PROPERTIES AND COMPOSITION OF BIO-OIL HYDRODEOXYGENATION PRODUCTS

Auersvald M.*, Staš M., Šimáček P.

Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
**milos.auersvald@vscht.cz*

Abstract

Pyrolysis bio-oil could be used as a second generation biofuel; however, its undesirable properties must be improved. A detailed analysis is necessary to optimize an upgrading process and understand the behaviour of bio-oils during their hydrodeoxygenation. Therefore, we introduced commonly used methods for the quantification of individual groups of oxygen compounds as carboxylic acids, ketones, aldehydes and phenols. In addition, we developed a GC-MS method for the quantification of semi-volatile oxygen compounds which provides reliable results. These analytical techniques allowed us to study the composition of a bio-oil from the ablative flash pyrolysis of straw and products of its hydrotreatment over a commercial sulphided $NiMo/Al_2O_3$ catalyst at different pressures.

Introduction

First generation biofuels are currently the only commercially used biofuels. They are made from food crops and thus their production competes to food and feed production. Mainly due to this, the future directive of EU (REDII) proposing a gradual increase in the share of second generation and gradual reduction in share of first generation biofuels in the total biofuel amount in the fuel pool [1]. Fast pyrolysis seems to be the easiest process to convert lignocellulosic biomass into a liquid [2]. In this process, it could be possible to convert biomass into liquids (bio-oils) in one step and possible mobile application of ablative pyrolysis can lead to a decrease of biomass transportation cost [3].

Nevertheless, bio-oil has high amount of oxygen and water which causes its negative properties. Bio-oil contains many of acidic and phenolic compounds, which causes its incompatibility with wide range of materials. High content of aldehydes and other reactive compounds causes its thermal and chemical instability. And due to its polarity and high water content, bio-oil is immiscible with conventional petroleum fractions [2]. Thus, a decrease of oxygen content and thus improvement of these properties is a crucial step before widespread of bio-oil usage.

Hydrotreatment seems to be the most promising method for bio-oil upgrading. It leads to higher yields of products of higher quality[4]. For bio-oil hydrotreatment, different catalysts have been used. Although noble metals proved very good results in bio-oil hydrotreatment, they can be poisoned by the presence of even a small amount of sulphur compounds in the bio-oil [5]. So, sulphided catalysts are still the preferred choice.

To optimize bio-oil upgrading process, it is necessary to have a detailed overview of changes in the chemical composition. Bio-oil and its upgraded products are complex mixtures and the analysis of their chemical composition is very difficult and time-consuming. GC-MS is the most common analytical method used for the characterization of bio-oil composition [6]. Quantification by MS detector is not such easy as by FID and therefore, most of publication uses only qualitative analysis. Due to this, most of authors quantify the changes in composition relatively as the ratio of total peak area [7-8]. These results can lead only to the misleading understanding of bio-oil hydrodeoxygenation, mainly due to different response factors of oxygenates on MS detector and in any case, we do not get the results in wt% by this way.

By GC-MS, we analyse only changes in low molecular compounds. So for, better understanding of chemical changes in whole sample, it is good to use methods for quantification of total amount of some important chemicals groups in bio-oil. Not a long ago there were validated [9] and published methods for quantification of carboxylic acids [10], carbonyls [11] and phenols [12].

In this work, we hydrotreated a straw bio-oil over sulphided $NiMo/Al_2O_3$ catalyst at different pressures. Then, we performed detailed characterization of the obtained products. Except of physicochemical properties, we quantified the changes in chemical composition of these products.

Experimental

Hydrotreatment of bio-oil

Catalytic hydrotreatment of a bio-oil from ablative pyrolysis of straw (barley/wheat 1/1 w/w) with 0.5 wt% of DMDS was performed in a continuous-flow fixed bed reactor (i.d. 23 mm and length 320 mm). Conditions were as follows: temperature 320°C, pressure 2; 4 and 8 MPa, hydrogen flow rate 90 Nl·h^{-1} and WHSV equal approximately to 1 h^{-1} using a 55 g of a commercial sulphided NiMo catalyst (Ni 6.9 wt% and Mo 27.7 wt%). Particle size of catalyst was as follows: top and bottom layer 5.0 g, not crushed - (p.s. > 1 mm), transitional layer 5.5 g (p.s. 0.84 - 1.0 mm) and middle (main) layer 34 g (p.s. 0.25 - 0.42 mm). Products were labelled as follows: TTT/P = temperature (°C)/pressure (MPa).

