for the sugar fraction of pyrolysis oil. They concluded that, during HDO of these model compounds using a ruthenium on carbon (Ru/C) catalyst, the catalytic hydrotreatment route is preferred over the thermal decomposition that would lead to the formation of tar/solids (humins). The main products observed were polyols and gas products (mostly methane). Elliott and Hart²⁰ carried out semi-batch HDO experiments using acetic acid and furfural to represent pyrolysis products from hemi-cellulose and cellulose, respectively. From an un-catalysed initial test at 250 °C, a solid polymeric material from furfural was obtained. The conversion of furfural involves two reaction paths: cyclic ketone products (such as cyclopentanone) and cyclic ether products (such as THF). Some of these products reacted to alcohols and even further to CH₄ and CO₂. These results suggest that in the HDO of AFWA stabilisation is critical to avoid excessive polymerisation, but on the other hand high temperatures and hydrogen abundance can lead to substantial gas (methane) formation and unnecessarily high hydrogen consumption.

In this paper, HDO of pyrolysis oil fractions obtained by water addition to pyrolysis oil (AFWA, OFWA) was studied to better understand the HDO of whole pyrolysis oil and to evaluate the suitability of the oils produced from these fractions as feedstock

for co-processing in lab-scale refinery units. In the first part of this paper, product yields and properties obtained after HDO of the fractions are compared to those obtained after HDO of whole pyrolysis oil, identifying in this way possible upgrading routes. The results obtained by co-processing the OFWA and AFWA HDO oils in lab-scale refinery units (FCC and hydro-treater) are discussed in the second part of this paper and are used to assess the quality of the resulting HDO oils.

1. Experimental section

1.1. Materials

The oil used for this research was produced by VTT (Finland) in a 20 kg h⁻¹ process development unit²¹ using forest residue as feedstock. 2 wt% of isopropanol was added to the fresh oil, facilitating the separation of a top layer (10.6 wt%) containing a large number of extractives. The remaining fraction was the one used in this study ('whole pyrolysis oil', see Table 1) and used to prepare the OFWA and AFWA fractions. After receiving the oil from VTT, it was kept at -10 °C to avoid aging.

In order to know the amount of water needed to induce pyrolysis oil phase separation, different amounts of water (from 10 : 1 to 1 : 1 oil : water weight ratio) were added to the pyrolysis oil. They were mixed in an ultrasonic bath for an hour and then centrifuged to facilitate phase separation. The aqueous fraction (AFWA) was on top and had a light brown colour and the oil fraction (OFWA) was a dark brown viscous liquid. Each fraction obtained was analysed for water content and elemental composition. The distribution of organics into the two fractions can be seen in Fig. 1. It shows that at 10 : 1 ratio, no phase separation occurred. At 4 : 1 ratio, most of the organics remained in the AFWA. With increasing amount of water added, a plateau was reached yielding approximately 69 wt% and 32 wt% of organics in AFWA and OFWA, respectively. From these data, it was decided to use the minimum amount of water needed to reach the plateau, thus, 2 : 1 oil : water weight ratio was used to prepare the samples for HDO. Fig. 2 shows the molecular weight distribution (MWD) of the whole oil and its fractions (AFWA and OFWA). It can be seen that, in general, the light components present in the whole oil were transferred to the AFWA and the heavier ones to the OFWA.

Because of the large quantities of AFWA and OFWA needed for the HDO experiments presented in this work, another less laborious method was used to obtain the fractions. Water was

Table 1 Properties of the forest residue pyrolysis oil and the fractions obtained by water addition (2 : 1 oil : water weight ratio)

	Pyrolysis oil	OFWA	AFWA
Elemental composition and water content			
C dry (wt%)	54.3	62.6	53.4
H dry (wt%)	7.0	6.4	7.6
O dry (wt%) ^a	38.7	31.0	38.9
Water (wt%)	25.0	16.9	60.3
Carbon residue			
MCRT (wt%)	19.7	29.9	8.54
MCRT dry ^b (wt%)	26.2	35.9	21.5

^a By difference. ^b Corrected for water content.

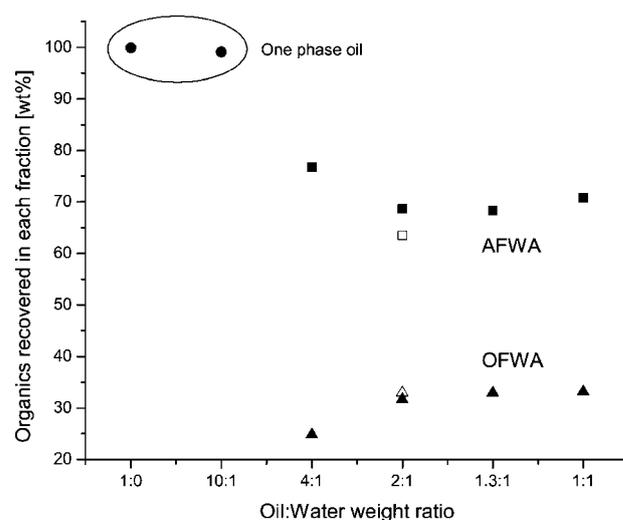


Fig. 1 Distribution of organics over AFWA and OFWA as a function of added amount of water to pyrolysis oil. Closed symbols correspond to results obtained using an ultrasonic bath for mixing and a centrifuge for separation. Open symbols correspond to results obtained by using a magnetic stirrer for mixing followed by 30 minutes gravity separation.

slowly added to pyrolysis oil while stirring with a magnetic stirrer. After adding the desired amount of water, the mixture was stirred for another 30 minutes. Then, the stirrer was turned off to allow the phases to settle. The distribution of organics using this method can also be seen in Fig. 1. The MWD of these fractions was the same as obtained using the ultrasonic method (results not shown).

The catalyst used for the HDO experiments was ruthenium on carbon (Ru/C) with a metal loading of 5 wt% and an average particle size of 14 μm. It was supplied by Sigma-Aldrich and it was used without any pre-treatment. This catalyst was selected because of its good HDO activity²² and to allow comparison with previous work¹ and literature.^{14,19,20}

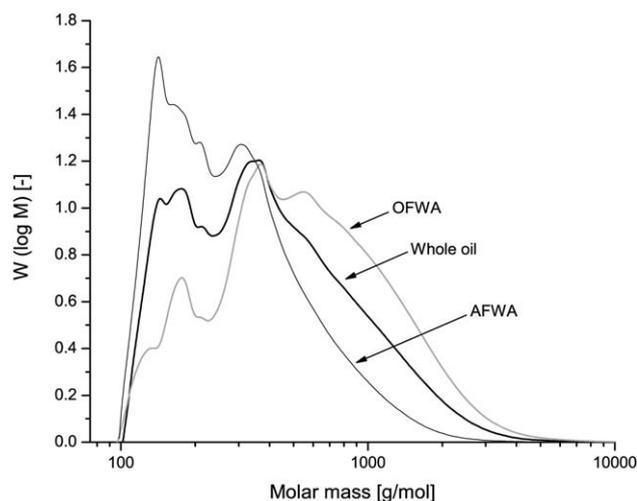


Fig. 2 Molecular weight distribution of the whole oil and its fractions (AFWA and OFWA).

1.2. Experimental set-up and procedure

Hydrodeoxygenation experiments were conducted in an intensively stirred autoclave from Autoclave Engineers with an internal volume of 0.6 l. The stirrer had a hollow shaft to induce gas–liquid mixing and thereby improve mass transfer. The maximum allowed temperature and pressure were 350 °C and 210 bar, respectively. For safety reasons, the autoclave was placed inside a high pressure box and it was monitored and controlled from outside. Fig. 3 shows a schematic representation of the set-up.

