Future?
Future?

Supply & Demand

- Worldwide trade of refined products
- Increased North American crude supply
  - Tight oil from shale formations
  - Canadian oil sands
- Shift gasoline production to kerosene/diesel

U.S. Government Mandates

- Clean Air Act & Amendments
  - Renewable Fuel Standards
    - Difference between 1st generation & advanced biofuels
- GHG Emissions Control
  - EPA CO2 Endangerment Finding
  - Carbon Capture & Storage
Supply & Demand
Worldwide trade of refined products

In general, U.S. prefers gasoline to diesel, whereas great deal of the rest of the world prefers diesel.

FCC-based refineries will still produce a great deal of gasoline even when trying to maximize diesel production. Foreign incentive to ship excess gasoline to US, especially to the East Coast from Europe.
  - 2008 gasoline imports suppressed the cost of gasoline relative to crude oil.

US refineries increasing the installation of Hydrocracking to produce diesel for export, especially along the Gulf of Mexico.

“U.S. petroleum product exports increase in 2013,” April 2014
http://www.eia.gov/todayinenergy/detail.cfm?id=15951
European Refining Main Trends

Decline in demand

- European refineries had been configured to maximize gasoline production.
- Had expected increase in gasoline consumption, but actually peaked in late 1990s.

Reduced US gasoline import requirements

- Peak exports over 400,000 bpd gasoline to US, 2013 Q1 only 280,000 bpd.
- Expect trend to continue since US gasoline demand decreasing.
  - Higher engine efficiencies
  - Colonial pipeline to link US Gulf Coast to US East Coast & will reduce need for European imports into the US East Coast.

Environmental compliance

- Multiple European environmental regulations & constant changes in policy by the European Commission (EC) – generated uncertainty & increased compliance costs

Threat from Asia and the Middle East

- New production coming out of Middle East & Asia. Large refinery projects in the Middle East will come on stream in the next few years.
- Rapid refinery expansion in Asia (in particular in China & India).
- Lose market share in North America & facing challenge to compete for market share in Africa.

Ref: http://www.refinerlink.com/blog/Europe_Still_Waiting/
Tight Oil from Shale Formations

Tight oil production made possible by improved technology: directional drilling & hydraulic fracturing

Tight oil from the Bakken has made North Dakota the 3rd largest producing state in the US

Oil production outside areas of existing pipeline infrastructure

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Canadian Oil Sands

Heavy oils produced by various technologies

- Surface mining & hot water extraction
- In situ heating
  - CSS (Cyclic Steam Stimulation)
  - SAGD (Steam Assisted Gravity Drainage)
- Upgrading
  - Exported product much lighter than feedstock

http://www.ogj.com/unconventional-resources/oil-sands.html

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Tight Oil & Oil Sands Considerations

Tight oil tends to be light & sweet – replacement to WTI

Products from oil sands depend upon production technology

- Mining & in situ SAGD production gives heavy & sour product – compete with other imported heavy oils
  - Must be mixed with light diluent to allow transport (“dilbit”)
  - Excess naphtha & LPG in the northern region viewed as source of diluent
- Product from upgraders would be light – compete with tight oils
- Oil Sands projects tend to be very expensive & require high crude oil market price for cost recovery
  - Largest undeveloped projects are Canadian oil sands projects requiring estimated $128 to $159 per bbl

Expectation is that each type will separately displace imported oil from the US refiner’s crude slate

Transportation Infrastructure is Key

Keystone XL Pipeline proposed to bring oils sands to Gulf Coast

U.S. government approval status

- Had been rejected November 2015 after 6 years of evaluation
- Reinstated January 2017

In many respects the section south from Cushing was the most important part to improve flow of all mid-continent oil.

- Started flow early 2014, up to 700,000 bpd capacity
- The differential between WTI & Brent started to close up at this time

Transportation Infrastructure is Key

Rail became preferred method to bring incremental barrels out of Bakken & Eagle Ford

- Safety concerns – train derailments July 2013 Quebec (40 dead), December 2013 ND, & others
- Concerns from communities
  - Increased emissions, especially in California
  - Advertising timing of oil shipments could be a matter of home security
- ANSI & API released new recommended practices for shipping crude by rail (ANSI/API Recommended Practice 3000) in September 2014

Transportation by Rail in U.S.


