Deoxygenation of fast pyrolysis vapors using zeolites

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Abstract
Process optimization of a bench scale fast pyrolysis set-up has been performed in order to screen the performance and stability of modified MFI zeolites in the ex-situ upgrading of straw and wood derived pyrolysis vapors. Repeated regeneration of the parent zeolites was demonstrated at the bench scale unit. Harsh regeneration conditions led to temperature peaks and permanent loss in the zeolite’s acidity. A certain extent of mesopores is introduced to the parent zeolites by post-synthesis desilication to increase the zeolite’s active time on stream.

Introduction
Fast pyrolysis of biomass produces a high yield of bio-oil at optimized process conditions [1]. Reducing the oxygen content of the obtained bio-oils increases its stability and heating value [2], which can render the upgraded bio-crude suitable for further processing in oil refineries. Downstream catalytic upgrading of the pyrolysis vapors over solid acid catalysts in a close-coupled process can offer processing and economic advantages over high pressure hydrotreating [3].

To date, the medium pore size ZSM-5 zeolite yields a high aromatic yield and the least amount of coke [4] in upgrading of pyrolysis vapors. However, the reactive pyrolysis vapors still lead to rapid coking of the zeolite, which must be regenerated by oxidative burnoff. At the high operating temperatures, the water introduced by the biomass moisture and from the pyrolysis process itself can lead to permanent deactivation of the zeolite structure via steaming. By modifications of the zeolite, this study aims to improve both the active time on stream and the long-term stability throughout multiple regeneration cycles. The Si/Al ratio and the operating temperature are main parameters for the catalyst’s performance. Also combinations of several types of catalysts have been demonstrated for physically mixing microporous with mesoporous catalysts [5] and dual beds comprised of solid acid and basic catalysts [6]. Furthermore, the yield of aromatics can be improved by metal incorporation [7].

Despite promising laboratory results, long term experiments of pilot plants showing stable catalyst operation with multiple regeneration steps are needed to prove the economic attractiveness of bio-oil plants.

Specific Objectives
It is investigated how the operation and interaction of the pyrolysis unit, hot gas filtration and catalyst fixed bed (Fig. 1) influences the product distribution. While mostly nitrogen is used as sweeping gas, the recycling of non-condensable pyrolysis gases may have a positive effect on the oil yield [8] and is currently being investigated.

Results and Discussion
The performance of the ZSM-5 type zeolite for pyrolysis vapor upgrading is influenced by the operating temperature and the zeolite’s acidity and pore structure. Mesopores have been introduced into the microporous bulk structure via NaOH leaching in order to reduce diffusion limitations and prolong the catalyst’s active
operation by reduced coking. The characterization of the modified zeolites via nitrogen and argon physisorption, NH1-TPD, XRD, XRF and TEM analysis confirmed the successful introduction of mesopores (Fig. 2) and the accompanied reduction in acid sites (Fig. 3) due to the removal of Al containing framework. Thus, it is desirable to obtain a considerable amount of mesopores without loosing too much of the micropore bulk volume containing the majority of active sites.

Figure 2: Argon physisorption and TEM confirm the introduction of mesopores.

Figure 3: Change in acidity and relative micro/mesopore volume of modified MFI zeolite.

The yield of organic liquid obtained from wood derived pyrolysis vapors decreases considerably once the vapors are passed over the zeolite (see Fig. 4). This is mainly due to the enhanced CO/CO2 production and formation of water during the vapor cracking reactions. Table 1 lists a comparison of the oxygen content and heating values (HHV) of the wood feedstock and the derived oils from pure pyrolysis and from ZSM-5 vapor upgrading. The energy content of the upgraded oil is increased.

Table 1: Comparison of feedstock and bio-oil oxygen content and higher heating values

<table>
<thead>
<tr>
<th>source</th>
<th>oxygen [wt%]daf</th>
<th>HHV\text{\textsubscript{db}} [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood feedstock</td>
<td>40.8</td>
<td>22.0</td>
</tr>
<tr>
<td>heavy fraction of pyrolysis oil obtained</td>
<td>30.8</td>
<td>25.4</td>
</tr>
<tr>
<td>without recycling gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heavy fraction of catalytically upgraded</td>
<td>22.6</td>
<td>29.9</td>
</tr>
<tr>
<td>pyrolysis oil (parent ZSM-5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the upgrading of straw derived fast pyrolysis vapors a repeated intermittent oxidative regeneration step was conducted. The injection of 5% oxygen allowed regeneration to occur in a similar time frame compared to the catalyst’s time on stream; however, it also lead to permanent loss of the zeolite’s acidity (Table 2).

Table 2: Comparison of acidity of parent and frequently regenerated zeolite determined via NH3-TPD

<table>
<thead>
<tr>
<th>catalyst</th>
<th>acidity [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh zeolite</td>
<td>1.02</td>
</tr>
<tr>
<td>used zeolite, removed from beginning of bed</td>
<td>0.75</td>
</tr>
<tr>
<td>used zeolite, removed from end of bed</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Conclusion
The parent zeolite deactivates rapidly due to coking, thus, it requires modifications. The pore structure of the ZSM-5 type zeolite with an acidity range relevant for the upgrading of biomass derived fast pyrolysis vapors can be tuned by introduction of a certain extent of mesopores. Too harsh leaching conditions lead to significant loss of pore volume and acid sites.

Future work
A selection of the most promising modified zeolites in terms of acidity and mesoporosity will be tested for their catalytic performance. This way it is aimed to obtain further insights how the interplay between pore structure and distribution of acid sites affects catalyst activity. Improvements of the zeolite’s hydrothermal stability are needed in order to speed up regeneration cycles and limit the extent of dealumination via steaming. The current reactor dimensions will be increased to allow collection of larger amounts of upgraded bio-oil for more thorough characterization.

References