Performance of Mesoporous HZSM-5 for the Upgrading of Wheat Straw Derived Fast Pyrolysis Vapors in Bench Scale

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Background of project: Concept of Polygeneration

Biomass $\xrightarrow{\text{Low Temperature Circulating Fluidized Bed (LT-CFB)}}$ Char/ash (fertilizer) + Bio-Oil + Electricity + Heat

Catalyst testing in a separate ablative bench scale unit ($\sim 200 \text{ g/h}$)

$\sim 20 \text{ kg/h}$

fuel flexibility
Ablative bench scale fast pyrolysis unit

- Biomass to ~200 g/h
- Nitrogen at 8 Nl/min

Temperature and equipment:
- $T = 400 ^\circ C$ gas preheater
- $T = 450 ^\circ C$ centrifugal reactor
- $T = 530 ^\circ C$ catalytic reactor
- $T = 350 ^\circ C$ ceramic hot gas filter
- $T = 500 ^\circ C$ HTV
- $T = 4 ^\circ C$ condensation

- 2 interchangeable reactors for catalyst loadings of ~60 ml and ~300 ml

Vapor upgrading:
- $T = 530 ^\circ C$
- $dT = 1 ^\circ C/min$ from 250–550 °C, 2 Vol% O$_2$

Regeneration:
- $T = 500 ^\circ C$
- $dT = 1 ^\circ C/min$ from 250–550 °C, 2 Vol% O$_2$

Equipment:
- NDIR CO, CO$_2$, O$_2$ analyzer
- GC-TCD/FID
- Ventilation
- Cumulative flow meter
Catalyst system: HZSM-5 zeolite

- In comparison with other zeolites, HZSM-5 yields more aromatics and less coke, which is attributed to shape selectivity (micropores with ~5.5 Å diameter)
  - Limitations: diffusion restrictions & blocking of pore entries by coke

- The SiO$_2$-to-Al$_2$O$_3$ (SAR) ratio of the HZSM-5 zeolite determines the acid site strength and density

- Steam (present during reaction conditions) initially steeply reduces the Brønsted acidity


C. Engtrakula et al., Catal. Today, 2015

L.H. Ong et al., Microporous Mesoporous Mater., 2012

100% steam at 450 °C, Si/Al = 87
Why using hierarchical HZSM-5 for catalytic fast pyrolysis of biomass?

- Better accessibility of bulky reactants to strong Brønsted acid sites via the newly created mesopores → shorter diffusion path of reactants and products

- Preservation of shape selective properties to favor monoaromatics and limit coke formation

- Open structure may prolong the accessibility to active sites in micropores while for conventional HZSM-5 the pore entries may rapidly become blocked by coke

- Benefits for hierarchical HZSM-5 reported in literature:
  - Higher activity in alkylation, isomerization, cracking of heavy substrates and condensation reactions.
  - Longer catalyst lifetime for MTH and aromatization reactions.
Research questions

I. What yields of deoxygenated pyrolysis oil can be obtained from ex-situ catalytic fast pyrolysis of wheat straw over conventional and mesoporous HZSM-5?

II. Can the oil yield be increased by the introduction of mesopores for a similar degree of deoxygenation?

III. Does mesoporous HZSM-5 retain its activity for a longer time compared to its original counterpart when evaluated at similar original zeolite mass?
Experimental—Feedstock

milled wheat straw pellets <1.4 mm

Proximate Analysis [wt%]

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>moisture [a.r.]</td>
<td>6.2</td>
</tr>
<tr>
<td>volatiles [d.b.]</td>
<td>75.5</td>
</tr>
<tr>
<td>ash [d.b.]</td>
<td>5.9</td>
</tr>
<tr>
<td>fixed carbon (by difference)</td>
<td>17.4</td>
</tr>
<tr>
<td>HHV_{daf} [MJ/kg]</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Ultimate Analysis [wt% daf]

<table>
<thead>
<tr>
<th>Element</th>
<th>wt% daf</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1.3%</td>
</tr>
<tr>
<td>C</td>
<td>48.2%</td>
</tr>
<tr>
<td>H</td>
<td>5.0%</td>
</tr>
<tr>
<td>O</td>
<td>45.4%</td>
</tr>
<tr>
<td>S</td>
<td>0.14%</td>
</tr>
</tbody>
</table>

Elemental Analysis [wt% db]