CRUDE OIL BY RAIL
Originations vs. Terminations, 2007-2016

America’s freight railroads support the nation’s energy renaissance by moving domestic energy resources such as crude oil. Since 2009, when domestic crude oil production started to surge, U.S. railroads have originated more than two million carloads of crude oil. To help ensure the safety of crude oil movements, freight railroads have implemented new operating protocols and advocated for stronger tank car design standards, while federal regulators have issued more stringent safety regulations related to crude oil transport.

Notes: Data are for U.S. Class I railroads
Source: Association of American Railroads

https://www.aar.org/Pages/Crude-Oil-Rail-Traffic.aspx

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Rail Safety

New rules from US DOT & Canadian transportation officials go into effect Oct. 1, 2015

- New tank cars must have an outer shell, a thermal lining, improved top and bottom fittings and thicker 9/16ths-inch steel walls
- By Jan. 1, 2021, trains of at least 70 cars must have electronically controlled brakes to automatically stop all the cars in a train at the same time

Implications

- Will require replacing all DOT-111 & non-jacketed CPC-1232 cars for Packing Group I within 5 years

New rules:


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Alternate Pipeline Projects

450 Mbpd Dakota Access line was to open Q4 2016
- To allow flow of Bakken oil to gulf coast
- Change flow of this oil to east & west coasts by rail
- Multiple owners, including Phillips 66, Marathon Petroleum, & Enbridge Energy Partners
- Reinstated January 2017 & started operating June 2017

Challenges to Process Tight Oil

In general, light & sweet, very paraffinic in nature
- May give poor cold properties (cloud & pour points)
- May destabilize asphaltenes when mixed with heavier crudes
  - Deposition in crude heat exchange trains

Properties can have considerable variability
- Solids loading in desalters can be highly variable

Finished fuels may require more processing & additives because of the paraffinic & low sulfur natures.

Table 2: Physical properties of Eagle Ford shale oil samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Yellow</th>
<th>Red</th>
<th>Black</th>
</tr>
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<tbody>
<tr>
<td>API</td>
<td>55</td>
<td>44.6</td>
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<tr>
<td>TAN, mg KOH/g</td>
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<td>0.07</td>
<td>&lt; 0.05</td>
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<tr>
<td>Sulfur, wt%</td>
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<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
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<td>Na, ppm</td>
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<td>1.6</td>
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<tr>
<td>K, ppm</td>
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<td>Mg, ppm</td>
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<tr>
<td>Ca, ppm</td>
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<td>2.8</td>
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<tr>
<td>Asphaltenes, wt%</td>
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<td>0</td>
<td>0.1</td>
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<tr>
<td>Resin, wt%</td>
<td>0.5</td>
<td>3.2</td>
<td>1.6</td>
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<tr>
<td>Filterable solids, PTB</td>
<td>176</td>
<td>295</td>
<td>225</td>
</tr>
</tbody>
</table>

What Does This Mean for U.S. Refiners?

Tight oil production should ensure domestic supply of sweet crude for the next 10 – 15 years

- Expected to peak @ 4.8 million bpd in 2021 (EIA, Dec. 2013)

Investments to allow processing of sour crudes might limit the ability to utilize this tight oil

- Exporting tight oil while importing heavy oil is very possible

Environmental concerns could put the brakes on this production

- High energy requirements for producing Canadian oil sands
- High water quantities needed for tight oil & oil sands production
- Public concerns about hydraulic fracturing
- Public concerns about oil transport by rail

Fairly quick production drop-off in shale formations – low oil prices have led to less drilling, leading to falling production rates


Shift gasoline production to diesel
Shift From Gasoline to Middle Distillate Production

Basis

- Growth of middle distillates (diesel & jet fuel) & petrochemicals much greater than gasoline
- Feedstock will be relatively heavy crude oil requiring desulfurization of intermediates & products
- Naphthas converted to petrochemicals
  - Light Naphtha to olefins (primarily propylene & ethylene)
  - Mid & Heavy Cat Naphtha to aromatics (BTX)

