Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels

K. Magrini, J. Olstad, B. Peterson, R. Jackson, Y. Parent, E. Christensen, K. Iisa, C. Mukarakate

April 29, 2021
Outline

• Catalytic Fast Pyrolysis (CFP) Oil Production
  – Catalysts and Feedstocks
  – Pyrolyzer/DCR System
  – CFP Oil Composition

• Co-Processing (CP) to Fuels
Catalysts and Feedstocks

Feedstocks
- Miscanthus
- Pine residues
- Debarked clean pine

Johnson Matthey Catalysts
- HZSM-5 (SAR = 30), 25 and 40% [HZSM-5]
- Ga-HZSM-5
Produce high quality CFP oils with modified FCC catalysts and biomass pyrolysis vapors at the small pilot scale to produce refinery compatible intermediates of:

- 10-20% oxygen content
- High carbon efficiency in the 20-25% range, but tied to oxygen content for economic optimum
- Goal to lower (modeled) costs, consistent with BETO's goal of a $2.50/GGE range fuel production cost
Pyrolyzer/DCR Modifications for CFP and CP

(1) Stripper cyclone addition returns entrained catalyst to the stripper
(2) PolyArc total carbon detector: total C content of feed/product gases simplify C mass balance
(3) Fractional condensation train: improve product recovery
(4) Developed multi feed, independently heated nozzles for co-processing

Improvements provide a feedstock flexible (vapors, liquids, co-feeds) DCR FCC system
Catalyst and Feedstock Impacts
2D GC² TOFMS Oil Analysis

Feedstock Impact: Pine vs. Oak
+ Alkenes, aromatics
+ Buta/enone
Possibly due to differences in lignin/hemicellulose/cellulose contents

Catalyst Impact: CP783 vs. CP758
(25, 40% zeolite/same binder – possibly ketonize)
+ aromatics, – alkenes/alkynes
+ 1-, 2-ring ketones, pentenone
– buta/enone
Catalyst and Feedstock Impacts
2D GC² TOFMS Oil Analysis

**Catalysts**
- ZSM-5
- Ga/ZSM-5
  - increased aromatics, phenols
  - reduced oxygenates (furans, carbonyls: cellulose deoxygenation)

**Feedstocks**
- Pine and pine forest residues (FR)
- Miscanthus
- Pine, FR and Miscanthus
  - Pine and FR similar oxygenates
  - Miscanthus: reduced phenolics (less lignin), enhanced carbonyls and furans

**Compound Classes**
- Unknown
- Oxygenates
- Aromatics
- Alkenes/Alkynes

**Oxygenates**
- Ethers
- Acids
- Methoxies
- Phenols
- Furans
- Esters
- Carboxyls
- Carbons
- Alcohols

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MS Area Percentage</td>
<td><strong>Unknown</strong></td>
<td><strong>Oxygenates</strong></td>
<td><strong>Aromatics</strong></td>
<td><strong>Alkenes/Alkynes</strong></td>
<td><strong>Ethers</strong></td>
<td><strong>Acids</strong></td>
<td><strong>Methoxies</strong></td>
<td><strong>Phenols</strong></td>
<td><strong>Furans</strong></td>
<td><strong>Esters</strong></td>
<td><strong>Carboxyls</strong></td>
</tr>
<tr>
<td>ZSM-5 Pine</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Ga/ZSM-5 Pine</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>ZSM-5 FR</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Ga/ZEM-5 FR</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>ZSM-5 Miscanthus</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Ga/ZEM-5 Miscanthus</td>
<td>0%</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Searchable Database of Process Conditions, Catalysts, Feedstocks, Oil Compositions

- Data comprises process, operating, feed and product compositions, BC content per refinery pathway (FCC, HT/HC)

- Similar to petroleum database http://www.crudemonitor.us/

- Database is searchable, to be linked with FCIC feedstock database (LabKey), and to be published for refiner use

- Potential users: 136 US refineries, multiple catalyst and instrument manufacturers, research community

Mockup of the final LabKey User Interface for the website of the published database. Potentially link with the FCIC feedstock database.
Co-Processing: FCC co-processing of bio-oils leverages existing refining infrastructure leverages with billions US$ in CAPEX and 5 million bpd of crude refining

Objective: Produce fungible bio-oils that can be co-processed in petroleum refineries to produce biogenic carbon containing fuels

Outcome:
- Tailoring CFP oil composition for refinery insertion
- Modified refinery compatible FCC catalysts
- Co-processing strategies to refiners

Impact: Faster introduction of renewable fuels into the transportation sector to reduce GHG by 2030

* FP: Fast pyrolysis oil
  CFP: Catalytic fast pyrolysis oil
Catalyst Impact to Fuel Chemistry: FCC Co-Processing

Targeted FCC catalyst development produces bio-oils for varied refinery insertion points

FCC of VGO, oak or CFPO, and 10% oak—90% VGO mixture over E-Cat and Johnson Matthey CP758 at 550 °C, product analysis with GC-MS.

**E-Cat co-processed product has:**
- **Enhanced aromatics**, CO, CO₂
- **Reduced alkanes**

**Figure:**

- **Bar chart** showing products identified by GC-MS: CO, CO₂, alkanes, alkenes, aromatics, oxygenates.

