

## FAST PYROLYSIS BIO-OIL UPGRADING VIA HYDROTREATMENT FOR REFINERY INTERMEDIATES PRODUCTION

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### ABSTRACT

Biomass-based fast pyrolysis bio-oil is an oxygen-rich liquid product that is unsuitable for use as transportation fuel, however after a mild upgrading step it can be used as a reliable co-feed in underlying refineries for the production of hybrid transportation fuels. The current study investigates the upgrading of bio-oil to high-quality refinery intermediates via catalytic hydrotreatment, as part of the BioMates project. The bio-oil used in this research was produced via ablative fast pyrolysis of a mixture made from barley and wheat straw at 50 wt.% each. The aim of the study was to improve via mild HDO, the bio-oil quality in order to be used as an intermediate feed in a typical refinery for co-processing targeting transportation fuels. During the research, various operating parameters of HDO were investigated, including three reaction temperatures (300°, 330° and 360° C), two pressures (580 and 1000 psi) and two H<sub>2</sub>/Oil ratios (3000 scf and 5000 scf). The results have shown that the properties of the upgraded bio-oil were improved as the initial viscosity, TAN and density reduced in a high manner. The successful removal of oxygen and water content from initial bio-oil feed renders this technology as a very promising way to upgrade and promote the use of bio-oil for transportation fuel production.

### INTRODUCTION

In the last years, the EU and other countries have established specific action plans for the promotion of biofuels (Directive 2003/30/EC, Renewable Energy Directive 2009/28/EC, Amendment to the Fuel Quality Directive 2009/30/EC etc.). The first-generation biofuels (biodiesel and bioethanol) are based on energy crops (fresh oils) which limit their environmental benefits (GHG emissions) while leading to incompatibility problems with their fossil-based counterparts and combustion systems<sup>[1]</sup>. In addition to lipids, bio-oil has been recently considered as a promising alternative bio-based feedstock due to its favorable origin from non-food biomass. In general, bio-oil can be obtained by fast heating of solid biomass, typically lignocellulosic biomass including wood, forestry and agricultural residues<sup>[2]</sup>. However, biomass-based fast pyrolysis bio-oil is an oxygen-rich liquid product that is unsuitable for use as transportation fuel, thus a mild upgrading step is important to transform this liquid to a reliable co-feed that can be used in underlying refineries for the production of hybrid transportation fuels. The current study investigates the upgrading of bio-oil to high-quality refinery intermediates via catalytic hydrotreatment, as part of the BioMates project<sup>[3]</sup>.

### TARGETS & METHODOLOGY

The aim of the current study is the upgrading of a bio-oil to higher quality refinery intermediates via mild hydrotreatment by investigating various operating conditions. The bio-oil used was produced via ablative fast pyrolysis of a mixture made from barley and wheat straw at 50 wt.% each, supplied by the company Erhard Meyer. The bio-oil feedstock was produced via ablative fast pyrolysis by Fraunhofer UMSICHT, Germany; more details can be found elsewhere<sup>[4,5]</sup>. The key properties of flash pyrolysis bio-oil are presented in Table 1. It should be noted that a small

quantity of DMDS (Dimethyl Disulphide) was introduced into the feed in order to keep constant the activity of the hydrodeoxygenation catalyst.

According to Table 1, bio-oil presents high density which exceeds the maximum diesel specification (0.820-0.845g/ml). Furthermore, it has high oxygen content which explains the increased values of TAN and dissolved water. Therefore, an upgrading step is important to transform this heavy feedstock to higher added value liquid. Hydrotreatment should focus on oxygen removal as well as on cracking of heavy molecules.

