Residue2Heat

Project title: Renewable residential heating with fast pyrolysis bio-oil

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Type:	R	R	- Report
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DISCLAIMER

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Executive summary

This deliverable is the first one in a series of deliverables describing the physico-chemical properties of fast pyrolysis bio-oil (FPBO) blends of different feedstock. It is known that blending of bio-oils may not necessarily yield similar products than producing bio-oils from mixed feedstocks. Therefore, both approaches will be tested in the *Residue2Heat* project:

- Blending of the produced FPBO of different feedstock;
- Blending of different feedstock to produce FPBO.

In this deliverable various FPBOs from different feedstock have been blended in different ratios (1:3, 1:1, 3:1) with the objective of producing a homogenous bio-oil. If FPBOs can be blended by various ratios the fuel oil properties of these bio-oils can be adjusted to meet required emission limits in combustion. Also the blending of degraded FPBOs has been studied.

Blending of pine and straw FPBOs as well as pine and forest residue FPBOs were successfully carried out and homogenous FPBO blends were obtained. It is concluded that FPBOs can be blended to reach target fuel properties, like maximum sulphur and nitrogen contents. More blending tests including different FPBOs and thermal stability tests are ongoing and will be reported in the next deliverable.

The series of deliverables (D3.6 – D3.8) related to FPBO blending are primarily used for *Residue2Heat* internal documentation although they are marked as public. The follow up deliverables will include more details and analysis concerning benchmarking of processes, comparison of data between different feedstock and the performance of measures for optimal blending.

Table of Contents

List of Abbreviations

ES	Ether Solubles
FPBO	Fast Pyrolysis Bio-Oil
FR	Forest Residue
HMM	High Molecular Mass
LMM	Low Molecular Mass
MCR	Micro Carbon Residue
WIS	Water-insolubles

1 Introduction

Over time, fast pyrolysis bio-oil (FPBO) forms separated phases due to purely physical phenomena (phase stability) or chemical composition changes in storage (aging reactions). Bio-oil multiphase behaviour [Oasmaa 16] and the formation of separated phases are controlled by the complex chemical composition of these oils. Fast pyrolysis bio-oils from woody biomass are typically observed in a single phase. However, feedstocks with high extractives content and/or high ash content commonly produce oils with more than one phase (an aqueous phase, an upper layer, and a decanted heavy oily phase) [Oasmaa 15].

The hydrophilic fraction of FPBO consists of water and the most polar organic compounds, such as anhydrosugars, polyols, and other compounds with many hydroxyl groups. The second is the WIS fraction, which is mainly composed of lignin degradation products and some dissolved wood extractives (e.g., fatty acids and resin acids). The third fraction consists of C1−C6 oxygenated molecules that include aliphatic and aromatic acids, aldehydes, ketones, alcohols, and phenols. The first and second fractions are poorly soluble to each other, but the third fraction, i.e., the C1−C6 oxygenated compounds, acts as a co-solvent for the first two. Bio-oil is considered homogeneous when no separation of lignin and aqueous phase could be determined visually or with a microscope. Figure 1 shows the correlation between the chemical composition (the above-mentioned three fractions) and the homogeneity of fresh and aged bio-oils in a ternary-phase diagram. Blue circles and red squares represent one- or two-phase bio-oils, respectively. Their positions in the diagram show their chemical composition. Small arrows attached to the axes point to the directions of how to read the diagram. The composition of normal fresh bio-oils is typically 55:20:25 (weight ratio of water and sugars/WIS/co-solvents). After 1 year of aging, their composition change to approximately 55:25:20, but they remained homogeneous. After 4−8 years of aging, the WIS content increases and the solvent content decreased to as low as 55:40:5 and the bio-oils separate to two phases. The change in chemical composition during aging is highlighted with the blue dashed arrow in the diagram. Aged bio-oils appear in the bottom of the diagram because the amount of WIS content increases and the amount of C1−C6 oxygenated compounds decreases during repolymerization. The composition of fresh dry bio-oils (water content less than 10 wt %) was also homogeneous, but their position was slightly further away from the polar bottom left corner compared to wet bio-oils having an average composition of about 45:30:25. Although the water content was lower, the solvent fraction was similar to wet bio-oils.