Physicochemical properties

Density and viscosity of the samples were measured using an SVM 3000 Stabinger Viscometer (Anton Paar) that consists of two systems: an oscillation U-tube for density measurements and a rotation tube cell with an integrated magnet for viscosity measurements. The density measurements were performed at 15 °C in agreement with ČSN EN ISO 12185 and the viscosity measurements were performed at 40 °C in agreement with ASTM D445.

Elemental composition (C, H, N, S) was determined using an elemental analyser Vario EL Cube (Elementar) according to ASTM D5291-16 and the sulphur content was determined according to DIN 51724-3. The oxygen content was determined by difference.

Water content was determined by a volumetric Karl Fischer titration using an automatic titrator METTLER TOLEDO DL38 and HYDRANAL (Riedel den Haën) was used as titrant. The measurements were in agreement with ASTM E203.

Higher heating value (HHV) was determined using IKA C 2000 (Merci) calorimeter equipped with a separate water cooler in agreement with ČSN DIN 51900-1. Lower heating value (LHV) was calculated from the HHV by subtracting the evaporation heat of water in the sample and water generated from hydrogen during the analysis.

Micro-conradson carbonisation residue (MCR) of the tested samples was determined by Conradson micro method using NMC 420 (Normalab Analysis) device. The measurement was performed in agreement with ASTM D 4530.

Quantitative GC-MS and functional groups analysis

Carboxylic acid number (CAN) was determined by automatic titration using Metrohm DMS Titrino 716, by method based on ASTM D664 modified for bio-oils, where tetrabutylammonium hydroxide is used as a titrant. The obtained results were recalculated to mmol of COOH·g^{-1} of bio-oil sample.

The total content of carbonyls was obtained using potentiometric titration described in detail elsewhere [13]. The same apparatus and electrode system were used as for the CAN measurements. The method is based on the reaction of carbonyl group with hydroxylamine hydrochloride at 80 °C. Released HCl directly consume presented Triethanolamine and the unreacted triethanolamine is determined by titration by HCl.

GC-MS analysis. Instrument control, data acquisition and analysis were performed using an Xcalibur 2.2 software (Thermo-Fisher Scientific). The sample (≈100 µL) was dissolved in about 1.7 mL of acetone and 10 µL of internal standard (a mixture of 1-butoxypropan-2-ol and 2-naphthaldehyde, each 34 mg·mL^{-1}) were added. GC-MS spectra were evaluated using NIST 14 mass spectra library. A gas chromatograph Trace Ultra connected to a DSQ mass spectrometer (both Thermo-Fisher Scientific) was used for analyses. Conditions of the GC analysis were as follows: injection: temperature 250 °C, split 1:20, injected volume 1 µL; carrier gas: helium 5.5, gas flow 1 mL·m^{-1}; temperature program: 32 °C (8 min), then 5 °C·min^{-1} to 300 °C (10 min); column: ZB-5MSi, W/Guardian, 30 m (+5 m Guardian end) x 0.25 mm x 0.25 µm; interface temperature: 280 °C. Conditions of the MS measurements were as follows: EI +70 eV; analyser: quadrupole; solvent delay: 3.0 min; data acquisition: full scan; scanning range: 20–500 Da; scanning frequency: 4 scans·s^{-1}. For quantification, a mixture of 64 standard compounds (1 mg·mL^{-1}) was used. For each compound, at least four point calibration curve covering concentration from 25 to 1000 µg·mL^{-1} was made. The calibration points were obtained as the intensity of one or two most intensive ions specific for each compound. For all calibration curves, the R^2 value was higher than 0.99. Other compounds were quantified based on the response factor of the structurally most similar compound.

Results and discussion

Bio-oil hydrotreatment

The experiments were performed in the order of decreasing pressure to avoid coking reaction expected at 2 MPa. The real average temperatures on the catalytic bed at selected experimental conditions and time on stream of

these experiments are shown in Table I. At all conditions tested, separation into an organic and aqueous phases occurred. At 320 °C and 4 MPa, the organic phase had lower density than water and it created thus upper phase. With the increasing reaction pressure, the amount of organic phase of products decreased up to 54.3 wt% at 320 °C and 8 MPa. It was caused by higher degree of deoxygenation and thus higher amount of aqueous phase was created.