**Table 1.** Bio-oil properties.

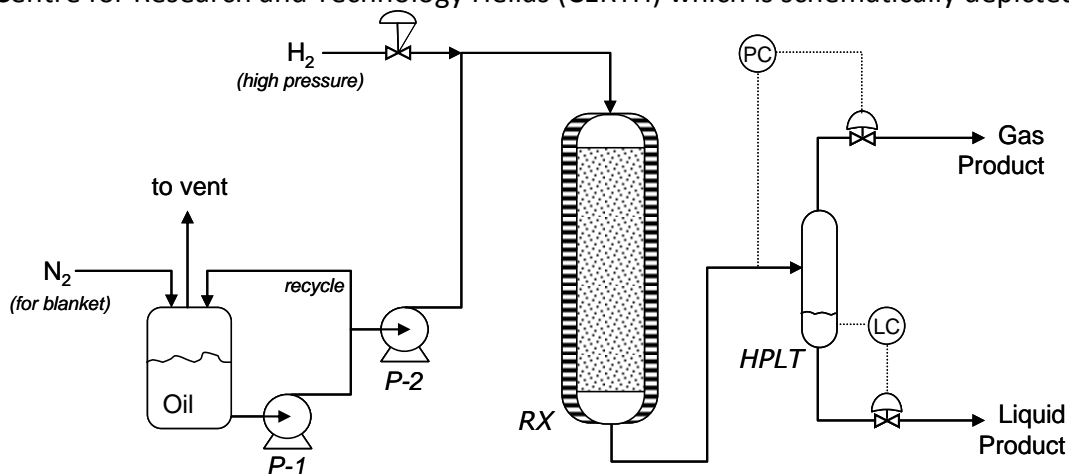


Properties	Units	Bio-oil
Density	gr/ml	1.024
Sulphur	ppm	1183
Hydrogen	wt%	8.32
Carbon	wt%	53.92
Oxygen	wt%	37.64
Dissolved water	wt%	21.86
TAN	mgKOH/g	79.92
Kin. viscosity	cSt	116

For this study, a custom-made NiMo/Al<sub>2</sub>O<sub>3</sub> based catalyst was developed from Ranido s.r.o. as part of the BioMates project. In order to maintain a desired LHSV, the catalyst was diluted with an inert material to ensure that it would be effectively dispersed throughout the reactor for achieving good heat and mass transfer. Catalyst presulfiding was performed by a procedure defined by the catalyst manufacturer.

## EXPERIMENTAL PROCEDURE

The main premise of this study was to evaluate the effect of temperature (300°, 330° and 360°C), pressure (580 and 1000 psi) and H<sub>2</sub>/oil ratio (3000 and 5000 scfb) on the upgrading of bio-oil via mild hydrodeoxygenation. During the investigation of each condition all the other operating parameters were remained constant. All experiments were carried out in a small pilot hydroprocessing plant of the Chemical Process and Energy Resources Institute (CPERI) of the Centre for Research and Technology Hellas (CERTH) which is schematically depicted in Figure 1.



**Figure 1.** Schematic diagram of laboratory scale hydroprocessing plant

Each experiment (condition) was considered complete when the reactions reached steady state, usually after 2-3 days on stream (DOS) (determined by monitoring the product density and sulfur

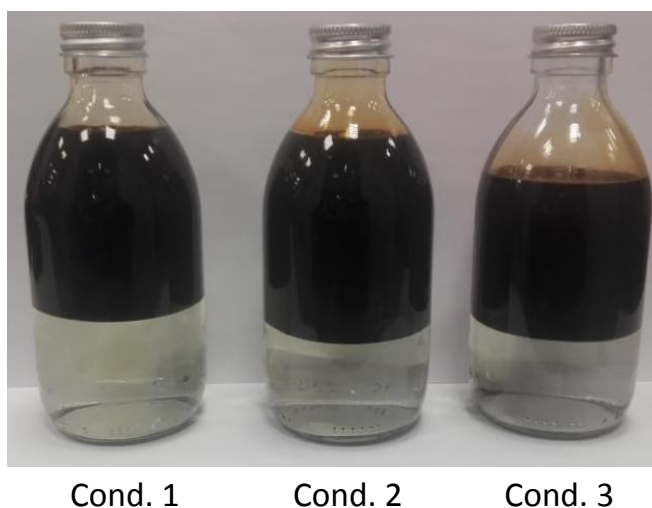
content). The total liquid product collected on the last day of each condition was analyzed in more detail. The gas product collected on the last day (after steady state was achieved) was chromatographically analyzed on-line as well. Table 2 presents the 5 conditions that were investigated.