**Table:**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Catalyst</th>
<th>% Bio-based Carbon (%Cbio)</th>
<th>(%C$<em>{feed}$)product/ (%C$</em>{feed}$)feed</th>
<th>Wt.% coke</th>
<th>Breakthrough Mass % Liq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO</td>
<td>E-Cat</td>
<td>0.0</td>
<td>NA</td>
<td>2.75</td>
<td>NA</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat</td>
<td>9.7</td>
<td>1.01</td>
<td>1.09</td>
<td>6.03</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/MFI 5 wt% Mn</td>
<td>7.3</td>
<td>0.76</td>
<td>0.83</td>
<td>5.19</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/MFI 5 wt% La</td>
<td>9.2</td>
<td>0.96</td>
<td>0.62</td>
<td>0.49</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/MFI 5 wt% Ca</td>
<td>5.5</td>
<td>0.57</td>
<td>0.68</td>
<td>5.39</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/MFI no meso</td>
<td>10.4</td>
<td>1.08</td>
<td>2.8</td>
<td>4.25</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/MFI meso</td>
<td>8.8</td>
<td>0.91</td>
<td>1.1</td>
<td>1.88</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/HZSM-5</td>
<td>5.4</td>
<td>0.66</td>
<td>0.23</td>
<td>1.80</td>
</tr>
<tr>
<td>VGO/CFPO</td>
<td>E-Cat/HZSM-5</td>
<td>5.9</td>
<td>0.72</td>
<td>Nd</td>
<td>2.33</td>
</tr>
</tbody>
</table>

**La/MFI and MFI zeolites optimized product**

%BC, wt% coke, oxygenate breakthrough – to be tested for FCC CP
FCC Co-Processing
High biogenic C incorporation demonstrated

Co-processing in FCC

<table>
<thead>
<tr>
<th>Product ID</th>
<th>VGO (vol %)</th>
<th>CFP Oil (vol %)*</th>
<th>% BC* in CFP/VGO</th>
<th>% BC in HC Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>na</td>
</tr>
<tr>
<td>V/C_99/1</td>
<td>99</td>
<td>1</td>
<td>0.8</td>
<td>na</td>
</tr>
<tr>
<td>V/C_97/3</td>
<td>97</td>
<td>3</td>
<td>3.0</td>
<td>na</td>
</tr>
<tr>
<td>V/C_95/5</td>
<td>95</td>
<td>5</td>
<td>3.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Rcn. T, P = 520°C, 25 psig; Feed rate = 1.2 liter/h
CP758 Johnson Matthey zeolite catalyst
Pine CFP oil in VGO
* Biogenic carbon measured by $^{14}$C analysis

>80% biogenic carbon incorporation in fuel products for:
- Woody CFP bio-oils with VGO
- Potential for MSW-derived biomass feedstocks

Simulated distillation shows similar BP range (expected at the low CFP concentrations)
Hydrotreated CFP Oil: 100% Biogenic Fuels

DCR conditions:
- CP758 zeolite, 550°C
- Residence time ~1s,
- 20% carbon efficiency with 500°C pine pyrolysis vapor at a 1:1 biomass:N₂ ratio.
- Hydrotreating:
  - 400 °C
  - LHSV 0.20h⁻¹ for ~90 h

<table>
<thead>
<tr>
<th>Net Weight (g)</th>
<th>Percent</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler Initial</td>
<td>51.53</td>
<td>100%</td>
</tr>
<tr>
<td>Lights</td>
<td>1.68</td>
<td>3</td>
</tr>
<tr>
<td>Gasoline (71-182)</td>
<td>23.91</td>
<td>46</td>
</tr>
<tr>
<td>Diesel (182-320)</td>
<td>20.20</td>
<td>39</td>
</tr>
<tr>
<td>Fraction Recovery</td>
<td>45.79</td>
<td>89%</td>
</tr>
<tr>
<td>Total Recovery</td>
<td>49.97</td>
<td>97%</td>
</tr>
<tr>
<td>Losses</td>
<td>1.57</td>
<td>3%</td>
</tr>
<tr>
<td>Gasoline: RON</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>MON</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>AKI</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>P_vapor Psig</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Diesel: CN</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

- Challenges: fuel composition
  - Low octane numbers due to naphthenes (cycloparaffins)
  - Low cetane numbers due to multi-ring compounds
  - Ring opening and/or C-C coupling required, less hydrogenation for gasoline
Summary

• Consistent quality CFP oils produced with a coupled pyrolyzer/FCC system

• Feedstock impact on oil composition:
  – Pine enhances aromatics, alkenes and buta/enone compared to oak, possibly due to lignin/hemicellulose/cellulose content
  – Pine and pine FR CFP oils are similar
  – Miscanthus produces less phenolics (less lignin)

• Catalyst impact on oil composition:
  – Ga addition to HZSM-5 increases aromatics as does increased [HZSM-5]
  – Ga increases phenolics, reduces carbonyls

• Biogenic carbon in hydrocarbon fuels from CFP oil co-processing with VGO approaches 80%

• Hydrotreating pine CFP oil produces gasoline, jet and diesel hydrocarbons
Acknowledgements

Bob Baldwin
Earl Christensen
Kristiina lisa
Rebecca Jackson
Calvin Mukarakate
Jessica Olstad
Yves Parent
Brady Peterson
Glenn Powell
Reinhard Seiser
Mike Sprague
Anne Starace

Huamin Wang
Miki Santosa
Igor Kutnyakov
Cheng Zhu
Oliver Gutierrez
Matt Flake
Yuan Jiang
Sue Jones
Jal Askander
Charlie Doll
Andrew Plymale
Corinne Drennan

Zhenghua Li
James Lee
Douglas Ware
Thomas Geeza
Oleg Maltseve
Jacob Helper

Industrial Collaborators
Casey Hetrick (BP America)
Jeff Lewis (Equilibrium Catalysts)
Gordon Weatherbee (WR Grace)
Mike Watson, Andrew Heavers, Luke Tuxworth (Johnson Matthey)
Larry Doyle, Chris Brown, Sean Murray (Zeton)
Kevin Stup (Vacuum Analytics)

SDI Program: Liz Moore, Jim Spaeth

NREL/PR-5100-79136