Opportunities for Biomass-Based Fuels and Products in a Refinery
– A Preliminary Investigation

1. HIGH-LEVEL IMPACT ASSESSMENT
2. SURVEY OF POTENTIAL 2022 BIOMASS AVAILABILITY NEAR PETROLEUM REFINERIES
3. CONSIDERATION OF BIO-INTERMEDIATE COMPATIBILITY WITH PETROLEUM INTERMEDIATES
4. A REFINER’S PERSPECTIVE

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Scope of Study

- **Technical Focus**
  - High level assessment of impact of incorporation of bio-derived intermediates in U.S. petroleum refineries
  - Surveys availability of biomass near petroleum refineries in the 2022 timeframe
  - Preliminary considerations of bio-intermediate compatibility with petroleum intermediates
  - Offers a refiner’s perspective
  - Public document

- **Data Sources**
  - KDF for biomass resources
  - EIA for refinery resources
  - Publically available bio-intermediate data

- **Mission Impacts**
  - Supports understanding of infrastructure use
  - Addresses entire barrel
  - Considers advanced biofuels
High-Level Impact Assessment

What refining capacities and capabilities currently exist in the US?

- Per EIA, 149 refineries total, 136 sufficiently detailed
- ~20 million barrels/day total capacity (136 refineries)
- Categorized into three main types:
  - Non-conversion & non-hydrotreating
  - Middle-distillate hydrotreating capability
  - Full conversion – fluidized catalytic cracking and hydrocracking
Q: Proximity of biomass suitable for 20% co-processing?

A: Initial look suggests refineries & biomass may fit.

* 20% additional yield loss
$60/ton farm gate
85 gal/dry ton conversion

**US refinery sites with highest est. fuel volumes
100 mile radius around each refinery
FCC and HCK refineries only (Cat 3)
Equiv. biofuel intermediate into any refinery limited to 20% of total crude capacity
Considerations for Bio-intermediates Compatibility

**How do bio-intermediate properties compare with conventional?**

- Partially hydrotreated pyrolysis more cyclic than crude derived cuts
- Very little published data
- No data for diesel or heavier cuts available

<table>
<thead>
<tr>
<th></th>
<th>Light Naphtha Cut (15 - 75 °C)</th>
<th>Heavy Naphtha Cut (75 - 165 °C)</th>
<th>Kerosene Cut (165 - 250 °C)</th>
<th>Diesel Cut (250 - 345 °C)</th>
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</thead>
<tbody>
<tr>
<td>Wt% Yield</td>
<td>5</td>
<td>13</td>
<td>12</td>
<td>17</td>
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<tr>
<td>Aliphatics (vol%)</td>
<td></td>
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<tr>
<td>Paraffins</td>
<td>86</td>
<td>46</td>
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<td>Isoparaffins</td>
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<td>Naphthenes</td>
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<td>39</td>
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<td>Aromatics (vol%)</td>
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<tr>
<td>Olefins (vol%)</td>
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<td>0.01</td>
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<td>Benzene (vol%)</td>
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<td>0.4</td>
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<td>30</td>
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<td><strong>TOTAL</strong></td>
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<td><strong>99</strong></td>
<td><strong>96</strong></td>
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<tr>
<td>H/C molar ratio</td>
<td>2.23</td>
<td>1.96</td>
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<td>1.75</td>
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<tr>
<td>Acidity*</td>
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<td>0.03</td>
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<td>RON</td>
<td>71</td>
<td>64</td>
<td>67</td>
<td>88</td>
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Further Considerations for Bio-Intermediates Compatibility

Co-processing bio-derived oils up to 20% of FCC feed potentially feasible, but…

- Raw pyrolysis oil needs pre-treatment to be miscible with petroleum feeds
- Little published data, mostly small scale FCC type applications

Graph Sources: Agblevor, F.A., et al., Co-processing of standard gas oil and biocrude oil to hydrocarbon fuels. *Biomass and Bioenergy*, 2012. 45: p. 130-137
<table>
<thead>
<tr>
<th><strong>Risk</strong></th>
<th><strong>Type of Bio-oil Intermediate</strong></th>
<th><strong>Insertion</strong></th>
<th><strong>Refinery Challenges</strong></th>
</tr>
</thead>
</table>
| Lowest | Well defined, consistent quality, such as single molecules (e.g., ethanol, butanol, farnesene)                                           | Blending units                | • Blending, product performance and distribution of products that include the bio-component  
• Evaluating and managing potential stability, toxicity and environmental issues                                                                                                    |
| Medium| Intermediates requiring only minor treating (e.g. triglycerides, some direct liquefaction oils, some catalytically derived sugar oils) | Hydrotreating followed by blending | Challenges identified above, plus:  
• Understanding process performance on new feeds and blends with petroleum-based feeds  
• Enabling larger fractions of bio-oil blending stocks while still meeting product specs.  
• Providing sufficient hydrogen to meet hydrotreating demands (for reducing oxygen or aromatic contents) |
| Highest| Intermediates needing boiling range & composition changes for acceptable gasoline, diesel and jet fuel blending stocks (e.g. fast pyrolysis oils, some hydrothermal liquefaction oils, some catalytic pyrolysis oils) | Off-site or dedicated on-site hydrotreating followed by cat- or hydro-cracking | Challenges identified above, plus:  
• Understanding the impact of bio-oils on all refinery processes  
• Meeting product quantity and quality needs with feedstocks with less data on conversion behavior |
Preliminary Conclusions

- Most U.S. refineries have sufficient capabilities
  - Processing units
  - Capacity (at least at this level of analysis)

- U.S Gulf Coast refining important
  - Bulk of capacity
  - Proximity to projected biomass availability

- Limited co-processing data available
  - Some data expected from 2012 BETO bio-oil commoditization awards
  - Some data from NABC
  - Concern around the scale and duration of necessary testing
  - How much will be made public?
    (PNNL 11.2.2.2 FY14 task focusing on FCC and HCK performance and cost modeling using publically available data)

- Methods and standards needed for characterizing and predicting the impacts of bio-based blendstocks and intermediates on conventional petroleum processing and tuning of product slates
On the Path Forward

- **Improve resource assessment**
  - Focus on Gulf Coast
  - Consider biomass availability and projected yields through 2022
  - Consider implications of INL feedstock densification work

- **Improve bio-intermediate characterization**
  - Incorporate development metrics meaningful to refineries (pour point, cetane, API, D86, etc.)
  - Improve characterization of bio-intermediate and predictions of “processability” and conversion

- **Validate, refine and guide Bioenergy Technologies Office with input from refiners, biofuel producers and technology developers**
  - Workshops
  - Formation of a guiding consortium
  - Collaborative research

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