Table I Experimental conditions

Experiment	**320/2**	**320/4**	**320/8**
Average T in catalyst bed (°C)	320.4	317.9	319.3
Pressure (MPa)	2	4	8
TOS (h)	69	26	7

Physicochemical properties of feed and products are compared in Table II. The best properties had in all cases product obtained at 8 MPa. With the increasing hydrotreatment temperature, density of organic phase decreased from 1.133 to 0.947 $g \cdot cm^{-3}$. Kinematic viscosity at 40 °C decreased from 123 up to 15.1 $mm^2 \cdot s^{-1}$. Water content of organic phase decreased from 22.6 to 1.0 wt%. Oxygen content decreased from 21.3 to 6.6 wt%, which means that 77.5 % of oxygen were removed. Micro Conradson carbonization residue (MCR) expressing propensity to cooking reaction decreased from 15.0 up to 2.8 wt%

Table II Physical and chemical properties of feed and selected organic phase of products

Sample	**Feed bio-oil**	**Products**		
		320/2	**320/4**	**320/8**
Yields of organic phase (wt%)	-	68.7	55.4	54.3
C *(wt%)	70.62	79.78	79.53	81.69
H * (wt%)	7.18	9.34	9.85	10.84
N * (wt%)	0.83	0.02	0.03	0.05
S * (wt%)	0.06	1.00	0.92	0.79
O * (wt%)- to 100 %	21.31	9.86	9.67	6.62
Density at 15 °C ($g \cdot cm^{-3}$)	1.133	1.054	0.997	0.947
Kinematic viscosity at 40 °C ($mm^2 \cdot s^{-1}$)	123	90.2	31.2	15.1
Water (wt%)	22.6	3.87	2.31	1.00
MCR (wt%)	15.0	7.9	3.3	2.8

*The elemental composition is given on dry basis, i.e. subtracting bio-oil water content determined by Karl-Fischer titration

Using GC-MS, we were able to quantify 33 % of all oxygenates in the feed. The total amount of oxygenates quantified by GC-MS in products at 2 MPa significantly increased up to 56 % and then with the increase of pressure it decreased to 26 %. From these results, we can assume that this sharp increase was caused by the deoxygenation of high-molecular-weight compounds of pyrolytic lignin. It was confirmed by an increase in the concentration of phenolic compounds at 2 MPa compared to feed namely the increase in amount of pyrocatechol (2x), 4-ethylguaiacol (2x), 3-/4-ethylphenol (3x), phenol (3x) and even 10x in case of 3-/4-propylphenol, see Table III.
Regarding other typical compounds in bio-oil, levoglucosan, hydroxyacetone and furfural were deoxygenated already at 2 MPa. Isoeugenol, as a representative of unsaturated compounds, was completely hydrogenated into 4-propylguaiacol at 2 MPa. 2-Methylcyclopentanone and syringol were completely deoxygenated at 4 MPa. Pyrocatechol and all guaiacols were completely removed at 8 MPa. Amount of acids decreased but at 320 °C and 8 MPa acids have not yet been completely removed.
For a better overview of changes in carboxylic acids and carbonyls in whole sample, we quantified their total amount by titration and Faix method respectively, the results are shown in Figure I. In high boiling fractions, the content of carboxylic acids was lower in comparison with carbonyls. We found that we quantified more than 66 % of all acids by GC-MS. The total amount of carbonyls was more than three times higher than we determined by GC-MS. Carbonyls groups were present in the most reactive pyrolytic lignin molecule probably in aldehydes group and thus its amount decreased more than two times at 2 MPa compared to feed. The different trend in the decrease of

carbonyl compounds by GC-MS and by Faix method is caused mainly by different reactivity of ketones compared to aldehydes, which were completely removed at 2 MPa.

