Straw-based bio-oil to hybrid fuels production

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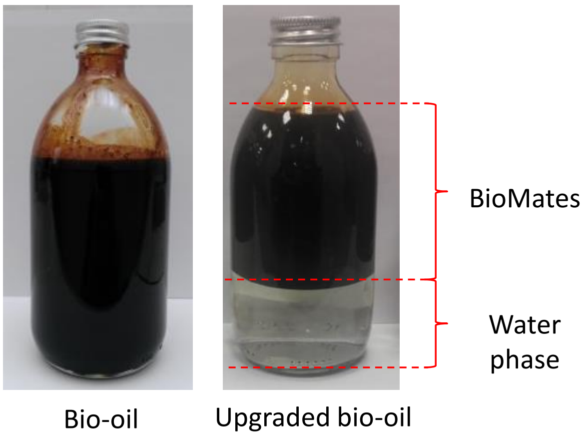
Pyrolysis bio-oils have been recently considered a promising alternative bio-based feedstock due to its applicability to lower grade waste/ non-food biomass. However, the complex composition of the current liquids and their physical-chemical properties prevent their direct blending with petroleum fractions. As a result, bio-oils need to be upgraded in order to be used as blending components with conventional refinery streams. To that aim, the current research is focused on partially upgrading of ablative fast pyrolysis bio-oil from a 50/50 v/v mixture of barley and wheat straw. Mild hydrotreatement, over various operating conditions was examined (temperature, pressure, H_2/Oil ratio) in continuous flow pilot plant at CERTH, as presented in Table 1, towards the identification of the optimum operating window in terms of hydrogen consumption and product quality.

Table 1 Operating experimental window for bio-oil hydrotreatment upgrading

Parameter	Units	Cond 1.	Cond 2.*	Cond 3.	Cond 4.	Cond 5.
Temperature	°C	**300**	**330**	**360**	330	330
Pressure	psi	1000	1000	1000	**580**	1000
LHSV	hr^{-1}	1	1	1	1	1
H_2/bio-oil	scfb	5000	5000	5000	5000	**3000**

*Control condition

A representative image of the ablative fast pyrolysis and its mild-hydrotreatment product is exhibited in picture 1, where it is obvious that the total liquid product consists of an organic phase (BioMates) and an aqueous phase resulting from the underlying hydrodeoxygenation (HDO) reactions. According to the experimental testing, the higher reaction temperatures favour HDO and cracking reactions, reducing the viscosity and the boiling point of the BioMates product, as shown in Table 2. Furthermore, the higher reaction pressures and H_2/bio-oil ratios are preferable in terms of catalyst life expectancy. In general, the BioMates product was produced with almost zero oxygen and water content, low viscosity and improved TAN (see Table 2).



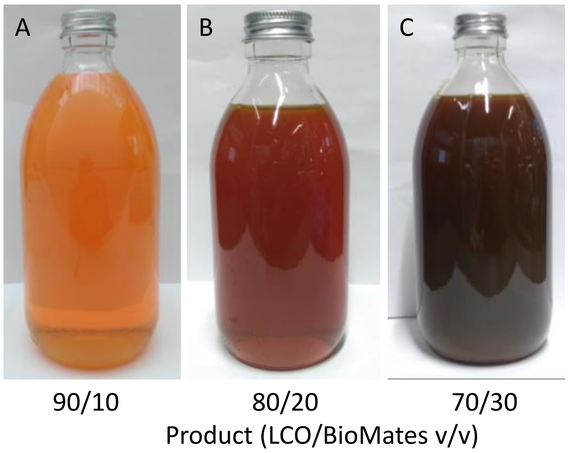
Picture 1 A) is the initial bio-oil feed and B) is the upgraded bio-oil after mild-hydrotreatment

Table 2 Properties of the initial bio-oil feed and BioMates

Properties	**Bio-oil**	**BioMates**
Density at 15°C (gr/ml)	1.024	0.927
Hydrogen (wt%)	8.32	11.68
Carbon (wt%)	53.92	85.40
Oxygen (wt%)	37.00	2.17
H_2O (dissolved) (wt%)	21.86	0.16
TAN (mgKOH/g)	79.92	0.87
Distillation		
Mass 10% (°C)	177.2	166.4
Mass 30% (°C)	226.2	236.0
Mass 50% (°C)	276.0	309.0
Mass 90% (°C)	468.4	537.0