**Table 2.** Operating experimental window.

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 <sup>-1</sup>	1	1	1	1	1
H <sub>2</sub> /oil	scf	5000	5000	5000	5000	3000

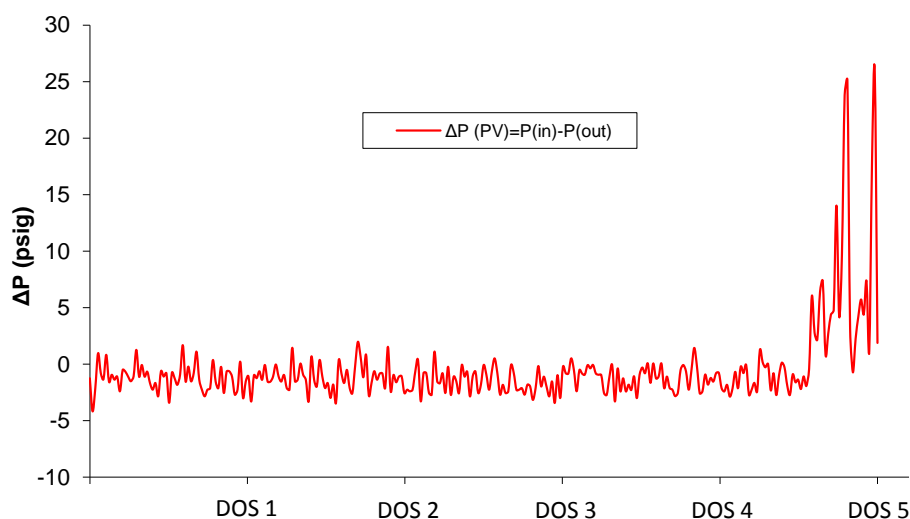
## RESULTS AND DISCUSSION

The effect of various operating parameters during mild hydrodeoxygenation upgrading of bio-oil will be presented in the current section. The aim of conditions 1, 2 and 3 was to investigate three reaction temperatures while keeping all the other parameters constant as presented in Table 2. It should be mentioned that the products consisted from an organic and an aqueous phase (resulting from HDO reactions) as shown in Picture 1. These two phases were separated via sedimentation and the organic phase was analyzed as the main liquid product.



**Picture 1.** Products from cond. 1, 2 and 3.

The catalyst clogging was daily monitored by the reactor  $\Delta P$  and the sulfur content in the liquid product. The reactor  $\Delta P$  did not show any appreciable change on the first days on stream. However,  $\Delta P$  was appeared on the fifth day of the experiment (DOS 5). At the 5 DOS an increase of  $\Delta P$  at 25 psi was occurred, for this reason the experiment was forced to stop. Similar to condition 1 are also the  $\Delta P$  plots of conditions 2 and 3, however for brevity reasons they are not presented in the manuscript.



**Figure 2.**  $\Delta P$  creation during condition 1

The aim of conditions 4 was to investigate the effect of pressure while keeping all the other parameters constant. As a result a pressure of 580 psi was investigated at the middle reaction temperature of 330°C and compared with the condition 2 (1000 psi and 330 °C) which was selected as a base case condition. The procedure followed on cond. 4 was the same with conditions 1, 2 and 3. High  $\Delta P$  was occurred during the third DOS reaching ~90 psi forcing in that way the termination of the experiment. The fast creation of  $\Delta P$  compared to previous conditions which were running on 1000 psi, shows the importance of higher pressures in the process. The catalyst clogging was revealed two DOS earlier compared to cond. 1, 2 and 3 (at 1000 psi).

In the case of cond. 5,  $\Delta P$  of 70 psi was occurred during the middle of DOS 3. Compared to the case of cond. 2 where pressure, temperature and LHSV were similar with the difference only on H<sub>2</sub>/oil ratio (con.2 was at 5000 scb), cond. 5 lasts less DOS. The current results show the importance of high hydrogen flows during HDO of bio-oil.

The properties of the organic liquid product from the third day of each condition are depicted in Table 2. It is observed that the second (water) phase range from 38 to 45 v/v % of the total liquid product depending from the operating window. The second phase of water shows the efficiency of hydrogenation reactions during hydrodeoxygenation. The aim of hydrodeoxygenation is the oxygen and water removal from initial bio-oil feed which was successfully completed. Furthermore due to oxygen removal, the TAN (total acid number) of the products is very low enhancing the quality of the organic phase. However, it was observed higher viscosity during 4 and 5 conditions. From the results, it is concluded that higher reaction temperatures favor HDO reactions and decrease the viscosity of the products. On the other hand, lower reaction pressure (580 psi) resulted in a product with three times higher viscosity (28.26 cSt) compared to the base case cond. 2 (8.99 cSt). Furthermore, the cetane number of cond. 4 was lower (27.37) compared to cond. 2 (35.24). It is easily noticed that lower reaction pressures results in lower quality products.