<table>
<thead>
<tr>
<th>Element</th>
<th>wt% db</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.10%</td>
</tr>
<tr>
<td>K</td>
<td>0.98%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.32%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.11%</td>
</tr>
<tr>
<td>P</td>
<td>0.11%</td>
</tr>
<tr>
<td>Mg</td>
<td>0.07%</td>
</tr>
</tbody>
</table>
Experimental—Catalyst

i. ZSM-5 was purchased from Zeolyst Int.: products CBV 3024E, CBV 5524G, and CBV 8014 with molar Si/Al ratio of 16, 29 and 39 (abbr. CBV30, CBV55 and CBV80)

ii. Desilication with NaOH solutions for 30 min at 65 °C at desired concentration and liquid-to-solid (L/S) ratio, followed by quench in ice water, washing/filtration, and drying at 105 °C overnight.

iii. Removal of Al debris by washing with diluted HCl solution for 6 h at 65 °C, followed by quench in ice water, washing/filtration, and drying at 105 °C overnight.

iv. Ion exchange with 1M NH$_4$NO$_3$ solution for 24 h at 80 °C, followed by quench in ice water, washing/filtration, and drying at 105 °C overnight.

v. Calcination at 550 °C for 5 h in air

vi. Steaming for 5 h at 500 °C with ~30 Vol% steam

vii. Empty catalytic reactor and SiC bed at 500 °C as non-catalytic reference

**Characterization:**

- Argon and nitrogen physisorption, TEM, XRF, TPD of NH$_3$ and Ethylamine, XRD
## Physicochemical properties of parent and desilicated HZSM-5

<table>
<thead>
<tr>
<th>Solid yield, %</th>
<th>$V_{\text{micro}}$ (cc/g)</th>
<th>$V_{\text{meso}}$ (m$^3$/g)</th>
<th>BET</th>
<th>$V_{p/p_0=0.99}$ (mmol/g)</th>
<th>Acidity (calcined), mmol/g</th>
<th>Acidity (steamed), mmol/g</th>
<th>Molar Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV30</td>
<td>0.21</td>
<td>416</td>
<td>0.36</td>
<td>1.02</td>
<td>0.73</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>CBV30/0.6B/0.06A</td>
<td>0.15</td>
<td>620</td>
<td>0.75</td>
<td>0.82</td>
<td>0.27</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>CBV55</td>
<td>0.23</td>
<td>424</td>
<td>0.45</td>
<td>0.56</td>
<td>0.30</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>CBV55/0.2B/0.02A</td>
<td>0.22</td>
<td>423</td>
<td>0.42</td>
<td>0.76</td>
<td>0.36</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>CBV80</td>
<td>0.20</td>
<td>431</td>
<td>0.24</td>
<td>0.44</td>
<td>0.24</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>CBV80/0.2B/0.02A (L/S = 15)</td>
<td>0.18</td>
<td>414</td>
<td>0.37</td>
<td>0.40</td>
<td>0.29</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>CBV80/0.2B/0.02A (L/S = 30)</td>
<td>0.17</td>
<td>454</td>
<td>0.44</td>
<td>0.64</td>
<td>0.24</td>
<td>22.9</td>
<td></td>
</tr>
</tbody>
</table>

B = concentration of base mol/L
A = concentration of acid in mol/L
Transmission electron microscopy investigations

mesoCBV30

mesoCBV55

mesoCBV80
XRD analysis (ASTM D5758−01)

- Comparison of steamed catalysts
- Desilication of Al-rich CBV30 suffered the highest loss in crystallinity (~30%) while crystallinity dropped by ~10% for desilicated CBV55 and CBV80
- Three cycles of vapor upgrading and regeneration further decreased the crystallinity of mesoCBV55 by 5%
Some results for microporous HZSM-5
Change in oil quality with increasing feeding of pyrolysis vapors over steamed CBV30 (Si/Al = 16)

<table>
<thead>
<tr>
<th>Mass catalyst</th>
<th>HHV_{db} [MJ/kg]</th>
<th>Energy yield [mg KOH/g]</th>
<th>TAN [mg KOH/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>- empty reactor</td>
<td>27.7</td>
<td>35.1%</td>
<td>n.d.</td>
</tr>
<tr>
<td>95 g thermal cracking</td>
<td>29.2</td>
<td>30.4%</td>
<td>52.3</td>
</tr>
<tr>
<td>CBV30-st, B:C = 1.4</td>
<td>39.4</td>
<td>17.2%</td>
<td>0.3</td>
</tr>
<tr>
<td>CBV30-st, B:C = 3.6</td>
<td>35.8</td>
<td>21.1%</td>
<td>3.0</td>
</tr>
<tr>
<td>CBV30-st, B:C = 6.1</td>
<td>34.3</td>
<td>26.2%</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Carbon yield (wt. %)