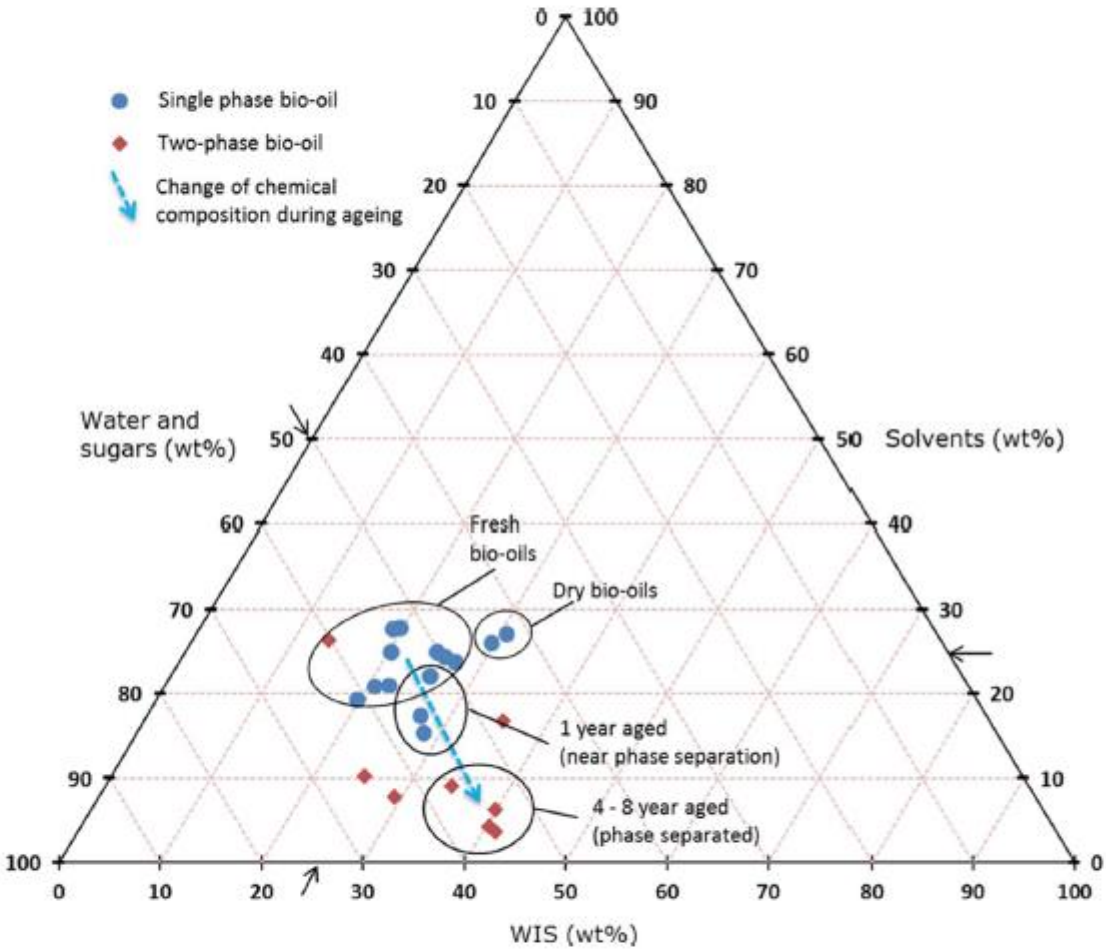

Figure 1: Ternary-phase diagram of phase stability based on chemical composition and homogeneity of fresh and aged bio-oils produced at VTT's pilot plant. [Oasmaa 15].

Blending of the feedstock (in task T2.2) is one strategy for producing homogenous FPBOs and another one is blending of different bio-oils from several feedstocks. The bio-oils have been produced in this project [Residue2Heat 17]. FPBOs were mixed after production to yield a homogenous FPBO. VTT will blend various FPBOs in different ratios (1:3, 1:1, 3:1) with the objective of producing homogenous bio-oil. If FPBOs can be blended by various ratios the fuel oil properties of these bio-oils can be adjusted to meet required emission limits in combustion. Blending of bio-oils may not necessarily yield similar products than producing bio-oils from mixed feedstocks. A comparison of results from the FPBOs produced from biomass blends and the blended FPBOs will be done.