In a typical experiment, approximately 250 g of pyrolysis oil or one of its fractions was loaded into the autoclave. Baffles were placed inside the autoclave to improve agitation. Then, 5 wt% (on wet basis) of fresh catalyst was added. The autoclave was closed and a first leak test was conducted with nitrogen at 170 bar. If the leak test was successful, nitrogen was vented, removing at the same time the remaining air that was inside. Afterwards, a second leak test was carried out using hydrogen at the typical reaction pressure of 190 bar. Then, the hydrogen was vented also removing the remaining nitrogen. A supply vessel with a known volume of 3.21 l was filled with hydrogen to a pressure of 300 bar. The pressure and temperature of this vessel were recorded as a function of time in order to calculate the hydrogen consumption (rate) during the reaction. The reactor was filled with 100 bar of hydrogen and an electric oven (jacket) was placed around it. At this moment, the high pressure box was closed and the monitoring and control of the process were done from outside. The stirrer (20 Hz) and the heater were turned on. The heating rate was 7–9 °C min⁻¹ at the beginning and 1.5–2.5 °C min⁻¹ when approaching the temperature set-point. This means that it took from 50 to 80 minutes to reach the desired reaction temperature and the low temperature stabilisation reactions were already occurring during this period (hydrogenation of olefins, aldehydes and ketones already occur at temperatures under 200 °C¹⁸). This was further confirmed by the high hydrogen consumption (rate) observed during the heating time, especially for the experiments using AFWA as feed

(see Fig. 4). Up to a temperature of ~150 °C, the pressure inside the reactor increased due to the temperature effects, however after that it started to decrease. Then, more hydrogen was slowly added to the reactor in order to obtain a pressure of 190 bar when the desired reaction temperature was reached. Although reactions had already occurred in the heating period, in this paper this final temperature will be referred to as ‘reaction temperature’. When the pressure inside the reactor dropped below the set-point, a reducing valve between the supply vessel and the reactor allowed hydrogen into the reactor, conducting in this way a semi-batch experiment. The reaction time was typically 4 h, excluding the heating time. After the desired reaction time, the heating was turned off, and the stirrer was kept on for 30 min more. Subsequently, the system was allowed to cool down overnight. When the system was at room temperature, the final pressure and temperature of the reactor and supply vessel were

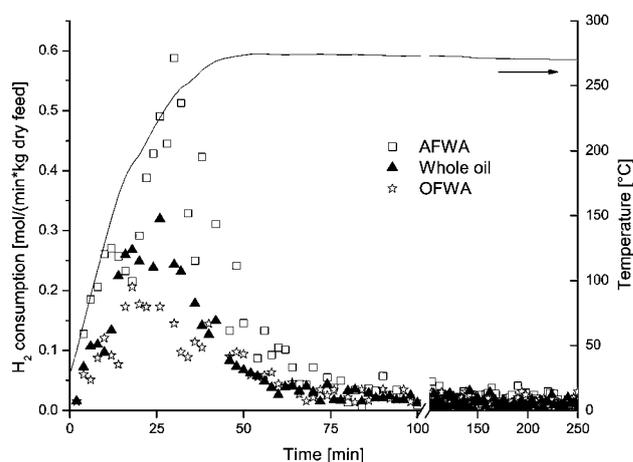


Fig. 4 Hydrogen consumption rate and temperature profile for the experiments at 270 °C using whole oil, AFWA and OFWA. This rate was estimated taking into account reactor and hydrogen supply vessel pressures corrected by the calculated water vapour pressure inside the reactor.

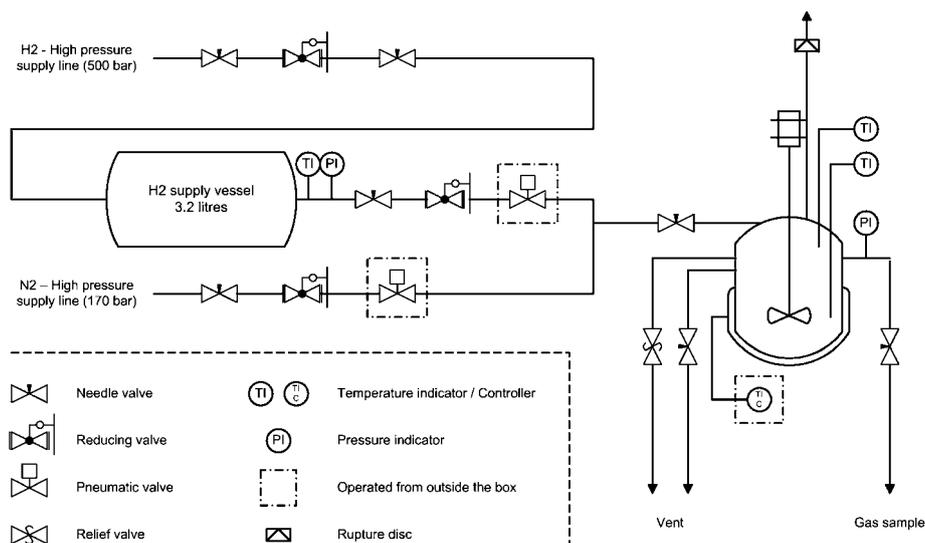


Fig. 3 Schematic overview of the HDO set-up.

noted and a gas sample from the reactor was taken for analysis. The total hydrogen consumption was calculated taking into account the initial and final number of moles of hydrogen in the supply vessel minus the number of moles of hydrogen that remained unreacted in the reactor. Next, the reactor was depressurised, opened and the liquid product, which normally consisted of different phases (see Section 3), collected and weighed.

The resulting HDO oils were co-processed in two different lab-scale refinery processes, *viz.* hydrodesulfurisation (HDS) and catalytic cracking. HDS experiments were performed by CNRS (Lyon, France), co-processing the upgraded oil with straight run gas oil (SRGO). The catalyst used was a commercial sulfided CoMo catalyst, the reactor temperature was 380 °C and the LHSV, 2 h⁻¹. Both SRGO and HDO oil (diluted in isopropanol to reduce viscosity) were fed using separate pumps, mixing them at the inlet of the reactor. Further details about this equipment and the SRGO used as co-processing fossil feed can be found elsewhere.²³ Catalytic cracking experiments were conducted by Shell Global Solutions in a MAT-5000 reactor. FCC equilibrium catalyst was used to co-process HDO oil with Long Residue fossil feed. The description of the set-up used and the properties of the Long Residue can be found in ref. 1.

1.3. Analyses

At the end of a HDO experiment, a sample of the remaining gasses was taken and analysed in a Micro GC Varian CP-4900 with three analytical columns: 10 m Molsieve 5A and 10 m PPG using helium as carrier gas and 10 m Molsieve 5A using argon as carrier gas for better hydrogen quantification.

The pyrolysis oil fractions and the HDO products were analysed for elemental composition (Thermo Scientific Flash 2000), water content (787 KF Titrino) and molecular weight distribution (Agilent HPLC 1200, with GPC columns). More details about the equipment and reactants can be found elsewhere.¹⁶

Micro-carbon residue tests (MCRT) were performed on all the feeds and oil products following the ASTM D4530 standard.

The SRGO and the co-processed products from the HDS unit were analysed on total sulfur content using an Antek 900 analyser. For these samples also the MWD was measured. In this case, an Agilent HPLC 1200 system with PLGel 5µm 50 Å and 5µm 500 Å (300 mm × 7.5 mm) was used.

The Long Residue and the products obtained by co-processing in the MAT unit were analysed using true boiling point (TBP) analysis following the ASTM D2887 standard, quantifying the yields of the different oil fractions.

