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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

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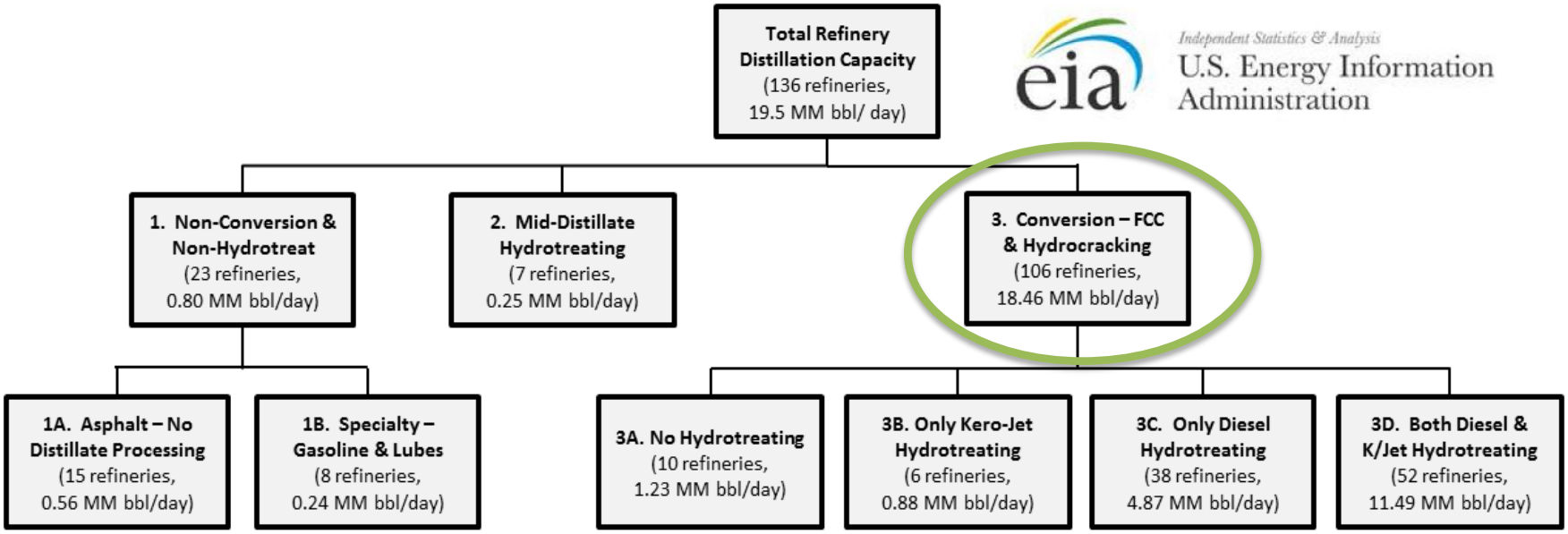
- Technical Focus
  - High level assessment of impact of incorporation of bio-derived intermediates in U.S. petroleum refineries
  - Surveys availability of biomass near petroleum refineries in the 2022 timeframe
  - Preliminary considerations of bio-intermediate compatibility with petroleum intermediates
  - 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



Survey of Projected 2022 Biomass Availability Near Petroleum Refineries

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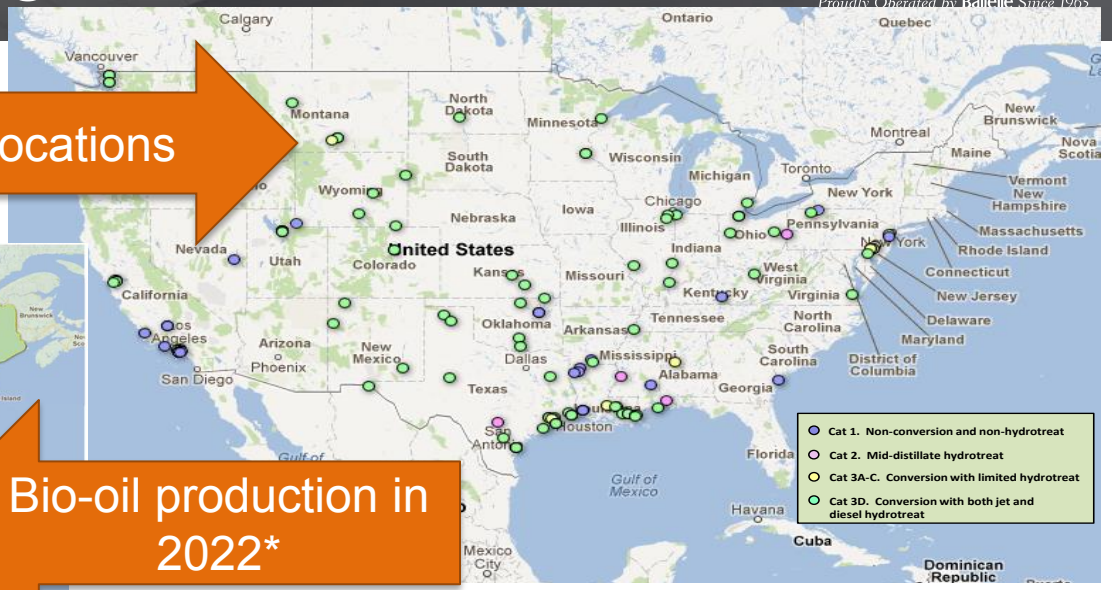
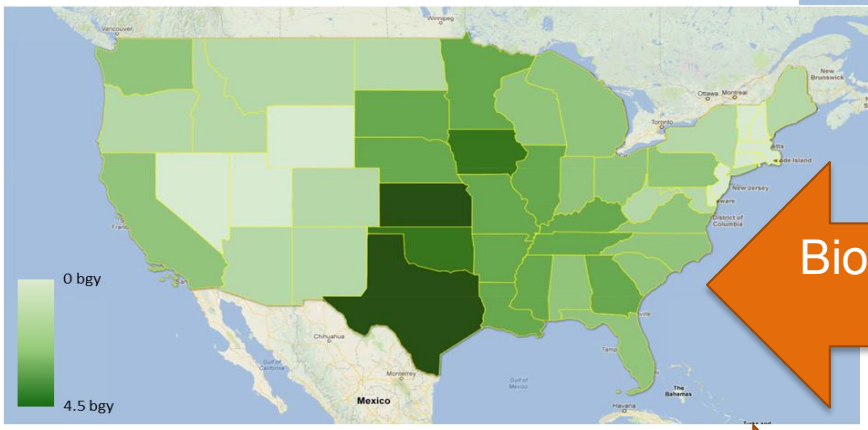
Q: Proximity of biomass suitable for 20% co-processing?