2 Materials and methods

The FPBOs chosen for the blending tests, their age, and their chemical composition indicated as weight ratio of water and sugars, WIS (HMM+LMM), and co-solvents (ES) are shown in Table 1. Physical properties of the FPBOs are presented in Table 2. Pine FPBO (R2H.BTG.001b) was separately blended with wheat straw (R2H.VTT.107) and forest residue (R2H.VTT.109). At the first stage, blending of FPBOs was performed using ratio 1:1.

Table 1: FPBOs for the blending tests[1].

FPBO		Age	Chemical composition, wt%		
			Water and sugars	WIS	Co-solvents
R2H.BTG.001b	Pine	Fresh	55.5 (21.5 water, 34.0 sugars)	26.2	18.3
R2H.VTT.107	Wheat straw	Fresh	54.4 (25.5 water, 27.9 sugars)	31.3	15.3
R2H.VTT.109	Forest residue	Freeze/fresh	57.2 (27.4 water, 29.8 sugar)	20.3	22.5

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3 Results

Microscopic images of blends are shown in Figure 2. Reference pine FPBO was blended with forest residue and wheat straw FPBOs in 1:1 ratio. Blending was successful and the blends homogenous FPBOs. Fuel oil properties of the blends are presented in Table 3. It is concluded that FPBOs can be blended to reach target fuel properties as mentioned before.

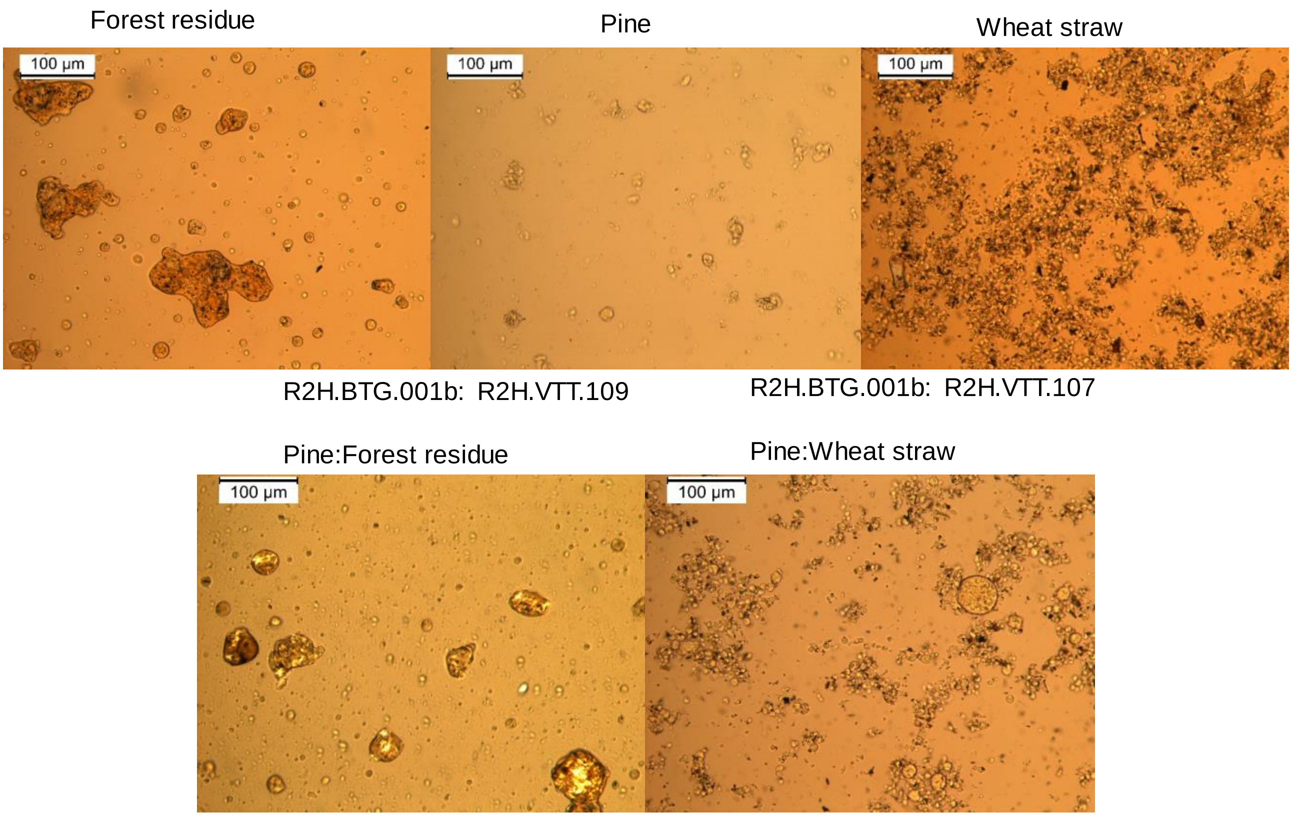

Figure 2: Blend (1:1) of pine and straw FPBOs.