Refinery configurations

- Existing refinery with FCCU – minimize gasoline yield
  - Shift FCC operations
- Grassroots refinery
  - Increased usage of Steam Crackers, Residuum FCC, & Hydrocracking

Ref: “Towards a zero gasoline production refinery,” Parts 1 & 2, B. Stamateris & D. Gillis, PTQ, Q3 & Q4 2013
Modify Existing FCC Refineries

Shift FCC operations to olefin production vs. naphtha
  - ZSM-5 addition shifts C₇-C₁₀ molecules to olefinic LPG

Shift LCN production to light olefins
  - Send LCN to 2nd FCC riser or to Steam Cracker
    - Steam cracker will produce more olefins but at a very high energy requirement

Convert MCN & HCN to aromatics
  - High severity Reformer operations increase aromatic content of reformate
  - Use PyGas (pyrolysis gas) from Steam Cracker
Modify Existing FCC Refineries (cont.)

Processing options for the additional C₄s

- C₄s to 2nd high-severity FCC for increased ethylene, propylene, & naphtha
- React n-butenes with ethylene to make propylene
  - Single fixed-bed reactor, equilibrium limited
- Polynaphtha oligomerization – flexible output
  - Create 100% naphtha range – send to FCC or Steam Cracker for propylene
  - Create 30% naphtha / 70% distillate – hydrotreat distillate to control freezing point & smoke point

Petrochemical integration
Future Refinery Configurations?

Minimize gasoline production
- Convert naphtha to LPG olefins & BTX aromatics
  - Modify operations of FCC
- No isomerization necessary
- No Alkylation in favor of Polymerization/Oligomerization

Increase middle distillate production (jet fuel & diesel)
- Increase hydrotreating to lower olefin & aromatic content (control freezing point & smoke point, increase cetane number)

Increase petrochemical production
- Increase Steam Cracking for increased LPG olefin production
New Configurations – SDA + DCU + HCU + RFCC

Delayed Coking to process resid with very high metals

- SDA maximizes feed to the Hydrocracker by separating saturates from Heavy Cracker Gas Oil
U.S. Government Mandates
Clean Air Act & Amendments

Series of Clean Air Acts
- Air Pollution Control Act of 1955
- Clean Air Act of 1963
- Air Quality Act of 1967
- Clean Air Act Extension of 1970
- Clean Air Act Amendments in 1977 & 1990

1977 Clean Air Act amendments set requirements for "substantially similar gasoline"
- Oxygenates added to make motor fuels burn more cleanly & reduce tailpipe pollution (particularly CO)
- Required that oxygenates be approved by the U.S. EPA
- MTBE & ethanol primary choices

California Phase 3 gasoline regulation approved by California Air Resources Board in December 1999 prohibits gasoline with MTBE after December 31, 2002
- Water quality issues
Recent Impacts from EPA Rulings

Decrease in sulfur in gasoline & diesel
- Gasoline sulfur reduced from 300 ppm to 30 ppm
  - Discussion started to further reduce to 10 ppm (ULSG)
- Diesel sulfur reduced down to 500 ppm (LSD) & 15 ppm (ULSD)

Reformulation of gasoline’s olefin & aromatic content & boiling ranges
- Specific reduction of benzene content from 1.1% to 0.62 vol%

Implementation of the 2007 Renewable Fuel Standard (RFS-2)
- Implementation of the Renewable Identification Number (RIN) program
Reducing gasoline’s sulfur in current refineries

Majority of the gasoline’s sulfur due to how the FCC is operated
   Challenge is to maintain the high octane from the olefins while removing the sulfur

Options
   Increased hydrotreating around the FCC
    • Increased severity in FCC feed pre-treatment
      o Remove sulfur before the olefins are formed
      o Increased H2 consumption & decreased catalyst cycle length
    • Post treatment of FCC Naphtha
      o Required for ULS Gasoline
      o For refiners with existing post treatment, increased severity may be required
   Use of Gasoline Sulfur Reduction additives in FCC
    • Additional cost, low sulfur removal