2. Hydrodeoxygenation of pyrolysis oil and its fractions

Three series of experiments were conducted using the three different feeds: whole pyrolysis oil, AFWA and OFWA. Each series consisted of three experiments carried out at different temperatures: 220 °C, 270 °C and 310 °C and a residence time of 4 h (at reaction temperature, thus excluding heating time). As said in the previous section, all the experiments were carried out at a constant total pressure of 190 bar by allowing hydrogen from the supply vessel to the reactor. However, for the experiment at 310 °C and using AFWA as feed, only 160 bar of H₂ was added

when the reaction temperature was reached, stopping the supply of hydrogen from the vessel, to be able to extend the reaction time to the typical 4 h. In spite of this measure, the experiment had to be stopped after 2 h because the pressure was exceeding 200 bar (safety limit) due to the production of gasses.

The properties and appearance of the liquid product depended on the type of feed used. When AFWA was used as feed, the product not only consisted of an aqueous phase but a new oily organic phase was created. This oil was completely adsorbed in the catalyst, forming a paste-like material. To recover the oil, this catalyst–oil mixture was dissolved in acetone and filtered (6 µm filter). The acetone was thereafter removed in a rotary evaporator, recovering the solvent-free oil while the catalyst and some char remained on the filter. The resulting oil had a dark brown colour and low viscosity. This oil will be referred to as AFWA_{oil} and the aqueous phase by-product AFWA_{aq}.

When OFWA was processed by HDO, two phases were obtained, *viz.* an aqueous phase (OFWA_{aq}) floating on top and an oil phase (OFWA_{oil}) at the bottom. The OFWA_{oil} was dark brown and very viscous. These phases were separated and quantified. The amount of OFWA_{oil} was determined by correcting for the catalyst intake. Because of the high viscosity of the OFWA_{oil}, filtration was difficult and it was not possible to separately determine the amount of char produced. Some of the OFWA_{oil} was filtered using a pressurised system (8 bar) and a steel wire mesh (5 µm) to obtain enough sample for analysis and co-processing.

For whole pyrolysis oil (whole oil), either a two or three phase product was obtained depending on the reaction temperature. If three phases were obtained, an oil phase was on top, an aqueous phase in the middle and another oil phase was at the bottom. Depending on the time the sample was allowed to settle after collecting it from the reactor, the amount of top and bottom phase changed (the sum remaining constant). For that reason, it was decided to separate the aqueous phase (whole-oil_{aq}) and mix both oil phases into a single oil phase (whole-oil_{oil}). This oil phase was filtered with the same filter as used for the OFWA_{oil}.

For all the experiments, the mass balance closure in wet basis was between 90 and 98 wt%; being between 87 and 98 wt% on dry basis. The lower balance closure, mainly for HDO of AFWA (see Table 2), was probably due to the small amount of organics present in the feedstock (water content 60.3 wt%), making small losses of organic material (especially during recovery of the oil product) more significant.

Table 2 shows the dry yields of all the experiments (for details on how these yields were calculated see ref. 16). It can be seen that when AFWA was used as feed, an oil phase (AFWA_{oil}) was produced, increasing its yield with the temperature, especially between 220 °C and 270 °C. Dedicated experiments on HDO of AFWA to determine the amount of sugars in AFWA feed and AFWA_{aq} product (using BRIX analysis²⁴ conducted by VTT, Finland) showed a reduction of the sugars present in AFWA_{aq} compared to AFWA feed, being this reduction more significant at higher reaction temperature. At 300 °C and 120 min reaction time, 80 wt% of the sugars from the AFWA feed was not present in the AFWA_{aq} anymore. This indicates that the new oil phase produced from the AFWA contains high amounts of sugars (derivatives). The amount of gas produced also increased considerably with the temperature, reaching 18 wt% at 310 °C,

Table 2 HDO product yields, hydrogen consumption and oil properties

Feed	AFWA			OFWA			Whole oil		
Temperature (°C)	220	270	310	220	270	310	220	270	310
Residence time (min) ^a	240	240	120	240	240	240	240	240	240
Dry yields									
Gas phase	4	12	18	2	3	5	3	4	6
Water produced	9	11	13	—	7	16	10	10	16
Aqueous phase	64	39	25	5	9	5	32	25	17
Oil phase + char	15	30	31	83	74	70	53	58	56
Char	3	2	2	N.A. ^b	N.A.	N.A.	N.A.	N.A.	N.A.
Mass balance closure	92	92	87	90	93	96	98	97	95
H ₂ consumption									
NL H ₂ per kg dry feed	487	674	442	188	253	375	247	299	401
NL H ₂ per MJ oil phase prod.	114	72	44	7	11	14	15	16	19
Product oil properties									
C (dry, wt%)	68.5	68.2	71.6	68.4	69.4	77.8	65.2	68.5	74.4
H (dry, wt%)	9.6	9.9	9.7	7.6	8.1	8.6	8.1	8.6	10.0
O (dry, wt%) ^c	21.9	21.9	18.7	24.0	22.5	13.6	26.7	22.9	15.6
H ₂ O (wt%)	12.1	7.7	0.8	7.5	7.6	6.7	14.7	7.6	4.4
HHV (wet, MJ kg ⁻¹) ^d	29.4	31.1	34.7	28.2	29.3	33.9	25.4	29.5	35.1
MCRT (wt%)	4.71	3.96	5.55	21.7	15.2	18.1	13.1	9.86	5.33
MCRT dry ^e (wt%)	5.36	4.29	5.60	23.4	16.5	19.3	15.3	10.7	5.57
H/C _{eff} ^f	1.20	1.26	1.23	0.80	0.91	1.07	0.88	1.00	1.30
H/C _{eff} blend ^g	1.67	1.68	1.67	1.60	1.62	1.64	1.62	1.64	1.68

^a Excluding the heating time. ^b Not available. ^c Determined by difference. ^d Calculated using Reed's formula.²⁶ ^e Corrected for water. ^f H/C_{eff} = (H - 2 × O)/C.^{27,28} ^g Blend 20 wt% in Long residue.

forcing an early stop of the experiment to prevent an excessive pressure in the reactor. The gas formation was the highest of the three feedstocks. It appears to be logical that the gas formation is much higher for AFWA than for OFWA, since the former contains lighter components than the latter (see Fig. 2). Excessive gas production during HDO of acetic acid using a Ru/C as catalyst was already observed by Elliott and Hart.²⁰ At temperatures higher than 250 °C they observed a considerable production of CH₄ and CO₂ while at temperatures lower than 200 °C, most of the acid remained unconverted. Wildschut *et al.*¹⁹ also found high gas formation (37% of the carbon was recovered in the gas phase) during HDO of glucose solution, as a representative of pyrolysis oil carbohydrate fraction, at 250 °C, 4.3 h reaction time and using Ru/C as catalyst. In the present work, the dry gas yield from the whole pyrolysis oil at 310 °C was 6 wt%. However, when pyrolysis oil is split into the AFWA and OFWA, the overall—weight fraction based—gas yield at the same temperature is 13 g gas per 100 g of dry whole oil (the contribution from AFWA to this value is 88%). This is clearly much higher than the gas yield as obtained for whole oil, which (in this comparison) contains the same quantity of light components as the AFWA. This could be a result of the ratio of catalyst to dry feed; for all the experiments, 5 wt% of catalyst on wet feed basis was used. This means that for the experiments using AFWA the amount of catalyst per amount of organics (12.4 wt%) was much higher than for the experiments with whole oil (6.7 wt%) and OFWA (6.0 wt%), which might have favoured the overall rate of (irreversible) reactions towards gas formation. The composition of the gas produced from the AFWA is also remarkable (Fig. 5): the main gas produced at 220 and 270 °C was methane. The high methane production is likely to be caused by the use of Ru based catalyst (known to favour methanation reactions²⁵). As indicated, at the highest temperature of 310 °C, the H₂ supply had to

be stopped earlier because of the pressure increase and associated safety issues, resulting in limited hydrogen availability. At the end of the experiment, after cooling down, only 9 mol% of the gas was H₂, compared to 90 mol% in the experiment at 220 °C. At the same time, the ratio of the produced CO₂/CH₄ strongly increased with the reaction (end) temperature (220 °C: 0.02, 270 °C: 0.06, 310 °C: 0.77). These results indicate that (a) the production of CO₂ is favoured over that of CH₄ in the case of shortage of hydrogen and (b) in the beginning of the experiment with an end temperature of 310 °C mainly hydrogenation occurred (low temperatures), followed by decarboxylation upon hydrogen shortage in the later phase (high temperature) of the experiment.

