Hot-injection slurry hydrotreating of lignin – Steering feedstock reactivity by advanced reaction control.

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Highlights

- Slurry hydrotreating of lignin in hot-injection semi-batches (HISB)
- Avoiding polymerization and condensations reactions during start up to retain higher reactivity of the Lignin Feedstock.
- Screening of different Lignin and Lignin-based Feedstocks.
- Comparison of traditional hydrotreating catalysts with cheap iron-based alternatives.

1. Introduction

Lignin is an aromatic natural polymer accounting for about 15-30% of dry biomass. Its high aromatic content makes it an attractive starting material to produce biomass-derived fine chemicals and fuels after removal of its high oxygen content. However, solid feedstocks like lignin are problematic to process in existing oil refinery infrastructure. Slurry hydrotreating is an exciting process to convert solid lignin to liquid products with reduced oxygen content, which can be used as drop-in feedstock in petrol refinery. Due to the chemical properties of lignin, it can undergo polymerization and condensation reactions during process operation and especially heat-up. These changes lead not only to a change in its physical properties but also its reactivity. Therefore, avoiding these changes in the feedstock is a key aspect in the development of efficient process for the hydrotreating of lignin.

2. Methods

Two different types of experiments have been conducted. Semi-batch experiments and hot injection semi batches. For the semi-batch run, a mixture of vacuum gas oil (VGO), lignin and catalyst were placed in the reactor chamber. The reactor was pressurized with hydrogen and heated up to reaction temperature under constant stirring. A constant hydrogen flow was held for the entirety of the reaction time. Similarly, a mixture of VGO and catalyst were placed in the reactor for the HISB runs and the reactor was brought up to reaction conditions. After the reactor reached the desired temperature and pressure a slurry of VGO and lignin was fed through the bottom of the reactor. As catalysts a variety of traditional hydrotreating catalysts and cheap iron-based catalysts were deployed. To demonstrate the versatility of the process a selection of different lignin feedstock was used.

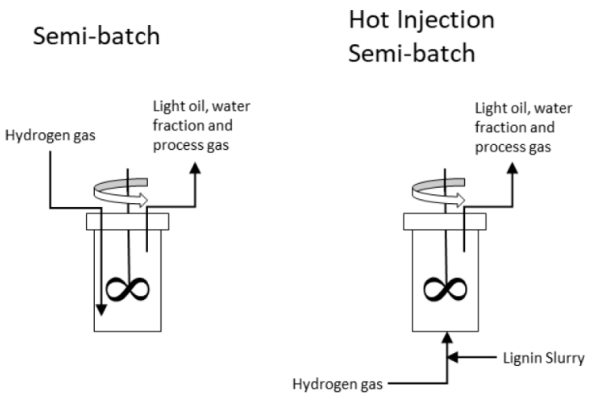

Figure 1. Reactor scheme of the semi-batch and hot-injection semi batch set-up (HISB)

3. Results and discussion

During semi-batch experiments lignin undergoes polymerization and condensation reaction starting at around 250 °C, leading to the formation of brittle agglomerates during the heat up of the reactor. These agglomerates were absent during HISB runs, allowing for shorter reaction times and more efficient conversion of solid lignin. Traditional sulfided molybdenum catalysts showed an overall better performance than the selected iron catalysts. However, all selected iron catalysts led to full conversion of solid Lignin with moderate catalysts concentrations making them an attractive alternative to the more expensive traditional catalysts applied in hydrotreating. Additionally, the possibility of the usage of different lignin feedstock has been demonstrated in the process.

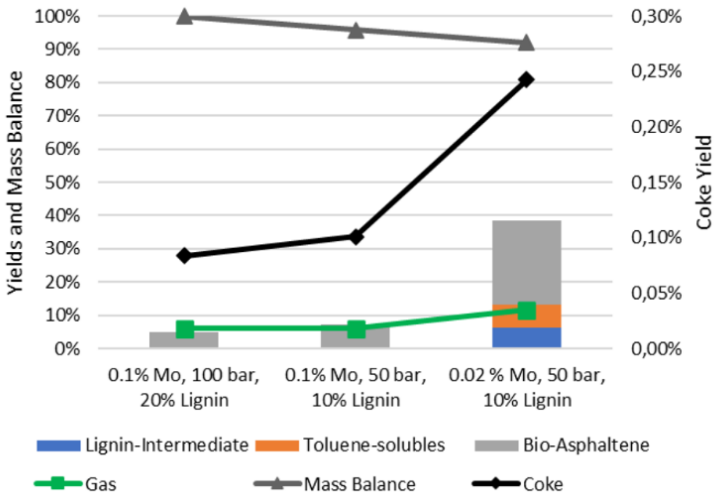

Figure 2. Product yields for HISB (425 °C, 2h) at different catalysts concentrations (gas and coke yield are based on the total mass; lignin intermediates, toluene-soluble and bio-asphaltenes are based on the lignin mass)

4. Conclusions

The hydrotreating of lignin feedstocks in hot-injection semi-batches is efficient process to produce biooil suitable for further downstream upgrading in existing oil refinery infrastructure. Through the avoidance of property changes of the feedstock during process operation it allows for the application of a variety of different lignin feedstocks. Next to traditional hydrotreating catalysts, iron-based catalysts have revealed themselves as a cost-effective alternative. Making it possible to reduce overall process cost.

References

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Keywords
Hydrotreating; Lignin; Biooil; Biorefinery