SCANFINING™ TECHNOLOGY: A PROVEN OPTION FOR PRODUCING ULTRA-LOW SULFUR CLEAN GASOLINE,
Kalyanaraman, Smyth, Greeley, & Pena
LARTC 3rd Annual Meeting 9-10 April 2014 Cancun , Mexico
2007 Renewable Fuel Standard (RFS2)

Replaced the RFS of the Energy Policy Act of 2005
Administered by the Environmental Protection Agency
http://epa.gov/otaq/renewablefuels/index.htm
EPA Clarifications & Adjustments

RFS-2 Advanced Biofuels amounts have had to be adjusted since 2010

- **Significantly** less development of cellulosic biofuels than had been anticipated in 2007

Adjustments required annually

- Have needed to drastically reduce Cellulosic Biofuel
- Increases in allowed biodiesel
- Have started to expand the types of allowable advanced biofuel
- Rules for 2017 lower than standard but higher than expected
- Final 2018 targets announced November 2017

---

EPA Clarifications & Adjustments

<table>
<thead>
<tr>
<th>Year</th>
<th>Renewable Fuel Bgal/yr</th>
<th>Advanced Biofuels Bgal/yr</th>
<th>Cellulosic Biofuel Bgal/yr</th>
</tr>
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<tr>
<td>2006</td>
<td>4.000</td>
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<td>4.700</td>
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<td>2008</td>
<td>9.000</td>
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<td>0.500</td>
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<td>2010</td>
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<td>2014</td>
<td>18.150</td>
<td>5.000</td>
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<tr>
<td>2015</td>
<td>20.500</td>
<td>6.000</td>
<td>5.500</td>
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<tr>
<td>2016</td>
<td>22.250</td>
<td>7.250</td>
<td>6.000</td>
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<tr>
<td>2017</td>
<td>24.000</td>
<td>8.500</td>
<td>6.500</td>
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<tr>
<td>2018</td>
<td>26.000</td>
<td>10.000</td>
<td>7.000</td>
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<tr>
<td>2019</td>
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<td>8.000</td>
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<td>2020</td>
<td>30.000</td>
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<tr>
<td>2021</td>
<td>33.000</td>
<td>16.000</td>
<td>9.500</td>
</tr>
<tr>
<td>2022</td>
<td>36.000</td>
<td>18.000</td>
<td>10.000</td>
</tr>
</tbody>
</table>

Biodiesel volumes actual. All other volumes ethanol-equivalent.

Advanced Biofuel:
Renewable fuel (other than corn starch derived ethanol) with 50% less than baseline lifecycle greenhouse gas emissions.

Cellulosic Biofuel:
Renewable fuel from lignocellulosic biomass with 60% less than baseline lifecycle greenhouse gas emissions.

Refs:
- [http://epa.gov/otaq/fuels/renewablefuels/regulations.htm](http://epa.gov/otaq/fuels/renewablefuels/regulations.htm)
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Refs:
- [http://epa.gov/otaq/fuels/renewablefuels/regulations.htm](http://epa.gov/otaq/fuels/renewablefuels/regulations.htm)
“Unforeseen” Issues with RFS-2

Production of advanced biofuels not increasing at rate expected & mandated by the law
  ▪ Both technology & commercial issues

The “blend wall” – Enough gasoline to incorporate all this ethanol?
  ▪ 136 B gal motor gasoline sold in US in 2012 – E10 can only incorporate 13.6 B gal
    • 2012 requires 15.2 B gal ethanol – 12% greater amount

Full amount of renewable fuel will suppress amount of gasoline in the market
  ▪ 36 B gal ethanol + 112 B gal gasoline will give energy equivalent of 2012’s 136 B gal gasoline – 82% of the
    2012 gasoline amount

Increased CAFE standards give further downward pressure on gasoline demand
  ▪ 2007 Energy & Security Act raises to 35 mpg by 2020
    • Increased to 35.5 mpg by 2016 by executive order
  ▪ 2025 target for passenger vehicles & light trucks 54.5 mpg
  ▪ Electric & plug-in hybrids will increase electricity demand at expense of petroleum

Ref: http://epa.gov/otaq/fetrends.htm
Is the RFS an Unworkable Policy?