Table III Directly quantified oxygen compounds with highest abundant

RT (min)	Elemental composition	Sample	Feed bio-oil	Products		
				320/2	320/4	320/8
3.24	C2H4O2	Acetic acid (wt%)	2.81	2.07	1.18	0.34
4.49	C3H6O2	Hydroxyacetone (wt%)	1.27	ND	ND	ND
6.00	C3H6O2	Propionic acid (wt%)	0.45	0.60	0.42	0.15
11.70	C5H4O2	Furfural (wt%)	0.29	ND	ND	ND
12.02	C6H10O	2-Methylcyclopentanone (wt%)	0.05	1.33	ND	ND
18.14	C6H6O	Phenol (wt%)	0.36	1.05	1.26	1.35
21.72	C7H8O2	Guaiacol (wt%)	0.80	1.10	0.11	ND
24.29	C8H10O	3-/4-Ethylphenol (wt%)	0.51	1.56	1.86	1.97
25.34	C6H6O2	Pyrocatechol (wt%)	0.57	1.21	0.67	ND
26.91	C9H12O	3-/4-Propylphenol (wt%)	0.04	0.42	1.10	2.36
27.60	C9H12O2	4-Ethylguaiacol (wt%)	0.76	1.55	0.20	ND
29.47	C8H10O3	Syringol (wt%)	0.75	0.26	ND	ND
29.98	C10H14O2	4-Propylguaiacol (wt%)	0.09	0.95	0.10	ND
30.96	C10H12O2	cis-/trans-Isoeugenol (wt%)	0.65	ND	ND	ND
33.42	C6H10O5	Levoglucosane (wt%)	0.56	ND	ND	ND
43.15	C16H32O2	Palmitic acid (wt%)	0.31	0.27	0.18	0.14
		Total amount of oxygenates by GC-MS (wt%)	**23.65**	**23.78**	**14.15**	**11.15**
		Total amount of oxygen in compounds by GC-MS (wt%)	**6.96**	**5.53**	**3.01**	**1.72**
		Ratio of oxygen in compounds by GC-MS (%)	**32.7**	**56.1**	**31.1**	**26.0**

ND – Not Detected

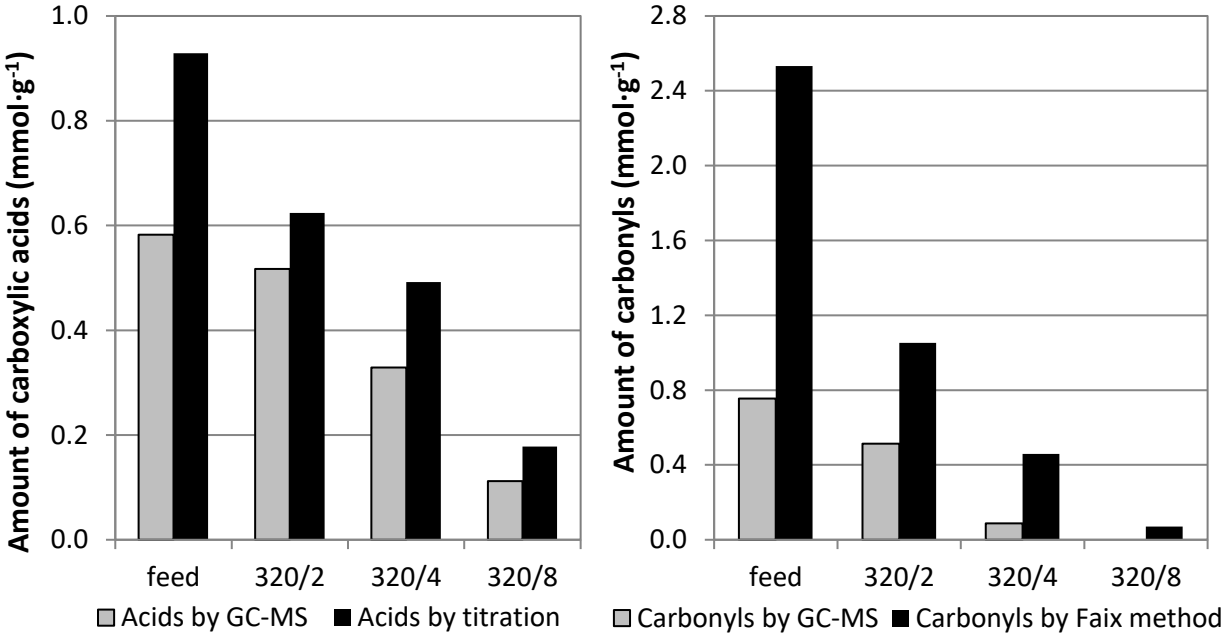

Figure I Amount of carboxylic acids and carbonyls by GC-MS and titration

Conclusions

In this work, we carried out the hydrotreatment of straw bio-oil from ablative fast pyrolysis at different pressures. In addition to changes in physicochemical properties, we quantified changes in chemical composition of volatile fractions by GC-MS. For a better overview of changes in most problematic groups of chemical compounds, we quantified total amount of carboxylic acids and carbonyls by titration and Faix method respectively. We found that at 8 MPa, only phenols, small amount of acids and negligible amount of carbonyls probably ketones were in product. Our results can contribute to a better understanding of bio-oil hydrodeoxygenation on sulphided catalysts.

Acknowledgement

The results were obtained in the BioMates project. This project has received funding from the European Union`s Horizon 2020 research and innovation program under grant agreement No 727463. The publication reflects only the authors' view and the Commission is not responsible for any use that may be made of the information it contains.

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