Newly Designed Reactor Inserts for Catalytic Hydrodeoxygenation of Biomass Pyrolysis Oil Model Compounds in a Continuous Slurry Reactor

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Highlights

- Hydrodeoxygenation was successfully performed in a continuous stirred slurry reactor
- Using inserts as catalyst containers prevented the catalyst from being crushed
- Using large amounts of catalyst as extrudates became possible
- The inserts did not create significant mass transport limitations

1. Introduction

Catalytic upgrading of pyrolysis oil is required to overcome its high acidity and reactivity, and poor combustion properties. This process has been performed in fixed bed reactors through hydrodeoxygenation at elevated temperatures and hydrogen pressures using various catalysts [1]. Nevertheless, fixed bed reactors are known to clog when the top of the catalyst bed is exposed to the very reactive bio-oil [2]. Slurry reactors are an interesting alternative, since the entire amount of catalyst and reaction liquid are vigorously stirred and well mixed. Furthermore, the fresh, reactive bio-oil is instantaneously diluted into already upgraded oil [3]. Nevertheless, catalyst crushing and attrition are known problems when operating slurry reactors, which can result in loss of catalytic material, leading to decreased catalytic activity, and plugging of tubes and filters [4].

Initial experiments with a continuous slurry set-up using an autoclave fitted with gas/liquid inlet and outlet tubes, led to an extensive crushing of the extrudate catalyst, particularly when operating at high stirring speeds and/or when large amounts of catalyst were employed. Furthermore, a fine filter on the product outlet tube, which prevented the catalyst from leaving the reactor, would often plug due to very small catalyst particles created from crushing. Due to this, reactor inserts functioning as catalyst containers were designed and developed to prevent the catalyst from crushing and to allow faster stirring speeds. Moreover, the filter in the outlet dip tube was removed to avoid plugging.

2. Methods

The inserts consisted of 8 perforated cylinders secured between two perforated circular frames. Figure 1 shows the assembly of the cylinders into the frame and how the inserts fit in the reactor.

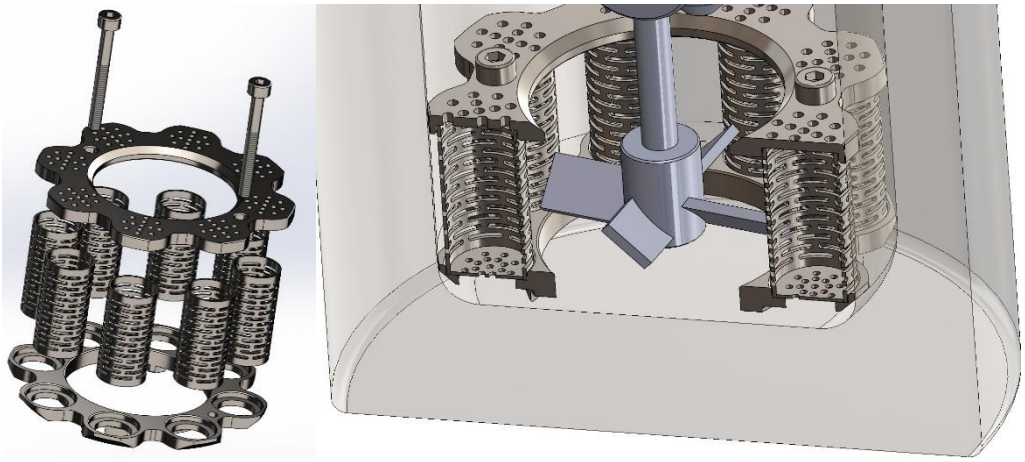

Figure 1. Reactor inserts design assembled; Detail of the inserts placed in the slurry reactor.

The inserts were fixed, while the stirrer rotated. The inserts were tested with 4, 6 or 8 cylinders in place.