**Table 1.** Properties of organic liquid product

Parameter	Units	Cond. 1	Cond. 2	Cond. 3	Cond. 4	Cond. 5
Density	gr/ml	0.9702	0.9202	0.9162	0.9675	0.9488
Sulphur	ppm	469.2	341.4	792.4	571.4	686.9
Hydrogen	wt%	11.03	11.68	11.41	10.88	11.31
Carbon	wt%	84.02	85.79	86.81	84.97	85.63
Oxygen	wt%	4.90	2.49	1.70	4.09	2.99
H <sub>2</sub> O dissolved	wt%	0.090	0.025	0.001	0.027	0.099
H <sub>2</sub> O 2 <sup>nd</sup> phase	v/v	40.41	40.48	38.63	37.14	45.60
TAN	mgKOH/g	2.77	0	0.01	1.57	0.87

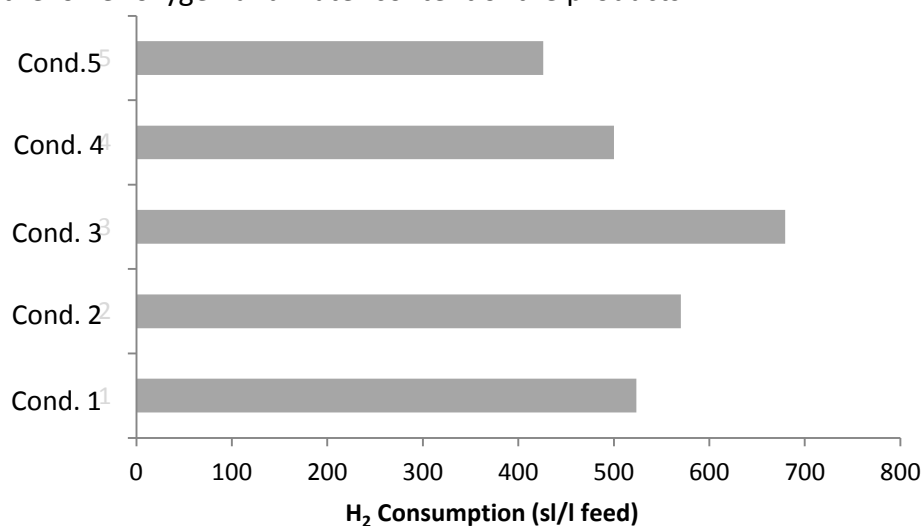
Cetane index	-	28.12	35.24	32.98	27.37	29.7
Kin. viscosity	cSt	61.98	8.99	4.94	28.26	14.60

Finally, catalytic hydrodeoxygenation consumes high amounts of hydrogen and thus is very important to optimize hydrogen consumption in order to improve the operating cost of the overall process. For this reason it is essential to estimate the H<sub>2</sub> consumption of the process. Hydrogen consumption was determined via the hydrogen mass balance according to the following equations:

$$H_{2Balance} = \frac{H_{2GasProd.} + H_{2LiqProd.}}{H_{2GasFeed} + H_{2LiqFeed}}$$

$$H_{2Consumption} = H_{2GasFeed} - \frac{H_{2GasProd.}}{H_{2Balance}}$$

The results of all conditions are depicted in Figure 3. According to the findings, Hydrogen consumption increased at higher reaction temperatures due to more cracking reactions that take place in the process. Furthermore, higher reaction pressures and H<sub>2</sub>/oil ratio result in higher hydrogen consumption. This is expected due to more deoxygenation reactions that take place confirmed by the lower oxygen and water content of the products.



**Figure 3.** Hydrogen consumption (Standard liter per liter feed)

## CONCLUSIONS

The proposed technology renders a promising intermediate for co-hydroprocessing with petroleum based fractions. In particular, the upgraded bio-oil is an excellent ignition quality intermediate feed that could be integrated in a mid process of a typical hydrotreating refinery. The successful removal of oxygen and water content from initial bio-oil feed via the proposed mild hydrotreating process render this technology as a very promising way to upgrade and promote the use of bio-oil for transportation fuel production. The properties of the upgraded bio-oil are improved as the initial viscosity, TAN and density reduced in a high manner. The results have shown that mild conditions are preferable from product quality view point and performance of the process. Finally it should be noted that although this technology is technically feasible, further research for reduced hydrogen consumption in order to improve economics is in progress.

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## LITERATURE

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