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Novel Ni-based catalysts for the hydrotreatment of fast pyrolysis oil

Agnes Ardiyanti, Arjan Kloekhorst, Y. Wang, Erik Heeres (University of Groningen)
S.A. Khromova, Vadim Yakovlev (BIC)
Robbie Venderbosch (BTG)
Content

› Introduction
  • Catalytic hydrotreatment
  • Objectives

› Results and discussion
  - Catalyst screening studies: identification of novel catalysts
  - Process studies

› Conclusions

› Acknowledgment
Pyrolysis 2.0: a biorefinery

Primary Processing
- Lignocellulosic Biomass
- Fast-Pyrolysis
- Char 10 – 15 wt%
- Gaseous 10 – 15 wt%
- Activated carbon
- Carbon black
- Soil improvement
- Pyrolysis oil 70 – 75 wt%

Secondary Processing
- Primary Fractionation
- Aqueous phase
- Sugars

Tertiary Processing
- Upgrading catalytic hydrotreatment
- Oil phase
- Chemicals Isolation
- Carboxylic Acids
- Phenol
- Aldehyde
- Furan
- Levoglucosan

Applications
- Transportation fuels
- Combustion engines
- Feedstock for refinery
- Alcoholic fuels
- Fuel gas/syngas
- Heat & Electricity

Aqueous phase
- Gasification
- Combustion

Oil phase
Catalytic hydrotreatment

\[-(CH_xO_y)- + cH_2 \rightarrow -(CH_x)^- + (H_2O, CO_2, CH_4, CO)\]

Typical conditions: 125-400°C, 20-200 bar pressure
Two stage hydrotreatment

Pyrolysis oil → Stabilisation → SPO → Deep Hydrodeoxygenation → DHPO → Refining

- Picula catalysts
- Conventional catalysts

Co-feeding in refinery

Hydrocarbons Applications: Biofuels Aromatics
Objectives catalytic hydrotreatment

› Process considerations:
  • Low hydrogen consumption
  • Active, stable and cheap catalysts

› Product considerations
  • Reduced oxygen content, exact amount depending on product application
  • Low viscosity
  • Low water content
  • Low coking tendency (improved thermal stability)
  • Preferably miscible with hydrocarbons
Stabilisation: catalyst developments

- Benchmark: Ru/C
- Bimetallic noble metal catalysts
- Ni-Cu catalyst on supports
- Improved Ni-Cu catalysts (Picula)

d. Venderbosch and Heeres; Chapter 17: Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment, Biofuel's Engineering Process Technology, Free download: http://www.intechopen.com, Patent application pending
Picula catalysts

Table 2 Catalyst composition

<table>
<thead>
<tr>
<th>Code</th>
<th>Active metal loading (wt%)</th>
<th>Support (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picula Cat B</td>
<td>Ni 58.3 Pd 0.7</td>
<td>SiO₂ 41</td>
</tr>
<tr>
<td>Picula Cat C</td>
<td>Ni 28.8 Cu 3.7</td>
<td>SiO₂ 33.8 Kaolin 33.8</td>
</tr>
<tr>
<td>Picula Cat D</td>
<td>Ni 57.9 Cu 7</td>
<td>SiO₂ 35.1</td>
</tr>
<tr>
<td>Picula Cat E</td>
<td>Ni 36.5 Cu 2.3</td>
<td>SiO₂ 12.6 ZrO₂ 37.2 La₂O₃ 0.9</td>
</tr>
</tbody>
</table>

- High Ni content (29-58 wt%)
- Promoted with Cu, Pd
- Various supports
- Prepared by BIC

Venderbosch and Heeres; Chapter 17: Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment, Biofuel's Engineering Process Technology, Free download: http://www.intechopen.com
Batch studies

- 150 °C, 1 h
- 350 °C, 3 h
- 200 bar
Batch studies

- Pyrolysis oil
- Atomic O/C (dry)
- Atomic H/C (dry)

- TG residue of upgraded oil (wt%)
- Atomic H/C (dry) of upgraded oil
Continuous experiments

- 4 fixed-bed reactors in-series
- Catalyst: Picula catalyst D
- $\text{H}_2$ pressure: 200 bar
- WHSV = 0.6 – 1 h$^{-1}$
- Variable: T

Analysis:
- Elemental composition, TGA, GPC, TAN, CAN, 2D-GC
Continuous experiments
Visual appearance

Pyrolysis oil      150°C      400 °C      distillates
2D-GC

150 C

400 C

polarity

b.p
Product is distillable
Two stage hydrotreatment

Stabilisation → SPO → Deep Hydrodeoxygenation → DHPO → Refining

Picula catalysts → Conventional catalysts

Co-feeding refinery → Hydrocarbons Fuels Aromatic

Date 25.06.2010
Conclusions

› Novel catalysts for pyrolysis oil stabilisation by catalytic hydrotreatment have been identified