When OFWA was used as feed, an increasing reaction temperature led to a decrease in the oil phase product (OFWA_{oil}) yield (Table 2). However, when looking at the carbon distribution (Fig. 6), the carbon that remained in the OFWA_{oil} was approximately constant. The decrease in oil yield can be attributed to the removal of oxygen from OFWA_{oil} (from 24.0 to 13.6 wt%, on dry basis) by water formation and to a smaller extent CO₂ formation (Fig. 5). Although the dry yield OFWA_{aq} was low when compared to HDO of AFWA and whole oil (factor of 3–4 lower), a remarkable trend can be observed. The highest yield of OFWA_{aq} was obtained at the intermediate reaction temperature of 270 °C. At 310 °C, the OFWA_{aq} yield decreased again by the production of gas and/or water. The CO₂/CH₄ ratio for the produced gasses favoured CO₂, especially at low temperature (220 °C: 16.5, 270 °C: 7.8, 310 °C: 1.7). In all cases the ratio was (much) higher than when AFWA was used as feed. With increasing temperature, and without hydrogen shortage, CH₄ formation appears to be favoured. Furthermore, part of the components that were in the OFWA_{aq} at 270 °C, disappeared at 310 °C forming CH₄.

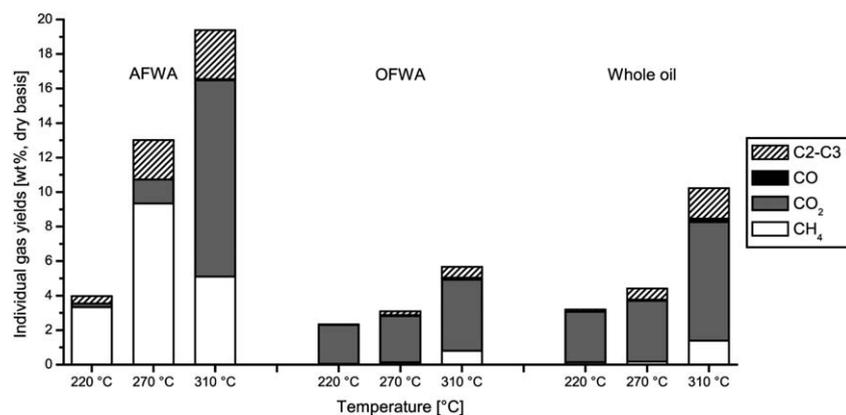


Fig. 5 Individual gas yields for HDO experiments at different temperature and feedstock. C2 and C3 are mainly ethane and propane, respectively.

For the experiments using the whole oil as feedstock, the yield of oil phase product (whole-oil_{oil}) remained approximately constant and the reduction of organics in the resulting aqueous phase product (whole-oil_{aq}) appears to be due to the formation of gas and water (Table 2). However, similar to the case of OFWA, the carbon distribution over the product phases reveals more information (Fig. 6). The increase in carbon recovery in the whole-oil_{oil} with the reaction temperature indicates that components with initially higher affinity for the whole-oil_{aq} changed their polarity due to the HDO reactions and were transferred to the whole-oil_{oil}. The observed constant whole-oil_{oil} yield was due to the accompanying reduction of oxygen content (from 26.7 to 15.6 wt%, on dry basis). These results are in line with results in our previous study.¹ This transfer of organics is further evidenced by the results in this study that show that it is possible to produce an oil phase product from HDO of AFWA. The main gas produced was CO₂ for all the reaction temperatures; the production of C2–C3 and CH₄ became more significant at 310 °C. The CO₂/CH₄ ratio (220 °C: 7.9, 270 °C: 7.4, 310 °C: 4.9) was lower than for the case of OFWA, except for the highest temperature, probably due to methanation of components typically present in AFWA. Similar to OFWA, methanation appears to be favoured with increasing temperature (no hydrogen shortage occurred in these experiments).

The first observation in Fig. 7 is the large difference in results as obtained for various feedstocks. Compared to the results

obtained for whole oil, OFWA_{oil} has a lower O/C, but also a lower H/C. Recent studies showed that the H/C might be a better quality indicator than O/C when considering co-processing in FCC units.¹ On the other side of the diagram,

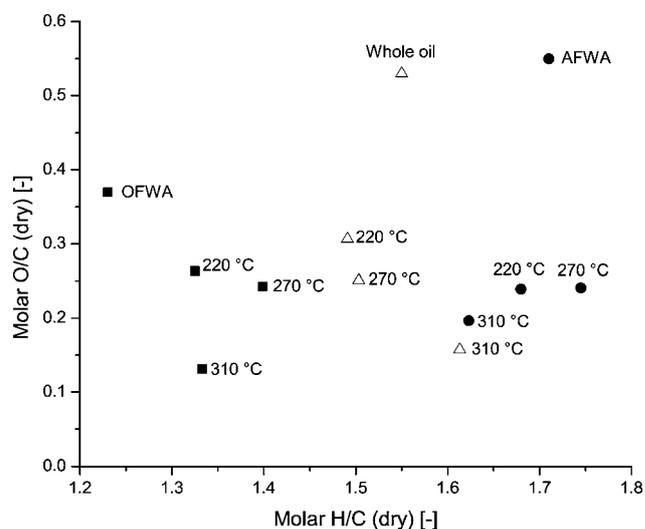


Fig. 7 Van Krevelen diagram for the (dry) HDO oil phase products (from AFWA, OFWA and whole oil respectively) obtained at different temperatures. Dry analyses of the 3 feedstocks included.

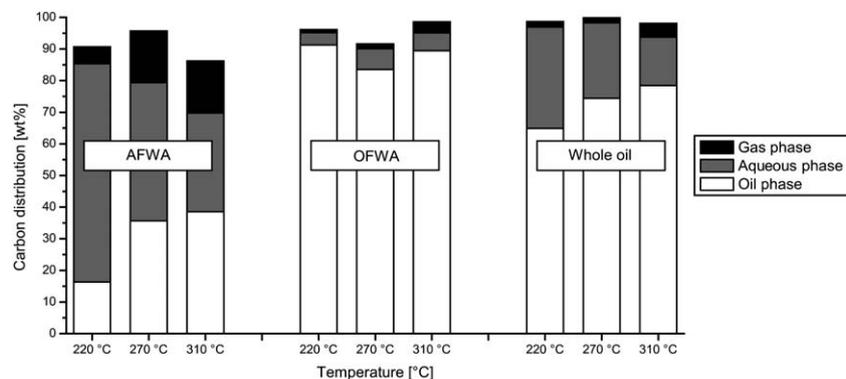


Fig. 6 Carbon distribution over the product phases using different feedstocks and reaction temperature.