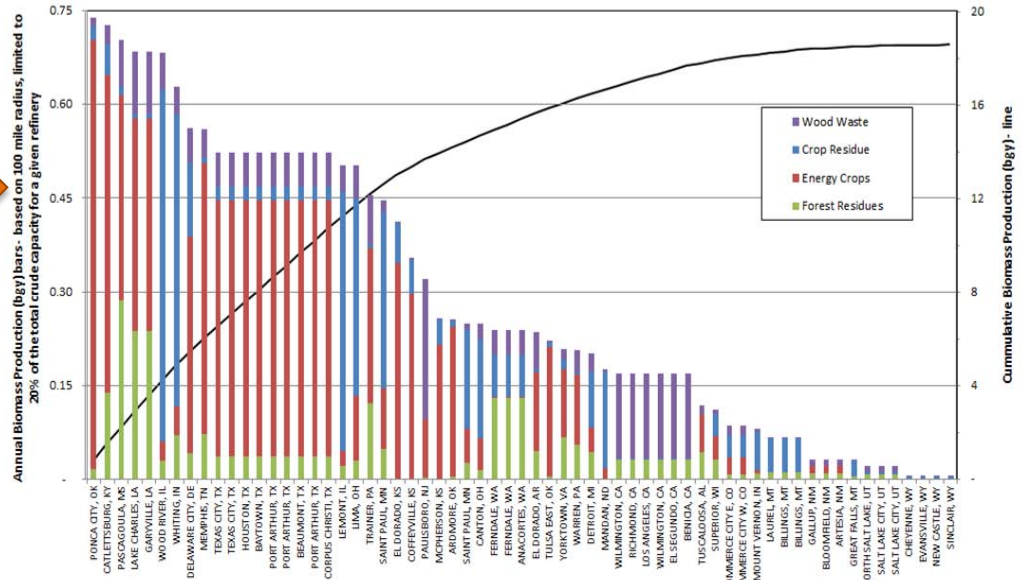
Refinery locations





Bio-oil production in 2022*

Refinery sites with highest likelihood of biofuel production**



* 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

A: Initial look suggests refineries & biomass may fit

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

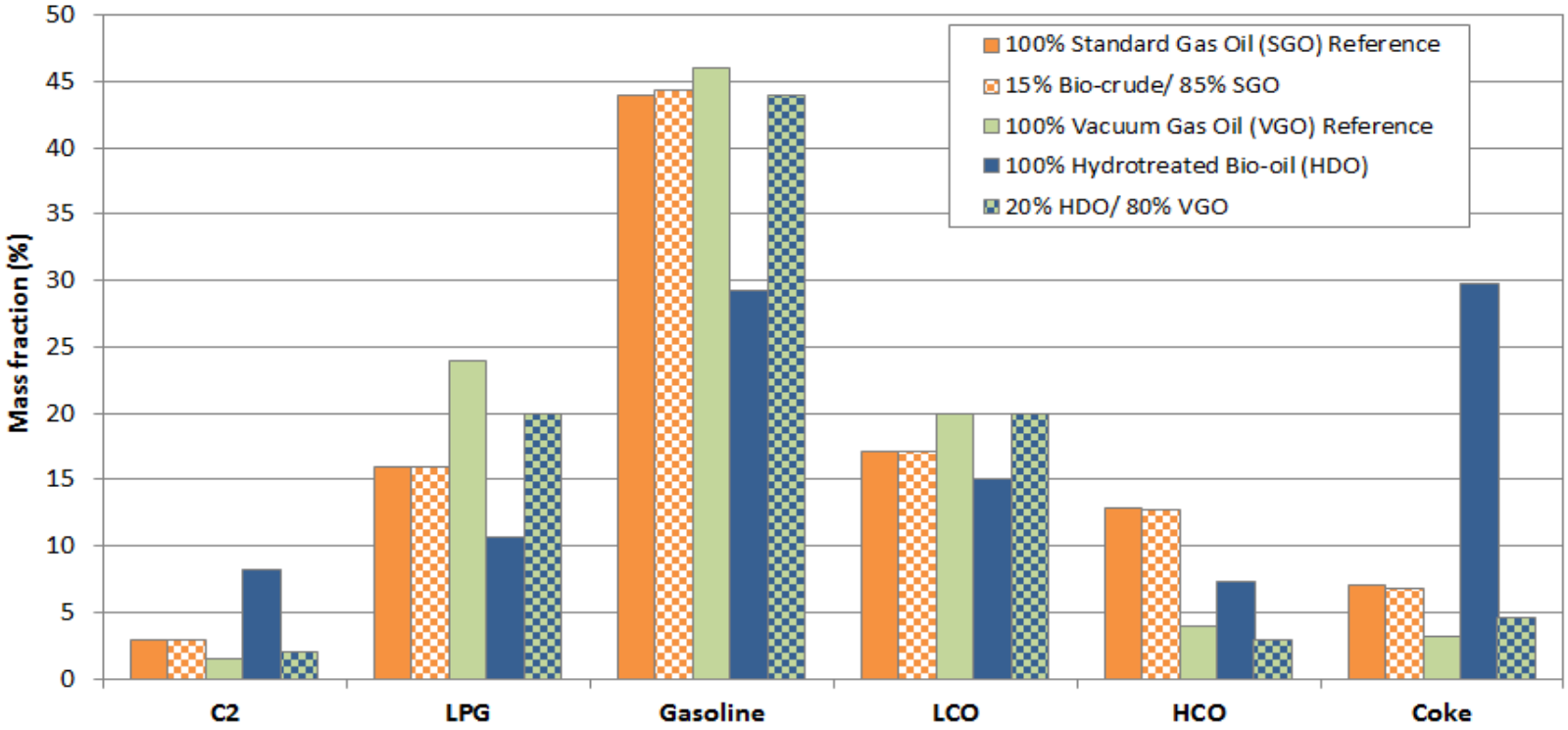
	Light Naphtha Cut			Heavy Naphtha Cut			Kerosene Cut			Diesel Cut		
	15 - 75 °C	C5 - 71 °C		75 - 165 °C	71 - 182 °C		165 - 250 °C	182 - 260 °C		250 - 345 °C	260 - 338 °C	
	North Slope Crude	Hydrotreated Pyrolysis Oil from Biomass		North Slope Crude	Hydrotreated Pyrolysis Oil from Biomass		North Slope Crude	Hydrotreated Pyrolysis Oil from Biomass		North Slope Crude	Hydrotreated Pyrolysis Oil from Biomass	
		8.2% O	0.4% O		8.2% O	0.4% O		8.2% O	0.4% O		8.2% O	0.4% O
Wt% Yield	5	5	14	13	20	30	12	19	22	17	17	21
Aliphatics (vol%)												
Paraffins	86	7.9	28.3	46	15.4	5.9	37	10	33	30		
Isoparaffins		32.8	14.9		26.8	38.8						
Naphthenes	13	31.8	51.3	39	46	20.3	44			38		
Aromatics (vol%)		10.9	5.6	14	11.8	27	15	52	38	31		
Olefins (vol%)		16.7	0.07		0.01	8.3						
Benzene (vol%)		0.3	0.5		0.4	0.8						
Unidentified								30	25			
TOTAL	**99**	**100**	**101**	**99**	**100**	**101**	**96**	**92**	**96**	**99**		
H/C molar ratio	2.23	1.96	2.04	1.96	1.88	1.85	1.89	1.69	1.7	1.75	1.56	1.55
Acidity*	0.001	102	ND	0.009	123	ND	0.03	67	ND	0.098	20	0.1
RON	71	79	64	64	71	88						

*Table Sources: Christiansen, Earl, *et al.* "Biomass Fast Pyrolysis Oil Distillate Fractions" *Energy & Fuels* **2011**, *25*, 5462-5471
BP Crude Marketing, Alaska North Slope Crude Assay http://www.bp.com/extendedsectiongenericarticle.do?categoryId=16002777&contentId=7020196

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
Fogassy, G., *et al.,* Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Applied Catalysis B: Environmental,* **2010**. *96*(3-4): p. 476-485

A Refiner's Perspective

Refiner's Perspective – Safety, Reliability, Predictability, Profitability

Risk	Type of Bio-oil Intermediate	Insertion	Refinery Challenges
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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