The research was further extended with a co-hydroprocessing of BioMates with a compatible fossil-based refinery intermediate, aiming in a scoping study of the potential direct integration of BioMates in a refinery for hybrid fuels production. Light Cycle Oil (LCO) was selected as a compatible intermediate, based on a detailed preceding study as the most suitable refinery candidate from a miscibility perspective [1]. The organic phase of upgraded bio-oil

(BioMates) was blended with typical LCO that was provided from a BP refinery, at three blending ratios (10%, 20% and 30% v/v BioMates), none of which contained any additives.



Picture 2 Product (hybrid fuels) from co-processing of various LCO/BioMates blends. A) 90/10, B) 80/20 and C) 70/30 v/v

Table 3 Properties of hybrid fuels from various blends

Properties	90/10	80/20	70/30
Density at 15°C (gr/ml)	0.925	0.925	0.926
*Hydrogen (wt%)	10.43	10.56	10.69
*Carbon (wt%)	88.19	87.88	87.57
**Oxygen (wt%)	0.00	0.00	0.00
H_2O (dissolved) (wt%)	0.03	0.06	0.08
TAN (mg KOH/g)	0.06	0.21	0.23
Distillation			
Mass 10% (°C)	189.2	182.6	169.6
Mass 30% (°C)	244.0	243.0	236.0
Mass 50% (°C)	271.0	272.0	268.0
Mass 90% (°C)	348.0	360.0	396.0

*Values of C and H for the three blends were calculated based on the proportion of LCO and HDT bio-oil content

**Values of Oxygen were indirectly calculated assuming that the samples contain only C, H, S (wt%) and O

The addition of BioMates in LCO feed for co-processing results in a high-quality liquid product consisting of diesel and jet range hydrocarbons with almost zero water and oxygen content, low viscosity and improved TAN (Table 3). Furthermore, no ΔP creation was observed during the co-processing which shows that a small content up to 30% v/v of BioMates can be added in the unit without penalties on coke creation. Figure 1 shows the effect of BioMates integration in hydrogen consumption during co-hydrotreatment. A reduction of up to 8.9% on hydrogen consumption of the process was observed with the addition of the BioMates due to its lower sulphur content compared to LCO, bringing economic benefits to the refinery operation.

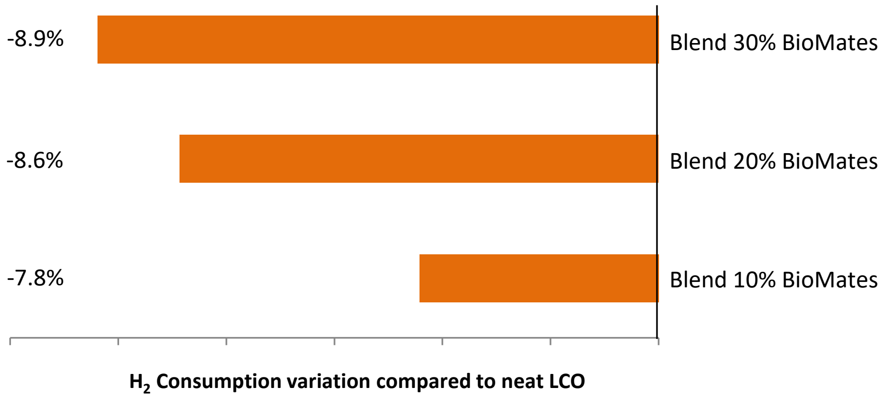


Figure 1 Effect of BioMates content on hydrogen consumption (H_2 consumption variation of LCO/BioMates blends compared to pure LCO)

To conclude, after a mild-hydrotreatment step, the organic phase of the produced total liquid product (BioMates) can be used as a blending component with petroleum-based feeds in a typical refinery hydroprocessing unit. This technology is well promising for green transportation fuels (hybrid fuels) production associated also with economic benefits for the refinery.

References

1. P. Manara, S. Bezergianni, U. Pfisterer. June 2018. Energy Conversion and Management 165:304-315

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