The experiments were performed with a bio-oil model compound mixture consisting of acetophenone (25 wt%), guaiacol (20 wt%), 2-ethylhexanol (20 wt%), furfural (15 wt%), diacetone alcohol (15 wt%) and octanoic acid (5 wt%). This mixture was further diluted in 2-ethylhexanol (60 wt% solvent, 40 wt% model mixture). The catalyst used was a sulfided $NiMo/Al_2O_3$ provided by Topsoe A/S as extrudates with approximately 1 mm in diameter and 5 mm in length. The reactor was a 500 mL stainless steel vessel from Parr which was operated at 100 bar of H_2 and temperatures from 200 to 350 °C, with continuous liquid/H_2 feed and product removal. The liquid and H_2 flow rates were 0.5 ml/min and 300 ml_N/min, respectively, and the liquid volume in the reactor was 100 ml, kept constant by product removal through a dip tube. The catalyst mass was between 2 and 6 g. The stirring speeds tested were 300, 500 and 750 rpm. Typical run times were 50 to 100 h per experiment.

3. Results and discussion

With the use of the inserts, it became possible to use catalyst extrudates and to operate at the maximum stirring speed (750 rpm) without leading to catalyst crushing, even after 100 hours. Previously, without the inserts, 300 rpm and a catalyst sieve fraction of 250 to 425 μm was used, to prevent catalyst crushing. The increase in stirring speed resulted in better mixing and improved conversions.

A main set of experiments was performed at 300 °C, with 2 g of catalyst in total in 4 inserts (0.5 g each). A 100-hour test at 750 rpm showed that no significant deactivation occurred, with conversions going from 83.2 % to 81.0 % for furfural and from 51.0 % to 46.5 % for acetophenone, between 50 and 100 h on stream. An increase in stirring speed from 300 to 500 rpm did not lead to major differences in the results. However, increasing it further to 750 rpm resulted in a conversion increase from 29.3 ± 1.6 % to 64.8 ± 2.2 % for guaiacol and from 36.5 ± 1.3 % to 54.4 ± 1.6 % for acetophenone. 750 rpm was then used for the remaining experiments. Increasing the number of cylinders used from 4 to 8, while still having 2 g of catalyst in total, resulted in a minor decrease in conversions, with furfural conversion changing from 87.2 ± 1.1 % to 85.3 ± 0.6 % and guaiacol conversion from 64.8 ± 2.2 % to 56.5 ± 1.5%. Increasing the amount of catalyst from 2 to 6 g, when using 4 cylinders, improved the results significantly, with conversions of 99.0 ± 0.1 % for furfural, 96.7 ± 0.2 % for guaiacol and 93.4 ± 0.3 % for acetophenone, and an overall degree of deoxygenation of 72.9 %. A temperature increase from 300 to 350 °C, with 6 g of catalyst in 4 cylinders, did not result in major improvements, as high conversions were already obtained at 300 °C, while decreasing the temperature to 250 °C led to a 2.5-fold decrease in the conversion of guaiacol and acetophenone, which can be attributed to the activity of the catalyst in use rather than to the inserts.

4. Conclusions

Using inserts as catalyst baskets in a continuous slurry reactor for hydrodeoxygenation of pyrolysis oil model compounds was successful at preventing crushing of the extrudate catalyst and allowed for faster stirring speeds. As a result, long run times were possible, achieving a stable and high degree of deoxygenation of the model bio-oil. By using the inserts, the removal of the outlet dip tube filter was possible. This prevented clogging in the fine filter from occurring, either by catalyst particles or by polymerization. This reactor concept thus seems very suited for bio-oil hydrotreating.

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References

[1] H. Wang, S.J. Lee, M.V. Olarte, A.H. Zacher, ACS Sustain Chem Eng 4 (2016), 5533-5545
[2] X. Hu, Z. Zhang, M. Gholizadeh, S. Zhang, C.H Lam, Z. Xiong, Y. Wang, Energy & Fuels 34 (2020), 7863-7914.
[3] R.V. Chaudhari, P.A. Ramachandran, AIChE Journal 26 (1980) 177-201
[4] J. Warna, M. Ronnholm, T. Salmi, K. Keikko, Computer Aided Chemical Engineering 10 (2002) 1009-1014

Keywords
Reactor inserts, Catalyst deactivation, Continuous slurry reactor, Upgrading of bio-oil