AFWA_{oil} appears to have a higher O/C and H/C than whole-oil_{oil}.

For the AFWA_{oil} and compared to AFWA feed, a drastic decrease in the O/C ratio is observed with only a relatively small change in H/C. Since the organics present in the untreated AFWA are water soluble (thus polar), this decrease in O/C appears to be necessary to create a new (hydrophobic) oil phase. When comparing the AFWA_{oil} at different temperatures, an increase in H/C ratio can be seen when increasing the temperature from 220 °C to 270 °C, keeping the O/C approximately constant. At 310 °C, both the H/C and the O/C decreased. This can be explained by the lack of hydrogen availability and/or the fact that hydrogenation reactions are favoured at lower temperature (150–250 °C) and deoxygenation/dehydration reactions are favoured at higher temperature (>~300 °C).¹⁸ Since the H/C of the AFWA_{oil} was not higher than the feed, the very high hydrogen consumption (Table 2) must overall be attributed to the high methane production, the production of water and the hydrogenation of the organics that remained in the AFWA_{aq}. Analysis of these organics in the resulting AFWA_{aq} indeed yielded very high H/C, between 2.11 and 2.27, and an O/C decreasing with temperature from 0.44 to 0.20 (see Fig. 8). The combined results at 220 °C (negligible CO₂ formation, considerable oil production with lower O/C but similar H/C as AFWA and high water production) further indicate that the mechanism by which AFWA_{oil} is formed from AFWA is first hydrogenation and then dehydration of AFWA_{aq}.

Processing the OFWA under HDO conditions gave an oil product with lower O/C than the feed. Although the O/C of the different OFWA_{oil}'s are similar to the AFWA_{oil}, the H/C is clearly much lower. At 220 °C, the production of water was not detected; consequently, the reduction of O/C can only be attributed to the production of CO₂ and the transfer of organics to the aqueous phase. The O/C of the OFWA_{aq} was 0.67, compared to the O/C of 0.26 of the OFWA_{oil}. This difference in O/C was also observed for the HDO of the AFWA. At 270 °C and 310 °C, the effect of the reaction temperature was similar as

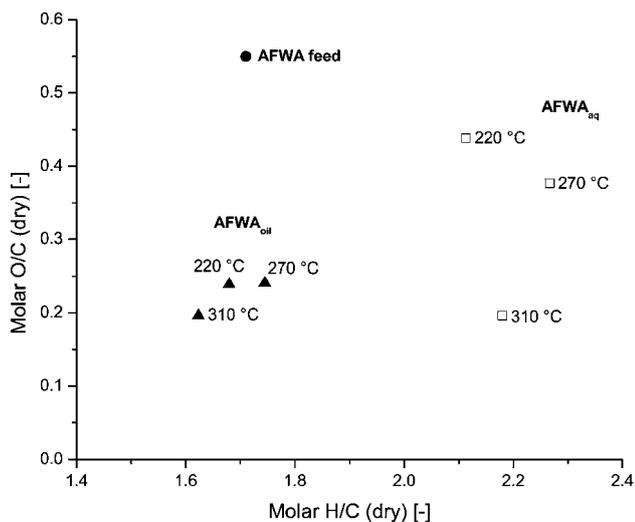


Fig. 8 Van Krevelen diagram showing the dry H/C and O/C ratios of the AFWA feed and the AFWA_{oil} and AFWA_{aq} products. Note that dehydration of AFWA_{aq} (220 °C) gives composition AFWA_{oil} (220 °C).

observed for the AFWA. For OFWA_{oil} and from 220 to 270 °C, there was an increase in H/C ratio while O/C remained similar. At the highest temperature (310 °C), a decrease of both H/C and O/C occurred. When looking at this low temperature hydrogenation and high temperature deoxygenation/dehydration during HDO, the same has been observed for aromatic structures such as phenol²⁹ and guaiacol,³⁰ molecules that are frequently used as model compound to represent the lignin structures present in pyrolysis oil.

The H/C and O/C of the different whole-oil_{oil}'s are also shown in Fig. 7. In all the experiments, the O/C was much lower than the ones for the feed. In this case, not only the hydro(deoxy)genation reactions have to be taken into account, but also the transfer of organics from one phase to the other (as observed in Fig. 6). The main cause for the reduction of O/C at low temperature is the change of polarity during HDO processing that induces a phase separation. In this process, components with low affinity for the aqueous phase (typically present in the OFWA) remained as whole-oil_{oil}, while most of the components with high water affinity (polar components typically present in the AFWA) were transferred to the whole-oil_{aq}. However, the higher H/C of the whole-oil_{oil} as compared to OFWA_{oil} as obtained in the experiments at 220 °C, indicates there was already a contribution to the whole-oil_{oil} from the organics originating from the AFWA. This is further confirmed by the AFWA_{oil} yield of 12 wt% at 220 °C (Table 2). This phase separation and transfer created a product oil with low O/C (similar to the HDO of the fractions) and an H/C which is typically between the H/C of the individual fractions. At 310 °C, opposite to the trend observed for HDO of AFWA and OFWA, the H/C of the whole-oil_{oil} increased (it should be noted that, for this experiment, there was no hydrogen shortage as in HDO AFWA at 310 °C). In this case, the increase in the whole-oil_{oil} yield due to the HDO of AFWA components (an oil with relatively high H/C) seems to compensate for the loss of hydrogen through dehydration reactions. It has to be noted that the results obtained for the whole pyrolysis oil are not just the weight averaged sum of the results for the individual fractions. The result of this weight average (using fractionation and product yields), for the case of 310 °C, gives similar O/C, but lower H/C (1.46, compared to 1.61 for the experimental value). Similar HDO experiments conducted in a bigger autoclave, at a higher pressure of 290 bar and at similar temperatures produced oils with similar O/C ratios (between 0.16 and 0.28), but higher H/C (~1.7, compared to ~1.5 to 1.6 in the present work).¹ This higher H/C could be because of the slower heating rate to reach the reaction temperature (30–40 min longer) allowing more time for hydrogenation reactions to occur (hydrogenation reactions are favoured at lower temperatures, see references above) and/or by the higher total pressure which increased the H₂ partial pressure and the amount of H₂ dissolved in the liquid. The hydrogen consumption of the experiments conducted at higher total pressure (at temperatures lower than 300 °C) was approximately 20% higher.

To define the quality of the upgraded oils towards further co-processing, the oxygen content has proven not to be the only parameter that should be taken into account. The MWD (Fig. 9), H/C (Fig. 7), H/C_{eff} (Table 2) and the MCRT (Table 2) of the HDO oils also give an indication of how well they will perform during pure or co-processing in a simulated FCC reactor.¹

