Engine fuels production via hydrotreatment of hydrothermal liquefaction biocrude oil and pyrolysis bio-oil

A. Dimitriadis[1], S. Bezergianni[1], N. Tourlakidis[1], G. Meletidis[1]

[1]Centre for Research & Technology Hellas (CERTH), Chemical Process and Energy Resources Institute (CPERI) Thessaloniki, 57001, Greece
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Presenting author email: adimitr@certh.gr

Biomass pyrolysis and hydrothermal liquefaction (HTL) are two comparable technologies, as they both render bio-based intermediate products (often referred to as bio-oil and biocrude oil respectively). There are, however, significant differences between these two technologies [1]. Feedstock drying is required for the pyrolysis process, while it is not necessary in the case of liquefaction which reduces the economic return of fuel production to a great extent due to the wet nature of the selected feeds [2]. Furthermore, the use of catalyst enabling the reactions is not common in pyrolysis, while the solvents employed for HTL act as catalysts, rendering higher quality products as compared to those obtained from pyrolysis. Finally, the HTL product has lower oxygen and moisture content and higher heating value in comparison to the pyrolysis product which reduces both the fixed and operative costs of handling equipment and storage [3], rendering the HTL technology more competitive for biomass conversion to fuel products. However, both products from pyrolysis and hydrothermal liquefaction required further upgrading to enable its end-use as fuel as well as its compatibility with the corresponding combustion systems. Various technologies have been developed especially for the upgrading of pyrolysis oil, however, there is none optimised technology for the upgrading of HTL biocrude oil yet. Catalytic hydrotreatment (HDT) of bio-oil as well as biocrude oil allowing stabilization and deoxygenation is considered the state-of-the-art technology.

To that aim the current work targets to investigate the HDT upgrading of both pyrolysis oil as well as HTL biocrude oil. The upgrading of both feeds was tested on the same operating window, utilising the same hydrotreating catalyst in order to find out which feed will render the highest quality liquid fuels and how will affect the catalyst performance. Three operating conditions were investigated with both feeds as described in Table 1. The aim was to investigate the effect of hydrotreating temperature as well as the effect of H2/oil ration on product quality and yields of the process. The HDT experiments were performed in the small-scale pilot plant TRL 3 of CERTH, which is a small industrial system that is operated to generate information about the behaviour of the system for use in design of larger facilities. For the purpose of the current investigation, a commercial hydrotreating NiMo catalyst was employed, however, as the catalyst is a commercial one, no further details could be provided.

Table 1 Operating parameters examined

Parameters	**Units**	**Condition 1**	**Condition 2**	**Condition 3**
Pressure	psi	1000	1000	1000
Temperature	°C	330	360	330
H2/oil ratio	scfb	5000	5000	3000
LHSV	hr^{-1}	1	1	1

The results have shown that hydrotreating of both pyrolysis oil and biocrude oil leads in a two-phase liquid product that consists from the organic phase and the aqueous phase. The water phase is formed via the decarboxylation and dehydration reactions [48], which is a typical side product of biomass catalytic hydrodeoxygenation. Both organic and water-phase products have a significantly different appearance over the initial feeds (color, odor, viscosity), while the organic phase was considered as the main product and was further analyzed.

In case of pyrolysis oil, the yields of aqueous phase for conditions 1 and 2 were between 40 and 38 v/v % respectively, which shows that there is no strong dependence on the reaction temperature. As far as cond. 3 is concerned, the results show that the density, the aqueous phase as well as the sulphur content of the product are higher compared to cond. 1. This shows that the deoxygenation reactions are competitive to desulphurization and cracking reactions. The presence of H2S to keep the catalysts in the sulfide state leads to incorporation of sulphur in the organic product as long as the deoxygenations take place. Once the oxygen content is low the remaining sulphur is removed since the applied NiMo catalysts are well-known desulphurization catalysts. Thus, the hydrogen is consumed mostly for deoxygenation reactions instead of cracking and desulphurization reactions. In addition, the oxygen content is slightly higher for cond. 3 compared to cond. 1. However, the difference is not significant and is a result of measurements accuracy. From the above findings, it is observed that at lower H2/bio-oil ratio the hydrogen is not enough to cover the needs of all hydrotreating reactions, thus higher H2/bio-oil ratio is preferable. In general, considering all conditions, the oxygen removal was so deep that over 90 wt% of the oxygen was removed from the bio-oil and thus the product at 330°C K contained less than 2 wt% of oxygen. Finally, hydrogen consumption increased at higher reaction temperature due to higher extent of HDO and cracking reactions. Furthermore, higher H2/bio-oil ratio resulted in higher hydrogen consumption. This was due to higher extent of deoxygenation reactions confirmed by the lower oxygen and water content of the products of condition 1 compared to 3.

In case of biocrude oil upgrading, the results have shown that the highest yields on naphtha and diesel like fuels were achieved in condition 1 at 330°C. Increased of T to 360°C resulted to more cracking reactions leading to higher naphtha yields at the expenses of diesel. Furthermore, at lower H2/oi ratio, the cracking reactions reduced as the yields of the heavy fraction in the products increased. Reduction of H2/oil ratio also led to higher pour point which is a result of the heavier HC. Furthermore, the lower bromine number of the products from condition 1, shows that there are less unsaturated aliphatic groups (olefins) in the products due to more cracking reactions. While, finally, the higher cetane number observed on the product of condition 1, shows that condition 1 has led to the highest quality liquid fuels.

For both feeds, it was found that the optimum operating condition is 1 at 330°C and 5000 scfb H2/oil ratio. From the comparison of the two products from condition 1 (see Table 2), it is observed that the product from biocrude oil has lower density fulfill diesel specifications (0.80-0.85 g/ml), lower viscosity, higher cetane number (fulfill diesel specifications >51) and more organic phase yields. From the comparison, it is easily observed that the biocrude oil hydrotreatment resulted in a higher quality product compared to pyrolysis oil hydrotreatment

Table 2 Properties of both feeds and products from condition 1

Analysis	**Units**	**HTL biocrude oil**	**Pyrolysis oil**	**HDT prod. from biocrude oil**	**HDT product from pyrolysis oil**
Density at 15°C	gr/ml	1.0018	1.0249	0.8415	0.9200
Sulphur	wppm	175	1183	104	341
H	wt%	9.64	8.3	13.44	11.68
C	wt%	64.26	53.92	86.36	85.79
O	wt%	26.08	37.66	0.00	2.49
Viscosity	cSts	-	156	5.362	8.99
Cetane index				56.18	35.24
Pour point	°C	21	-3	6	-
2nd aqueous phase	v/v%			34.5	40.5
Organic phase	v/v%			65.5	59.5
TAN	mgKOH/g	88.24	79.92	0.5	0.0
Carbon residue	wt%	13	15.7	1.18	-
Naphtha yields (<200°C)	wt%	7	21	10	20
Diesel yields (200°-360°C)	wt%	31	50	62	42
Heavy fuel yields (>360°C)	wt%	62	29	28	38

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