› Products are distillable, indicative for improved thermal stability

› Picula catalysts show unique performance
  - Improved product properties at low processing temperature
    - Low hydrogen consumptions due to limited methane formation
    - Good hydrothermal stability (run times up to 400 h have been demonstrated)

› Two stage hydrotreatment leads to deep deoxygenation and formation of hydrocarbons
Acknowledgement
Vacancy

Tenure Track Assistant Professor Green Chemistry and Technology (1,0 fte)

Deadline for applications: June 28, 2013

Contact: h.j.heeres@rug.nl
Carbonyl number

Alehydes and ketones are very reactive at low temperature

Formation of new compounds at about 250 °C
Elemental composition

Sequence:

- Hydrogenation
- Dehydration
- Hydrogenation
Molecular weight (GPC)

Sequence:

- Limited polymerisation till 250 °C
- Hydrocracking above 300 °C
Total acid number

Acids are very persistent, reactive only above 300 °C
$^{13}\text{C} \text{ NMR}$

Temperatures:
- 150°C
- 250°C
- 320°C
- 350°C
- 400°C

Frequencies:
- 0
- 50
- 100
- 150
- 200
Overview

Stabilisation (< 250 °C)
- Competition between hydrogenation and polymerisation
- Water formation by condensation reactions
- Slight increase in Mw
- Hydrogenation of aldehyde/ketones
- Sugar chemistry dominates

Mild hydrotreatment (250-350 °C)
- Hydrogenation-dehydration
- Reduction in Mw
- Water formation by alcohol dehydration
- Breakdown of higher Mw fractions
- Sugar-sugar alcohol chemistry dominates

Deep hydrotreatment (> 350 °C)
- Hydrocracking
- Further reductions in Mw
- Formation of aromatics and aliphatic hydrocarbons
- Acid conversion
- Lignin chemistry dominates
Reaction pathway

Pyrolysis Oil

- Hydrogenation
  - $+H_2$, catalyst, $T > 80 \, ^\circ C$
  - Stable fragments

- Hydrodeoxygenation
  - $+H_2$, catalyst, $T > 250 \, ^\circ C$
  - Non-polar fragments, aqueous phase

- Re-polymerisation
  - $T > 175 \, ^\circ C$, non catalytic, fast
  - High mol. fragments

- Hydrogenation
  - $+H_2$, catalyst, $T > 200 \, ^\circ C$
  - Stable fragments

- Hydrocracking
  - $+H_2$, catalyst, $T > 250 \, ^\circ C$
  - Non-polar fragments (low $M_w$), aqueous phase

- Charring
  - $T > 175 \, ^\circ C$, non catalytic, fast
  - Char

Catalytic biomass conversions RUG/CRE

<table>
<thead>
<tr>
<th>Biofuels</th>
<th>Biobased chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Catalytic pyrolysis oil upgrading</td>
<td>Platform chemicals</td>
</tr>
<tr>
<td>• Biodiesel from <em>Jatropha Curcas</em></td>
<td>• hydroxymethylfurfural</td>
</tr>
<tr>
<td>• Green gas by supercritical gasification in water</td>
<td>• levulinic acid/lactic acid</td>
</tr>
<tr>
<td></td>
<td>• methanol</td>
</tr>
<tr>
<td></td>
<td>• furanics based diols</td>
</tr>
<tr>
<td></td>
<td>• phenolics</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bio-based performance materials</th>
<th>Enabling science and technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Starch modifications in non-conventional solvents</td>
<td>• Catalyst development</td>
</tr>
<tr>
<td>• alcohols</td>
<td>• Process intensification using centrifugal contactor separators</td>
</tr>
<tr>
<td>• supercritical CO2</td>
<td></td>
</tr>
</tbody>
</table>
Fast Pyrolysis Oil

Lignocellulosic biomass $\rightarrow$ Fast Pyrolysis $\rightarrow$ Volatiles, Condensables, Fast Pyrolysis Oil $\rightarrow$ Char

450-600 °C, 1-2 s

BTG, Enschede
Fast pyrolysis oil characteristics

- High oxygen content (up to 50%)
- Immiscible with petroleum products
- Limited stability upon heating and storage (coke formation, repolymerization)

Pyrolysis oil composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
<td>40.1</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>7.6</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>52.1</td>
</tr>
<tr>
<td>Moisture (wt%)</td>
<td>23.9</td>
</tr>
</tbody>
</table>
Biomass application platforms

High T platform
Combustion
Gasification
Pyrolysis

Low T platform
Pre-treatment
/hydrolysis
Fermentation
Separation in fractions

Secondary conversions

Heat and Power
Transportation fuels
Biobased Chemicals
Biobased Performance materials