Higher GHG emissions?
- Double GHG emissions as farmers convert land to corn fields?
- Lower energy density means more frequent stops to refill

Land use
- RFS taking major toll on grasslands & wetlands?

Water use
- Does ethanol production from corn use 3 to 6 times the amount of water for gasoline?
- Water degradation from fertilizers, pesticides, & soil erosion?

Petroleum Company Renewable Fuels Investments

1st Generation Biofuels

Valero
- Purchased 7 corn dry mills from bankrupt VersaSun, 770 MMgal/yr capacity.
- Additional funding to Terrabon LLC (waste to liquid fuels)

Sunoco
- Purchased converted brewery from bankrupt Northeast Biofuels. Started up production July 2010.

Murphy Oil Company
- Exiting refining to focus on marketing. Ethanol part of this strategy.
  - Purchased 100 MMgal dry mill plant in Hankinson, ND
  - Negotiating purchase of 100 MMgal plant near Hereford, TX (July 2010)

Marathon Petroleum Company
- Co-owner of 110 MMgal/yr corn dry mill Greenville, OH, with Andersons
- Buying biodiesel plant in Cincinnati, OH

Advanced Biofuels

Phillips 66 (legacy ConocoPhillips)
- Announced renewable fuels center Louisville, CO (2008); not moving forward (2012)
- UK production green gasoline & diesel
- Alliance with NREL & Iowa State University – research cellulosic biomass conversion
- Will work with Sapphire Energy to collect & analyze data from co-processing of algae & conventional crude oil (2013)

BP
- Exiting biofuels (other than Brazilian sugar cane business) as of late 2014

ExxonMobil

Chevron

Royal Dutch Shell
- As of February 2011, narrowing from 10 technologies to 5.
- Raizen (joint venture with Cosan) will spend €1 billion on 8 ethanol plants

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Hydrodeoxygenation of Organic Oils

Organic oils can be hydrotreated to form “green” diesel

- Fully compatible with petroleum derived diesel
- Excellent cetane number but poor cloud point because of the straight chain nature

Challenges for catalyst design

- Oxygen relatively easy to remove, but large oxygen content
- Prefer to deoxygenate to CO₂ to maximize fuel usage of H₂

“Hydrotreating in the production of green diesel”
R. Egeberg, N. Michaelsen, L. Skyum, & P. Zeuthen
Petroleum Technology Quarterly, 2nd Quarter 2010

Updated: July 12, 2018
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## Green Diesel Production Examples

### Oleic Fatty Acid (18:1)

<table>
<thead>
<tr>
<th></th>
<th>Oil</th>
<th>Hydrogen</th>
<th>Water</th>
<th>Propane</th>
<th>Octadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>3$H$<em>5$-(OOC-C$</em>{17}$H$</em>{33}$)$_3$</td>
<td>H$_2$</td>
<td>H$_2$O</td>
<td>C$_3$H$_8$</td>
<td>C$<em>{18}$H$</em>{38}$</td>
</tr>
<tr>
<td><strong>Molar Mass</strong></td>
<td>885.4</td>
<td>2.0</td>
<td>18.0</td>
<td>44.1</td>
<td>254.5</td>
</tr>
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<td><strong>%C</strong></td>
<td>77%</td>
<td>0%</td>
<td>0%</td>
<td>82%</td>
<td>85%</td>
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<tr>
<td><strong>%H</strong></td>
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<td>100%</td>
<td>11%</td>
<td>18%</td>
<td>15%</td>
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<tr>
<td><strong>%O</strong></td>
<td>11%</td>
<td>0%</td>
<td>89%</td>
<td>0%</td>
<td>0%</td>
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<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>0.92</td>
<td>1.00</td>
<td>0.51</td>
<td>0.78</td>
<td></td>
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<tr>
<td><strong>Stoichiometric Coefficient</strong></td>
<td>1</td>
<td>15</td>
<td>6</td>
<td>1</td>
<td>3</td>
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<tr>
<td><strong>Mass</strong></td>
<td>885.4</td>
<td>30.2</td>
<td>108.1</td>
<td>44.1</td>
<td>763.5</td>
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<tr>
<td><strong>Volume (Liquid)</strong></td>
<td>962.4</td>
<td>108.1</td>
<td>86.5</td>
<td>978.8</td>
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<tr>
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### Oleic Fatty Acid (18:1)

