Hydrotreatment of fast pyrolysis bio-oil from pilot-scale CSTR to laboratory scale batch reactor: experimental downscaling for catalyst development

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Highlights

- Fast pyrolysis bio-oil hydrotreated in 2L CSTR and 200ml and 1L batch reactors
- Results of two different unsupported catalysts are compared
- Simple method to predict performance of a catalyst system in pilot scale is presented

1. Introduction

Bio-oil from thermochemical liquefaction of lignocellulosic biomass is a promising alternative feedstock for advanced biofuels for hard-to-decarbonize sectors, e.g. for aviation, to combat climate change and reach tightening regulations [1]. However, high oxygen content, thermal instability and biomass-based impurities limit and complicate the upgrading of bio-oils to drop-in hydrocarbon fuels in traditional fixed-bed hydrotreaters [2]. Recently, slurry hydrotreating of bio-oil in CSTR has gained attention as a promising, technically viable upgrading route for challenging feedstock [3, 4].

However, further investigation is required for optimizing catalyst composition and process conditions. CSTR experiments consume a significant amount of time, feedstock and catalyst. The aim of this work was to find robust methods to predict the performance of a catalyst in CSTR system from the batch results to support catalyst development and scale-up activities.

2. Methods

Typical biomass fast pyrolysis bio-oil produced from lignocellulosic biomass in commercial scale plant with characteristics presented in Table 1 was hydrotreated in three reactor setups: batch reactors with sizes 200mL and 1L and CSTR pilot plant with reactor size of 2.7L. Three different catalysts were used for these studies. Commercial supported NiMo catalyst procured from Ranido s.r.o (Czech Republic) was used in test runs in batch reactors, and in-house prepared unsupported CoMoS and Mo-ethylhexanoate precursor sulfided and forming MoS_2 in-situ were used in 200mL batch reactor and pilot scale CSTR test runs.

The performance of the catalysts was studied at 140bar temperatures ranging from 350°C to 410°C in CSTR test runs with residence time 1.5h. The performance is compared to batch reactor experiments of different experiment lengths, catalyst loadings and temperatures from 350°C to 380°C. Formed products were characterized for elemental composition, density, viscosity, and ^{13}C-NMR to study the change of physical properties, chemical functionalities and oxygen content.

3. Results and discussion

The preliminary results of the CSTR test runs are presented in Figure 1. Product oxygen content and carbon recovery to oil phase decrease as function of temperature, as both HDO and cracking reactions are promoted by high temperature, indicating the importance of process temperature in control of hydrotreatment severity and product properties. However, in comparison of the samples with pre-experiment of semi-batch hydrotreatment of bio-oil with VTT in-house prepared catalyst at 350°C presented in Table 1, the similar hydrotreatment performance as at 410°C in CSTR hydrotreatment is reached. This highlights the role of residence time and catalyst amount in the hydrotreatment process severity.

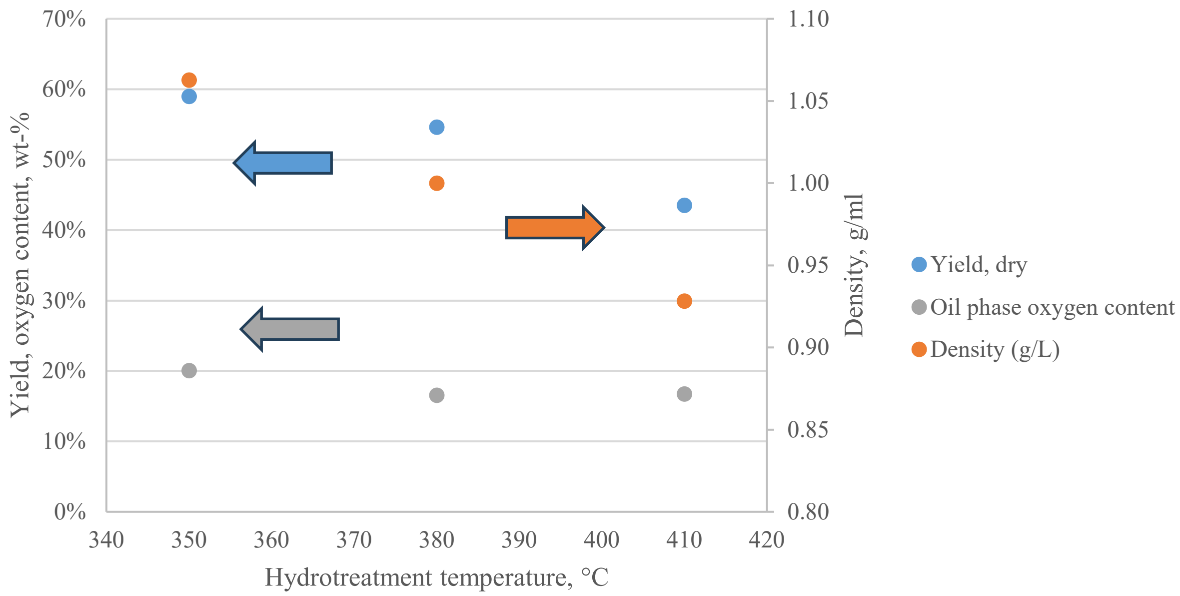

Figure 2. Oil yield, oil phase oxygen content and oil density as function of processing temperature in CSTR equipment, RT 1.5h, 140bar.

Table 1. Comparison of CSTR results to results previously achieved in semi-batch test run. a) semi-batch treatment 4h at 160°C and 4h at 350°C

	T (°C)	P (bar)	RT (h)	Catalyst loading g catalyst /g feed	C (wt-%)	H (wt-%)	O (organic) (difference)	Water content
Feed	Feed				39.7%	7.8%	32.4%	22.7%
CSTR	350	140	1.5	X	68.2%	9.1%	20.1%	2.9%
CSTR	380	140	1.5	X	69.9%	9.7%	16.6%	4.3%
CSTR	380	75	1.5	X	69.0%	9.9%	17.1%	4.5%
CSTR	410	140	1.5	X	70.6%	10.3%	16.8%	2.6%
Semi-batch	160 (4h) +350 (4h) a)	60	8 a)	4X	72.7%	9.1%	14.8%	3.8%

4. Conclusions

Slurry hydrotreatment of bio-oil was investigated in pilot-scale continuous reactor with different catalyst systems and temperatures. The same reaction was studied in semi-batch and batch reactor set-ups. The differences between these setups were compared and products characterized to reverse-engineer a method for predicting catalyst and process performance in pilot-scale CSTR equipment.

References

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Keywords
Bio-oil hydrotreatment; catalyst development; continuous stirred tank reactor; batch reactor