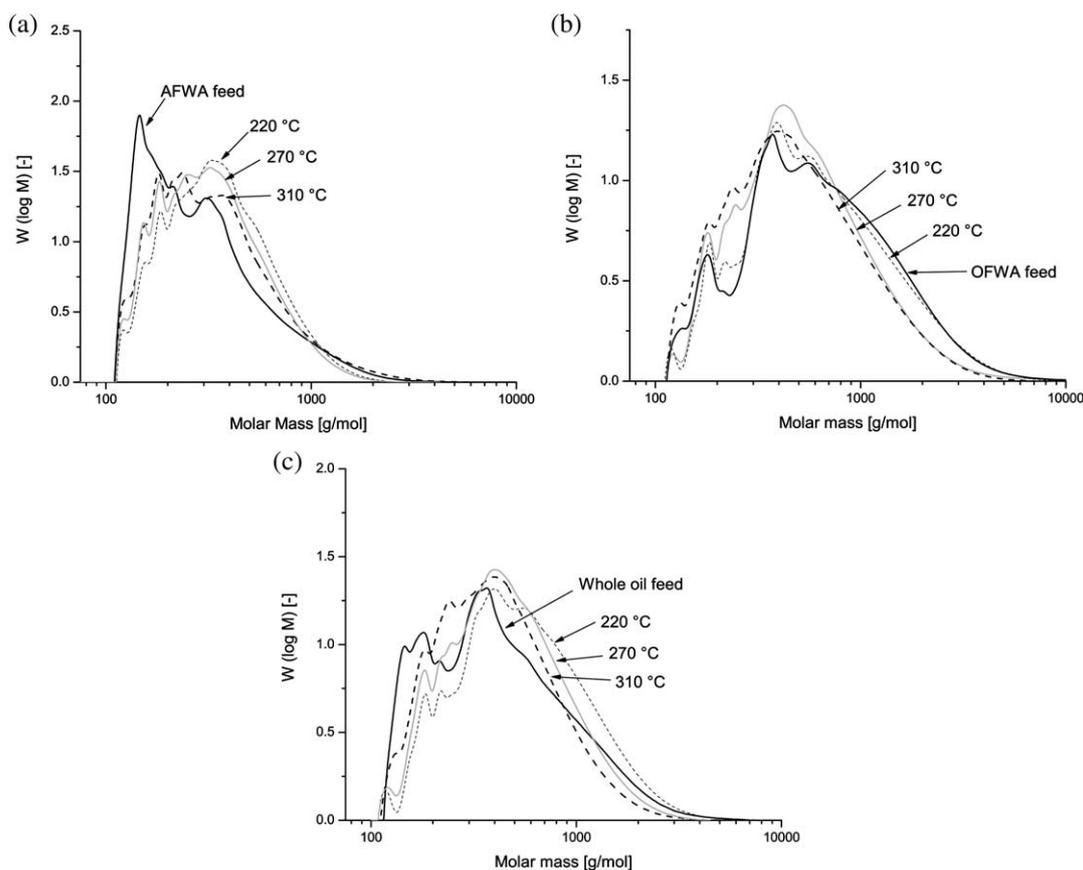


Fig. 9 Molecular weight distributions obtained by GPC analysis of the three different feeds and the corresponding HDO oil products obtained at different temperatures. (a) AFWA, (b) OFWA and (c) whole oil.

When looking at general quality differences between the oils produced from the different feedstocks, it can be seen that OFWA_{oil} has a higher MWD and MCRT and lower H/C compared to AFWA_{oil}. Product quality of OFWA_{oil} is thus expected to be lower than that of AFWA_{oil}. Quality parameters for whole-oil_{oil} are in between these two. A general trend between the H/C, MCRT and MWD can be observed: the higher the H/C the lower the MCRT and the MWD (with a few exceptions for the latter). Previous studies using whole pyrolysis oil as feed already showed the relationship between MWD and MCRT (or TGA residue).^{1,31}

Fig. 9a shows that AFWA_{oil} has a similar MWD as the feed. It should be noted that the tailing (at the high molecular weight region) for the AFWA_{oil}'s is equal (310 °C) or even shorter (220, 270 °C) than that of the feed. This shows that, in contrast to thermal treatment,¹⁶ in HDO processing strong polymerisation of the sugars constituents (main components of AFWA) can be prevented. The previously mentioned shortage of hydrogen in the experiment at 310 °C is probably responsible for the somewhat longer tailing as observed for this temperature in Fig. 9a. This is further supported by the MCRT values shown in Table 2, where the value for the experiment at 310 °C is somewhat higher than the values for 220 °C and 270 °C. This same trend (but inverse) also appears when looking at the H/C ratio. The experiment at 270 °C results in the highest H/C of the oil while for the experiments at 310 °C, this value decreased again. This

reduction in H/C was also observed during HPTT of pyrolysis oil¹⁶ and the processing of glucose at high temperature and pressure and it was attributed to dehydration reactions³² accompanied by polymerisation.

The MWD of the OFWA feed and the HDO oil products (OFWA_{oil}) show that the product obtained at 220 °C had a similar MWD to the feed, while for 270 and 310 °C the molecular weight was lower than that of the feed oil (Fig. 9b). In this case the MCRT does not follow this same trend, having the lowest value for the experiment at 270 °C. On the other hand, the trend observed for the H/C (from high to low 270 °C > 310 °C > 220 °C) matches the inverse of the trend of the MCRT (from low to high 270 °C < 310 °C < 220 °C).

In Fig. 9c the MWD of the whole oil and its HDO oil products (whole-oil_{oil}) can be seen. It shows that the whole oil feed contained both the lightest components (tall peak between 100 and 200 g mol⁻¹) and the heaviest (tailing). With increasing reaction temperature, the abundance of light components (originating from AFWA components) decreased, probably being converted to water soluble components and/or gas. This same effect is also seen when AFWA was used as feed. The abundance of heavy components (most of them belonging to the OFWA) also reduced as compared to the feed, this reduction being more significant with increasing reaction temperature. The same is observed when OFWA is used as feed, and it is likely caused by the depolymerisation of lignin structures.¹² Also in this case, the

MCRT and the inverse of the H/C follow the same trend. In literature, this reduction of molecular weight at increasing temperature using whole pyrolysis oil as feed is also reported^{1,31}

3. Upgrading routes

In Fig. 10, the carbon distribution from the whole pyrolysis oil and its fractions to the HDO products is shown. At the right side of the diagram, the sum of the carbon yields of the fractions is also shown for comparison purposes. The carbon recovery in the oil phase product is higher in the case of processing whole pyrolysis oil as compared to the recovery with intermediate fractionation. This can be attributed to the high carbon loss to the gas phase (due to the considerable gas formation when AFWA was used as feed), the larger amount of organics that remained in the aqueous phase product and the higher percentage of unrecovered carbon when fractions were used as feed.

When using whole pyrolysis oil as feed for HDO and at increasing the reaction temperature, a transfer of organics is observed from the whole-oil_{aq} to the whole-oil_{oil} (as already seen in previous studies¹). This study has confirmed that it is indeed possible to create an oil phase product from the AFWA. The formation of this product appears to be important to increase the

carbon recovery in the whole-oil_{oil} (Fig. 10). Although the oil obtained from HDO of AFWA (AFWA_{oil}) has a high oxygen content, which caused a higher O/C in the whole-oil_{oil} compared to OFWA_{oil}, it also has a high H/C_{eff} and a low MCRT, properties that appear beneficial for product quality.¹ Therefore, upgrading of whole pyrolysis oil leads to a high carbon recovery (oil from OFWA and new oil phase from AFWA), fair quality parameters (MCRT, H/C, H/C_{eff}, MWD) and also moderate hydrogen consumption.

Based upon pre-fractionation of pyrolysis oil into AFWA and OFWA, separate HDO of AFWA and OFWA is a possible process option. In this concept, the resulting oils can be routed towards different refinery units trying to valorise their difference in quality. Although the quality of the AFWA_{oil} (in terms of H/C, MWD and MCRT) is high, the high hydrogen consumption per MJ of product (see Table 2) and the low organic concentration of the feed increase the process costs. It should be noted that when processing AFWA, a considerable part of the hydrogen consumption was related to the production of low value gaseous products like methane. This suggests that removal of (some) light components, e.g. acids, either from whole pyrolysis oil or from the AFWA, might reduce hydrogen consumption. This would have the added benefit that at a given partial pressure of hydrogen in the HDO process, the total reactor pressure might be lowered. The light components could be recovered as value added chemicals or used for hydrogen production.^{33–36}

Another option that can be considered is the HDO of OFWA only, followed by co-processing of this HDO oil.⁴ As stated before, the AFWA could then be used for the recovery of chemicals and/or the production of hydrogen. In that case, the HDO of the OFWA would require less hydrogen than the HDO of the whole oil (Table 2), being beneficial for process economics. However, there are negative consequences to this approach. The total recovery of carbon in the HDO oil product would be 35 wt% from the initial pyrolysis oil which is low when compared to the 78 wt% when whole pyrolysis oil is processed. The reason for this is because the organics present in AFWA comprise ~62 wt% of the carbon in pyrolysis oil (see Fig. 10). Moreover, the quality of the OFWA_{oil}, when looking at H/C, MWD and MCRT, is lower compared to the whole-oil_{oil}. It appears that a higher HDO reaction temperature can reduce the molecular weight of the OFWA product (Fig. 9b), however, in this study, the H/C decreased and the MCRT increased at the same time.