[1] More detailed description of the analysis methods are presented in deliverable D3.3 [Residue2Heat 17b].

Table 2: Composition of FPBOs for the blending tests.

	Unit	R2H.BTG.001b Pine wet	R2H.BTG.001b Pine dry basis	R2H.VTT.107 Wheat straw wet	R2H.VTT.107 Wheat straw dry basis	R2H.VTT.109 Forest residue (FR) wet	R2H.VTT.109 Forest residue (FR) dry basis
Water	wt %	21.5	0	25.5	0	27.4	0
Solids	wt %	0.01	0.01	0.99	1.33	0.04	0.055
Ash	wt %	0.02	0.02	0.67	0.90	0.07	0.096
Carbon	wt %	44.6	56.82	42.1	56.5	41	56.5
Hydrogen	wt %	7.7	6.7	8.0	7.0	7.8	6.5
Nitrogen	wt %	0.1	0.13	0.6	0.8	0.6	0.8
MCR	wt %	18.3	18.3	19.9	26.7	19.8	27.3
Water increase (24h 80 °C)	%	4.2		7.2		2.6	
Water after test	wt %	22.4					
Carbonyl change (24h 80 °C)	%	26.0					
Carbonyl content	mmol/g	4.3					
Carbonyl content after test (24h 80 °C)	mmol/g	3.19					

Blended oils have a bit higher water increase after the stabilisation test compared to the original oils, especially in the case of pine and forest residue blend. Carbonyl content was similar in both blends, but lower in comparison to the pine FPBO before and after the stability test.

Table 3: Composition of oils after the blending of 1:1.

Ratio	Pine + straw R2H.BTG.2016.001b+ R2H.VTT.107 1:1	Pine + FR R2H.BTG.2016.001b+ R2H.VTT.109 1:1
Water, wt %	22,9	24,1
Nitrogen, wt %	0,3	0,3
Carbon, wt%	43,7	42,9
Hydrogen, wt%	7,5	7,5
Water increase , % 24h 80C	7,4	11,6
Water after test, wt%	24,6	26,9
Carbonyl increase, % 24h 80C	34,0	33,6
Carbonyl content, mmol/g	3,74	3,69
Carbonyl content after test	2,47	2,45
After test 24h 80C		
Nitrogen, wt %	0,3	0,3
Carbon, wt%	43,1	47,8
Hydrogen, wt%	7,6	7,7

4 Conclusions

This deliverable is the first one in a series of deliverables describing the physico-chemical properties of fast pyrolysis bio-oil (FPBO) blends of different feedstock. It is known that blending of bio-oils may not necessarily yield similar products than producing bio-oils from mixed feedstocks. Therefore, both approaches will be tested in the *Residue2Heat* project:

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Bibliography

[Oasmaa 15] Oasmaa, Anja; Sundqvist, Tom; Kuoppala, Eeva; Garcia-Perez, Manuel; Solantausta, Yrjö; Lindfors, Christian; Paasikallio, Ville. Controlling the phase stability of biomass fast pyrolysis bio-oils: American Chemical Society. Energy and Fuels, Vol. 29, No. 7, pp. 4373-4381, 2015.

[Oasmaa 16] Oasmaa, Anja; Fonts, Isabel; Pelaez-Samaniego, Manuel Raul; Garcia-Perez, Martha Estrella; Garcia-Perez, Manuel. Pyrolysis oil multiphase behavior and phase stability: A review: ACS Publications. Energy and Fuels, Vol. 30, No. 8, pp. 6179-6200, 2016.

[Residue2Heat 17] Evert Leijenhorst, Christian Lindfors; Delivery of Conditioned FPBO, Residue2Heat Deliverable D2.5 (2017), available at http://www.residue2heat.eu