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<tr>
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<th>Oil</th>
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<th>Carbon Dioxide</th>
<th>Propane</th>
<th>Heptadecane</th>
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<td>H$_2$</td>
<td>CO$_2$</td>
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<tr>
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<tr>
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<td>0%</td>
<td>0%</td>
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<td><strong>Density (g/cm$^3$)</strong></td>
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</tbody>
</table>
Expectations for Hydrotreating Fats & Oils

Configuration

- Expect to have similar configuration & materials of construction as hydrodesulfurization
- Different catalyst than hydrodesulfurization
- Lower severity expected?
  - Oxygen easier to remove
  - Fewer complex molecular structures
  - But experience shows higher reactor temperatures
- Additional processing of feed?

Hydrogen requirements

- 5X or more than hydrodesulfurization

Product considerations

- Remove the produced CO₂/CO/H₂O
- Fractionation required to remove light ends
  - Will get additional light ends from autothermal cracking
  - Propane & other light gases to LPG
  - Naphtha should go to Isomerization
- Distillate
  - Extremely high cetane number
  - May have cloud point issues
  - High portion of the boiling point fraction
GHG Emissions Control
EPA CO₂ Endangerment Finding

Endangerment finding

- April 2007 Supreme Court ruled in *Massachusetts v. EPA* that the Clean Air Act gives the EPA authority to regulate emissions of greenhouse gases if they are a threat to human health & welfare
- Dec. 2009 EPA finalized finding that greenhouse gases pose a threat to human health & welfare
- June 2014 Supreme Court ruling emissions of GHGs alone are not enough to trigger EPA enforcement, but sources already having to comply with mitigating effects of other pollutants could be required to do the same for GHGs

**Mandatory** reporting

- 25,000 ton/yr CO₂(e) threshold
- Fines for reporting late, ...
  - ExxonMobil fined $120,000 in July 2013 for late report for Torrence, CA refinery

"Submitting your first GHG report"
Baranski & Ternes
*Chemical Engineering Progress*, March 2010
Industrial & Typical Refinery Emissions

Industrial Emissions

- Power: 54%
- Refineries: 15%
- Ammonia: 6%
- Cement: 5%
- Ethylene: 12%
- Ethylene Oxide: 3%
- Gas Processing: 2%
- Hydrogen: 1%
- Iron & Steel: 3%
- Other: 2%

Refinery Emissions

- Process Heaters: 50%
- FCC & Hydrogen Plants: 35%
- Steam & Power Systems: 15%
CO2 Capture & Sequestration

Power Station/Industrial Facility

- CO2 stored in saline formation
- CO2 displaces oil
- CO2 replaces methane trapped in coal

- Enhanced Oil Recovery (CO2 displaces oil)

Updated: July 12, 2018
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## Carbon Capture & Storage (CCS) Technologies & Issues

<table>
<thead>
<tr>
<th>Technology</th>
<th>Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂ Capture</strong></td>
<td></td>
</tr>
<tr>
<td>• Post-Combustion</td>
<td>• High capital cost &amp; energy penalties</td>
</tr>
<tr>
<td>• Add capture to existing facilities</td>
<td>• 75-90% of the CCS cost</td>
</tr>
<tr>
<td>• Pre-Combustion</td>
<td></td>
</tr>
<tr>
<td>• Gasify &amp; capture CO₂ prior to final combustion</td>
<td></td>
</tr>
<tr>
<td>• Oxy-Combustion</td>
<td></td>
</tr>
<tr>
<td>• Burn with O₂ &amp; condense produced water</td>
<td></td>
</tr>
<tr>
<td><strong>Transport</strong></td>
<td></td>
</tr>
<tr>
<td>• Pipelines to final location</td>
<td>• Infrastructure right of ways</td>
</tr>
<tr>
<td></td>
<td>• Limited by economics of transport distance</td>
</tr>
<tr>
<td><strong>Storage / Sequestration</strong></td>
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</tr>
<tr>
<td>• Sub-surface</td>
<td>• Scientific &amp; operational basis for safe &amp; effective long-term storage</td>
</tr>
<tr>
<td>• Land possibilities</td>
<td>• Land &amp; mineral access rights for geologic storage</td>
</tr>
<tr>
<td></td>
<td>• Long-term liability</td>
</tr>
<tr>
<td><strong>Research Focus</strong></td>
<td>• Cost &amp; energy penalty reductions</td>
</tr>
</tbody>
</table>
CO₂ Sources & Disposition Options