For the determination of the optimal route, the possibilities to use the various product streams (including remaining aqueous streams) should be assessed and an overall economic evaluation performed. In the next section, the experimental performance of various HDO oils in lab-scale refinery units (FCC, hydro-treating) is discussed.

4. Co-processing upgraded pyrolysis oil fractions in refinery units

The HDO oils were evaluated as feeds in lab scale refinery units. HDO oils obtained by HDO of OFWA and AFWA (both at 310 °C) were co-processed in lab-scale catalytic cracking (with Long Residue) and HDS (with SRGO) units. This study only indicates if the HDO oils produced from

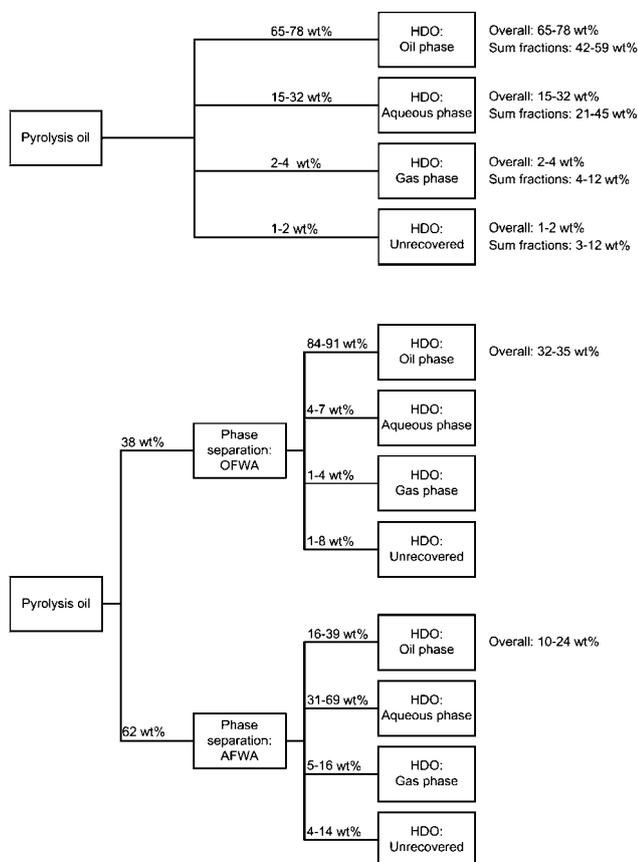


Fig. 10 Carbon distribution for HDO of the pyrolysis oil and its fractions. The range corresponds to experiments at different reaction temperature. Overall values correspond to the carbon recovered from the starting pyrolysis oil in the specific product phase.

Table 3 Product yields at constant 60 wt% conversion after catalytic cracking of 20 wt% AFWA_{oil} or OFWA_{oil} with Long Residue feed at 520 °C. Product yields (in wt%) normalised by the amount of produced water. Between parentheses, yields including produced water

	Long Residue reference	20% HDO oil from OFWA (310 °C)		20% HDO oil from AFWA (310 °C)	
Cat/oil ratio	3.2	3.2		3.5	
LPG yield	8.8	9.8	(9.4)	10.0	(9.6)
Gasoline yield	44.6	45.4	(43.6)	44.9	(43.2)
LCO yield	25.5	25.2	(24.2)	25.1	(24.1)
Dry gas yield	1.5	2	(1.9)	2.1	(2.0)
Coke yield	5.0	5.3	(5.1)	5.4	(5.2)
Other (HCO, slurry oil, CO and CO ₂)	14.6	12.3	(12.0)	12.5	(12.0)
Water ^a	—	—	(3.8)	—	(3.9)

^a Produced water calculated from the oxygen content in the feed, considering all the oxygen is transferred to water during catalytic cracking (CO and CO₂ yields were under 0.3 wt%).

fractions can be co-processed and how this affects standard operation. An extensive study on the influence of process conditions, catalyst type and product yield speciation during co-processing is beyond the scope of this paper.

Catalytic cracking

Co-processing of HDO oils (from AFWA and OFWA) with Long Residue was carried out successfully in the MAT reactor without plugging of lines. Table 3 shows the true boiling point (TBP) analysis of the products obtained after catalytic cracking of pure Long Residue (used as reference) and a blend of 20 wt% HDO oil/80 wt% Long Residue. In the same table, it can be seen that the cat/oil ratio needed to obtain 60 wt% conversion—defined as the sum of dry gas, LPG, gasoline range (C₅—221 °C) and coke—was the same for the reference and the co-processing of OFWA_{oil}, while it was slightly higher for co-processing of AFWA_{oil}. The product yield distributions were in all cases very similar and differences not significant.‡ The differences in quality for the various HDO oils as established in the previous sections are not confirmed by the co-processing results. It should be noted that the current product yields are similar to the yields obtained in a previous study using the same MAT reactor for co-processing of HDO oils from pyrolysis oil (produced at temperatures ranging from 230 °C to 340 °C and total pressures of 290 bar¹). Also in there, apparent differences in the product quality in HDO oils produced at different temperature did not result in substantial yield differences upon co-processing. A large excess of fossil feed, resulting in similar H/C_{eff} of the blends, was believed to contribute to this, and might also explain the similarity of results as obtained in this study (see Table 2). Although the MCRT values of the HDO oil were different, also the coke formation during catalytic cracking was alike and similar to the reference. This has been attributed to the hydrogen donation capacity of the fossil feed during catalytic cracking¹ which reduced the MCRT of the blends at least proportional but often more than that. After catalytic cracking of HDO oil from whole pyrolysis oil, phenolic components were detected in the total product, their level decreases with HDO operation temperature.¹

‡ Note that the overall yield to gasoline is 27 wt% (taking into account the OFWA_{oil} wet yield (63 wt%) and the gasoline yield after catalytic cracking (43.6 wt%)) which is similar to the gasoline yield of 30 wt% in the UOP LCC patent.⁴

Hydrotreating

The limit in sulfur content (10 ppm in 2009 in EC) in gasoline or diesel is one of the most drastic parameters that must be met by the refiners. Thus, the co-processing of an HDO oil and a Straight Run Gas Oil (SRGO) can be envisaged only if the competition between HDO and HDS reactions can be easily overcome by process adjustment. Preliminary studies performed on the co-processing of a SRGO with model oxygenated compounds such as guaiacol demonstrated that competition between HDS and HDO can occur, the severity depending on the type of components used.^{23,37}

