Impact of hydrogenation on miscibility of fast pyrolysis bio-oil with refinery fractions towards bio-oil refinery integration

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Keywords: bio-oil, hydrotreatment, hybrid fuel, wastes.
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Pyrolysis bio-oil is a mixture of oxygenated compounds formed during the decomposition of lignin, hemicellulose, cellulose and water (produced during the process and from the inherent moisture content of the biomass). Bio-oil differs from the petroleum refinery fuels in the heteroatom distribution, oxygen and water content, in density and the low heating value (Manara et al. 2018). In order to convert the low energy bio-oil in a compatible transportation fuel, an upgrading step is necessary, such as hydrotreatment. While stand-alone hydrotreatment of bio-oil is not economically attractive due to the associated high CAPEX and OPEX, bio-oil co-hydroprocessing with petroleum intermediates employing existing refinery hydrotreatment plants appears an attractive approach for bio-oil extensive use as a transportation fuel (Bezergianni et al. 2018). However, due to the unfavourable properties of bio-oil and miscibility limitations, a mild-hydrotreatment first step is unavoidable prior to co-processing. Within the BioMates project, a mild-hydrotreatment upgraded fast pyrolysis bio-oil is evaluated as a potential refinery co-processing feedstock.

In the present study, the potential compatible refinery entry points of a mild-hydrotreated bio-oil (BioMates) are investigated. In particular, a straw-based Ablative Fast Pyrolysis (AFP) bio-oil produced by Fraunhofer UMSICHT (Schulzke et al. 2016) was upgraded via mild-hydrotreatment at CERTH to be used as a blending component with fossil-based intermediates, in order to define the BioMates possible refinery entry points. The main purpose of the current work is to investigate the BioMates and petroleum intermediate blends in terms of miscibility and their properties. Based on the results of density, distillation data and the composition, in association with BP, the possible petroleum refinery entry points of BioMates include Straight Run Gas-Oil (SRGO), Gas-oil (GO), Fluid Catalytic Cracking Light Cycle Oil (LCO) and Heavy Cycle Oil (HCO), as well as Light Vacuum Gas-Oil (LVGO). All properties of AFP bio-oil, BioMates and afore-mentioned petroleum fractions are juxtaposed in (Table 1).

Table 1. Comparison between HDT bio-oil, straw bio-oil and refinery intermediates.

Property	Bio-oil	BioMates	SRGO	GO	LCO	HCO	LVGO
Surface tension (dyn/cm)	----	----	27.2	29.8	30.5	33.7	30.1
Density (kg/m^3)	1024.9	918.7	850.37	886.13	924.6	1077.5	855
Kin. Viscosity (cSt)	----	7.3871	1.5	20.5	6.9	140.6	21.99
Carbon content (wt.%)	53.92	83.91	87.2	86.37	88.51	89.46	85.48
Hydrogen content (wt.%)	8.32	11.65	12.37	12.5	10.32	7.95	12.68
Nitrogen content (wt.%)	0.00	0.68	0.02	0.047	0.08	0.26	0.14
Oxygen content (wt.%)	37.64	3.72	0.01	0.736	0.26	0.02	0.02
Sulfur content (wt.%)	0.12	0.96	0.4	0.347	0.83	2.31	1.68

A comparative analysis among the blends of bio-oil with the petroleum streams (30/70 v/v) and BioMates with the petroleum streams (30/70 v/v) was carried out in order to examine the effectiveness of bio-oil mild-hydrotreatment on its miscibility with the potential refinery entry points. To that aim, 2ml sample of each blend was examined in sedimentation chambers using the inverted microscope Nikon Eclipse SE 2000 (Stefanidou et al. 2018). The microscopy analysis started with a scan of the entire chamber bottom at low magnification (X45) to give an overview of the sample. This was followed by analysis at higher magnification (X100) in order to determine the existence of one or two separate liquid phases. Micrographs were taken using the Nikon DS-L1 microscope camera.