- oil fraction
- C_4+
- aq. phase
- gas
- char
- coke

molar H/C and molar O/C

- Straw
- empty reactor
- SiC
- CBV30-st, B:C = 6.1
- CBV30-st, B:C = 3.6
- CBV30-st, B:C = 1.4

Yield (wt-% of dry and ash-free biomass)
Carbon recoveries and oxygen content of phase separated oil fraction
Oil characterization

- Increase in oxygen content correlates with increase in TAN, charring during heating, and MW
- NMR ($^{13}$C, $^1$H, 2D HSQC) and GC-MS/FID: increased concentration of aromatics and reduced content of sugars, methoxy-groups and acids at low B:C.
- Decrease in BTX selectivity with decreasing yields of monoaromatics
- Oxygenates break trough towards higher B:C

<table>
<thead>
<tr>
<th>$^{13}$C NMR</th>
<th>Chemical shift range (ppm)</th>
<th>SiC</th>
<th>mesoCBV55-st, B:C = 2.5</th>
<th>mesoCBV55-st, B:C = 9.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes, ketones</td>
<td>220–180</td>
<td>7.8%</td>
<td>3.5%</td>
<td>6.1%</td>
</tr>
<tr>
<td>CO groups (carboxylic acids and derivatives)</td>
<td>180–160</td>
<td>7.6%</td>
<td>1.7%</td>
<td>2.6%</td>
</tr>
<tr>
<td>Aromatic carbons in phenol</td>
<td>160–140</td>
<td>12.6%</td>
<td>8.9%</td>
<td>12.7%</td>
</tr>
<tr>
<td>Aromatics and olefins</td>
<td>140–125</td>
<td>9.1%</td>
<td>42.3%</td>
<td>21.7%</td>
</tr>
<tr>
<td>Methoxylated phenols related to guaiacyl and syringyl lignin</td>
<td>125–105</td>
<td>14.2%</td>
<td>14.3%</td>
<td>16.0%</td>
</tr>
<tr>
<td>Levoglucosan, anhydrosugars, alcohols, ethers</td>
<td>105–60</td>
<td>8.3%</td>
<td>2.5%</td>
<td>4.6%</td>
</tr>
<tr>
<td>Methoxyl-group in lignin</td>
<td>57–55</td>
<td>3.9%</td>
<td>0.7%</td>
<td>1.9%</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
<td>55–0</td>
<td>36.4%</td>
<td>26.3%</td>
<td>34.3%</td>
</tr>
</tbody>
</table>
Experimental set-up micro-pyrolyzer

0.59 mg wheat straw (0.5 mg dry and ash-free) introduced via Autosampler

Pyrolysis
μ-reactor (530 °C)

Catalytic
μ-reactor (500 °C)

Catalyst, diluted in ~60 mg glass beads
quartz wool

Split gas out

Separation columns

TCD
MS
FID

GC Oven

8 mg SiC

8 mg mesoCBV55-st injection #16
B:C = 0.93–0.99

8 mg mesoCBV55-st injection #1
B:C = 0–0.06

CO and C1-3 hydrocarbons

relative intensities (FID signal)
time (min)
Monitoring of product yields (8 mg catalyst)

- Acids and sugars were completely converted.
- Slightly lower yield of monoaromatics for desilicated CBV55.
- Methoxyphenols break through earlier and increase steeper for parent CBV55.
Slightly lower yield of mono- and di-aromatics for desilicated CBV55
However: improved conversion of ketones, methoxy-phenols, acids, and especially sugars!
Benefits of mesopores become more apparent at higher B:C ratios (in line with bench scale observations)
Comparisons based on same volume (bench scale) and mass (micro-pyrolyzer) of catalyst show that the coking propensity increased for hierarchical zeolites.

No shift to lower coke combustion temperature as observed for purely mesoporous catalysts \((\gamma-Al_2O_3)\) → increased deposition of 'hard/catalytic' coke due to better accessibility of microporous domains.

Also surface based comparison confirms increased coking propensity of mesoporous HZSM-5.
Take home messages

- Adding mesoporosity to HZSM-5 increased the coke yields, but improved the tolerance towards deactivation.
- Mild desilication is preferred since...
  1) it better maintains crystallinity,
  2) it preserves more parent zeolitic material, and thereby
  3) it limits the increase in coking propensity.

...for more detailed information:

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  – Department of Nanotech (Size exclusion chromatography: Sokol Ndoni)
  – Department of Physics (XRD analysis: Prof. Christian Danvad Damsgaard)

• Haldor Topsøe A/S

• Iowa State University (Tandem micro-pyrolyzer: Alireza Saraeian, Prof. Brent H. Shanks)
Questions?

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