Upgrading of wheat/barley and miscanthus bio-oil over a sulphided catalyst

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Upgrading of wheat/barley straw bio-oil over a sulphided catalyst

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Cork, Ireland
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OUR AIM

- Straw and miscanthus bio-oils
- Sulphided x transition metals

Hydrogenation unit
- one-step fixed-bed reactor
- Optimization of T and P

Products characterisation
- Use advanced analytical techniques to shed light on product nature

AIM
- Low-cost petroleum-refinery-compatible feedstock

Bio-oil and catalysts
WHEAT/BARLEY STRAW BIO-OIL

Wheat/barley straw bio-oil

- $T_{\text{cond}}$ 2-5 °C
- Aqueous phase yield = 27.9 wt%
- Bio-oil yield = 20.9 wt%

- $T_{\text{cond}}$ 75 °C
- Bio-oil yield = 23.3 wt%

Chemical compositions:

- Left side:
  - S 0.06
  - O 38.6
  - C 52.4
  - N 0.7
  - H 8.2
  - Water content 22.6

- Right side:
  - S 0.05
  - O 36.2
  - C 55.1
  - N 0.6
  - H 8.1
  - Water content 20.5

Department of Petroleum Technology and Alternative Fuels
HYDROGENATION UNIT

- Fixed-bed, co-current flow
- Wheat/barley straw bio-oil
- 340 °C, 40 bar, TOS 80 h, LHSV 1h⁻¹
- Presulphided NiMoS/Al₂O₃

Based on our previous experiments

$S_{\text{BET}}$: 86.5 m²·g⁻¹
3.9% Ni and 15% Mo
0.8-1.2 mm particle size

2-5 °C and 75 °C
Hydrogenation of wheat/barley bio-oil 2-5 °C

Part 1: effect of thermoprofile
Hydrogenation of bio-oil (2-5 °C) at two different thermoprofiles: fast increase to 340 °C and smooth increase to 340 °C.
All hydrogenated products were separated at two phases: organic and aqueous phase (OP and AP).
• High catalytic activity loss after 12 hours TOS leads to decrease of products properties ("Fast")
Significant increasing MCR value can be assumed as the most negative point of “Fast” products even with other better properties.
Corrosivity of bio-oil products can cause huge problems in refinery – should be blended with crude-oil/distillates.
In all products were found alkanes, cycloalkanes/-alkenes that have not been observed in the raw bio-oil.
Hydrogenation of wheat/barley bio-oil 75 °C

Part 2: application of „smooth“ thermoprofile
• “Smooth” thermoprofile mode was applied for the hydrogenation of staged condensate bio-oil (75 °C) for 64 hours experiment
• After 40 h TOS organic phase density increased and all further products were not separated so well on two phases
HYDROGENATION OF STAGED CONDENSED BIO-OIL

- Higher loss of the catalytic activity during hydrogenation of staged condensed bio-oil was dominantly caused by higher CAN of feed (80 mg KOH·g⁻¹)
CONCLUSION

• Raw bio-oil is a complex mixture with unacceptable properties that should be upgraded to fulfil limits for transport fuels

• Hydrotreatment is a suitable technology for bio-oil upgrading in the fixed-bed reactor for producing low-cost petroleum-refinery-compatible feedstock

• Hydrotreatment thermoprofile play significant role in the upgrading process: „Smooth“ mode is preferred due to:
  • stable products properties
  • convenient unit operation

• Upgrading of bio-oil condensed at 2-5 °C gave more valuable products with similar properties at all TOS

**Future plans:** test two thermoprofiles for the hydrtotreatment of miscanthus bio-oil (2-5 and 75 °C) and beech-wood bio-oil
Thank you for your attention!

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