The results of the light microscopy analysis are shown in images (1) to (5). The untreated bio-oil was not miscible in any of the five intermediates while, after the mild-hydrotreatment upgrading step (BioMates) was miscible in all of them. In every bio-oil sample, the presence of two distinct phases between the bio-oil and the tested petroleum stream was clearly detected, as well as the bonds between the two phases (images 1-5). There were significant differences between these five mixtures to the size of the second phase areas, but none of them could be qualified as miscible. On the other side, the five blends of the Biomates/petroleum streams were perspicuous and the oil was miscible in all the refinery intermediates that were tested. The examination of these mixtures could only lead to the inference of the rare existence of a few dust particles, not related to the miscibility under examination.

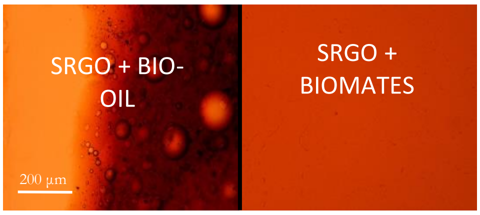

Image 1: Micrographs of SRGO with bio-oil/ BioMates.

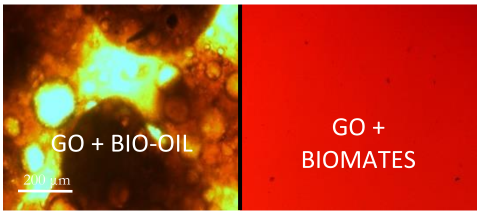

Image 2: Micrographs of GO with bio-oil/ BioMates

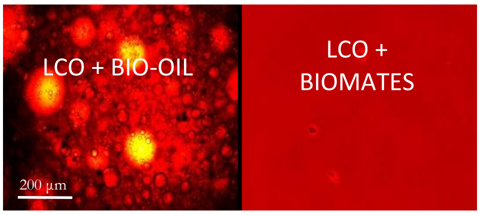

Image 3: Micrographs of LCO with Bio-oil/BioMates

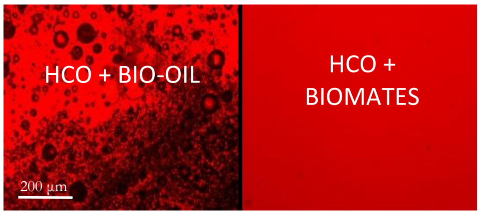

Image 4:Micrographs of HCO with Bio-oil/ BioMates

Image 5: Micrographs of LVGO with Bio-oil/ BioMates

The results from the HDT bio-oil blends show that they are all miscible and they consist of a single phase, based on the visual observations via microscope (Image 6). It is apparent that the mild-hydrotreatment converts all the non-soluble-to-hydrocarbons bio-oil components into compatible and miscible compounds that can be mixed with several refinery intermediates without any consideration. It is also noteworthy that non-hydrotreated AFP bio-oil has problematic miscibility with all petroleum fractions tested. This information expands the exploration of BioMates as a potential refinery co-feed of multiple petroleum fractions.

Image 6:(left to right) BioMates + (1. SRGO 2. GASOIL 3. LCO 4. HCO 5. LVGO)

References

P. Manara, S. Bezergianni, U. Pfisterer (2018) “Study on phase behaviour and properties of binary blends of bio-oil/ fossil-based refinery intermediates: A step toward bio-oil refinery integration”, Energy Conversion and Management, 165, 304-315

S. Bezergiani, A. Dimitriadis, O. Kikhtyanin, D. Kubicka (2018) “Refinery co-processing of renewable feeds”, Progress in Energy and Combustion Science, 68, 29-64

T. Schulzke, S. Conrad, J. Westermeyer (2016). Fractionation of flash pyrolysis condensates by staged condensation. Biomass and Bioenergy, 95, 287-95.

N. Stefanidou, S. Genitsaris, J. Lopez-Bautista, U. Sommer, M. Moustaka-Gouni (2018) “Effects of heat shock and salinity changes on coastal Mediterranean phytoplankton in a mesocosm experiment”, Marine Biology, 16