In the HDS unit, the HDO oils were processed according to the sequence: SRGO–(SRGO and HDO oil mixture)–SRGO, in this way, the deactivation of the catalyst after the introduction of the HDO oil could be examined. The AFWA_{oil} and OFWA_{oil} were diluted in isopropanol 2 : 1 and 1 : 1 weight basis, respectively, to reduce the viscosity and allow pumping. These diluted oils were co-fed to the reactor with a ratio of 70 : 30 (in weight basis) SRGO : diluted HDO oil. Similar to the catalytic cracking experiments, both HDO oils were successfully co-processed without plugging of the reactor. However, the presence of HDO oil affected the degree of desulfurisation. For the reference experiment, upon processing only SRGO, the sulfur content of the product was on average 136 ppm (from 13 500 ppm of the crude SRGO). When the AFWA_{oil} (310 °C, 120 min) was co-processed, the product contained ~2000 ppm of sulfur. Just after the co-processing test, SRGO was processed pure again. Then, the desulfurisation recovered its initial value, indicating that the reduction in desulfurisation activity was due to the competition between HDO and HDS and not due to permanent catalyst deactivation. This competition was already observed during co-processing SRGO with guaiacol as model compound.²³ When the OFWA_{oil} (310 °C, 240 min) was co-processed, the sulfur content in the product also rose compared to processing pure SRGO to a value of 376 ppm. This value is much lower than the one obtained when co-processing AFWA_{oil}, but it should be noted that because of the different dilution ratio in isopropanol the concentration of HDO oil was lower in the case of co-processing OFWA_{oil}. Also in this case, the catalyst recovered its HDS activity when processing pure SRGO thereafter, demonstrating again the competition between HDO and HDS. After the co-processing of both AFWA_{oil} and OFWA_{oil}, phenolic

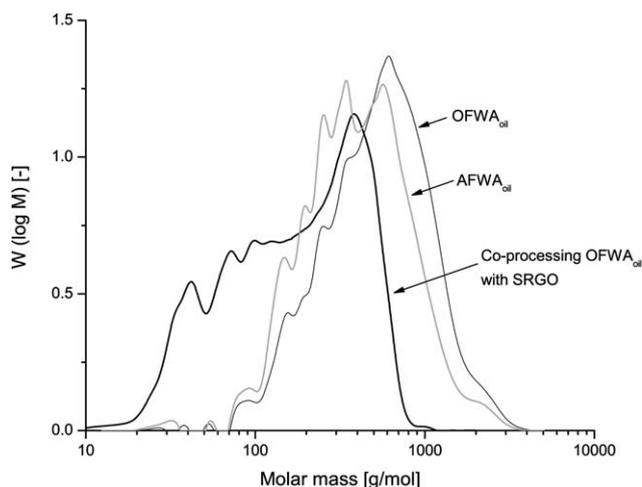


Fig. 11 Molecular weight distribution of the OFWA_{oil}, AFWA_{oil} and the product after co-processing SRGO and OFWA_{oil} in the HDS unit. Feed SRGO, processed SRGO and co-processed SRGO/AFWA_{oil} gave overlapping chromatograms with the co-processed SRGO/OFWA_{oil} product and are therefore not shown.

components were detected in the end product. The phenol C–O bond appears to be one of most resilient bonds in HDS/HDO conditions,²³ although it should be mentioned that the catalyst used was aimed at desulfurisation and not deoxygenation. Fig. 11 shows the MWD of OFWA_{oil} and AFWA_{oil} as well as the MWD of the product of co-processing the OFWA_{oil} with SRGO. Because the MWD of the feed SRGO and all the products of co-processing (including also processing of pure SRGO) were very similar and overlapping, only one HDS/HDO product chromatogram is shown. In the figure, it can be seen that the MWD of OFWA_{oil} is higher than AFWA_{oil} and they are both considerably higher than the MWD of the product oil obtained after co-processing. Therefore, during hydrotreating, not only the sulfur content was reduced but also cracking of large organic molecules originating from HDO oil occurred. This reduction of molecular weight during co-processing (at 380 °C) follows the same trend as observed in HDO of pyrolysis oil (fractions), which showed a decrease in molecular weight with increasing temperature (Fig. 9).

5. Conclusions

By addition of water to pyrolysis oil, a phase separation is induced creating two fractions, *viz.* an aqueous fraction water addition (AFWA) and oil fraction water addition (OFWA). The organic recovery in both fractions between a 2 : 1 and a 1 : 1 oil : water weight ratio remained constant. The AFWA had a higher O/C and H/C and approximately 62 wt% of the carbon was recovered in it. The OFWA had lower O/C but also lower H/C and the recovery of carbon in this fraction was approximately 38 wt%.

It was possible to create an oil phase (hydrophobic) product by hydrodeoxygenation (HDO) of the AFWA. The recovery of carbon in this oil phase increased substantially with the temperature, from 220 °C to 270 °C (16.3 wt% to 35.6 wt%), but less significant when further increasing the temperature to 310 °C

(38.5 wt%). This also explains the larger carbon recovery at increasing temperatures observed after HDO of the whole pyrolysis oil. The oil phase product obtained had a similar O/C as the product of whole oil but a higher H/C. This appears to be beneficial to reduce the coke formation tendency, which was confirmed by low MCRT values. On the other hand, the high H₂ consumption and the noteworthy production of CH₄ are downsides of this route. The H₂ consumption of HDO of OFWA was lower compared the HDO of whole oil. However, the oil product obtained had lower H/C and higher molecular weight and MCRT than the oil obtained from AFWA. Based on the differences in various quality parameters of the HDO oils from AFWA and OFWA, differences upon co-processing were expected.

The HDO oils produced from both AFWA and OFWA were successfully co-processed in catalytic cracking and hydrodesulfurisation (HDS) lab-scale units. Remarkably, the type of HDO feedstock did not change the product yield distribution after catalytic cracking, which is probably due to similar values of H/C_{eff} of the HDO oils/fossil feed blends. During co-processing straight run gas oil (SRGO) and HDO oils (obtained from pyrolysis oil fractions) in a HDS unit, competition between hydrodesulfurisation and hydrodeoxygenation was observed. When the oxygenated compounds from upgraded pyrolysis oil fractions were fed to the reactor, the sulfur content of the product was higher than when only SRGO was fed. After co-processing, pure SRGO was fed again and the degree of desulfurisation recovered its initial value showing no permanent catalyst deactivation. The molecular weight distribution of all the HDS co-processed products was similar and, at the same time, similar to the distributions obtained for (un)treated SRGO. It should be noted that the catalyst used in HDS co-processing was specifically targeted towards desulfurisation and not deoxygenation.

Considering the significant differences in HDO oil quality on one side, but the similarity in co-processing results on the other, further research on product speciation of the co-processed oils is recommended to see if initial differences in HDO oil product quality are eliminated in the co-processing procedures.

List of abbreviations

AFWA	aqueous fraction water addition (untreated)
AFWA _{aq}	aqueous phase product obtained by HDO of AFWA
AFWA _{oil}	oil phase product obtained by HDO of AFWA
FCC	fluid catalytic cracking
GPC	gel permeation chromatography
HDO	hydrodeoxygenation
HDS	Hydrodesulfurisation
HPTT	high pressure thermal treatment
H/C	dry molar hydrogen over carbon ratio
H/C _{eff}	H/C effective, $H/C_{eff} = (H - 2 \times O)/C$
LHSV	liquid hourly space velocity
MCRT	micro-carbon residue test
MWD	molecular weight distribution
OFWA	oil fraction water addition (untreated)
OFWA _{aq}	aqueous phase product obtained by HDO of OFWA

OFWA _{oil}	oil phase product obtained by HDO of OFWA
O/C	dry molar oxygen over carbon ratio
SRGO	straight run gas oil
TBP	true boiling point
THF	tetrahydrofuran
Whole-oil	untreated/not fractionated pyrolysis oil
Whole-oil _{aq}	aqueous phase product obtained by HDO of whole-oil
Whole-oil _{oil}	oil phase product obtained by HDO of whole-oil

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