“Study places CO₂ capture cost between $34 and $61/ton”
Oil & Gas Journal, Oct. 12, 2009

Source: NatCarb
Summary
Market for petroleum products is becoming more worldwide.

Petroleum feedstocks diverging:
- Tight oil from U.S. very light & sweet
- Worldwide becoming heavier & more sour

Changing product demand:
- Diesel expected to grow much more than gasoline
  - Decreased cat cracking & increased hydroprocessing
  - Outlet for crude oil’s naphtha?
- Impact of transportation technologies that do not require liquid fuels

Impact of regulations:
- Reduction in sulfur content
- Biofuels
- Greenhouse gas emissions
Alternatives to Keystone XL Pipeline

TransCanada’s Energy East pipeline would transport oil-sands crude to Canadian refineries & Atlantic Coast

Enbridge’s Northern Gateway pipeline opposed by aboriginal groups

Proposed AAR DOT-111 Railway Tank Car Upgrades

<table>
<thead>
<tr>
<th></th>
<th>Current Standard</th>
<th>Latest Proposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HIGH CAPACITY PRESSURE RELIEF VALVE</td>
<td>No Requirement</td>
</tr>
<tr>
<td>2</td>
<td>TOP FITTINGS PROTECTION</td>
<td>Protect integrity of valves and fittings used in loading in event of accident</td>
</tr>
<tr>
<td>3</td>
<td>HEAD SHIELDS</td>
<td>½ inch thick/ half height head shields on either end to improve puncture resistance</td>
</tr>
<tr>
<td>4</td>
<td>STEEL TANK</td>
<td>½ inch thickness for unjacketed cars 7/16 inch thickness for jacketed cars</td>
</tr>
<tr>
<td>5</td>
<td>BOTTOM OUTLET HANDLES</td>
<td>No requirement</td>
</tr>
<tr>
<td>6</td>
<td>JACKET AND THERMAL PROTECTION</td>
<td>Minimum ½ inch thick steel tank OR 1/8 inch thick steel jacket</td>
</tr>
</tbody>
</table>

http://www.slideshare.net/ParkerHannifin/proposaed‐aar‐dot‐111railway‐tank‐car‐upgradestank‐car‐safety

Updated: July 12, 2018
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Renewable Identification Number (RIN)

What is it?
- 38-character numeric code that is generated by the producer or importer of renewable fuel
- Way to demonstrate compliance to the RFS & track volumes

What info does the RIN code contain?
- Year the batch is produced/imported
- Producing/importing company registration information
- Production facility registration information
- Producer assigned batch number
- Equivalence Value for the renewable fuel (e.g., Biodiesel is 1.5 = “15”)
- Renewable type code (e.g, 1=cellulosic ethanol, 2=non cellulosic ethanol)

<table>
<thead>
<tr>
<th>D Code</th>
<th>Fuel Type</th>
<th>Fuel</th>
<th>GHG Reduction Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>D3 RIN</td>
<td>Cellulosic Biofuels</td>
<td>Cellulosic ethanol, cellulosic naphtha, ...</td>
<td>60%</td>
</tr>
<tr>
<td>D4 RIN</td>
<td>Biomass-based Diesel</td>
<td>Biodiesel, renewable diesel, ...</td>
<td>50%</td>
</tr>
<tr>
<td>D5 RIN</td>
<td>Advanced Biofuels</td>
<td>Sugar cane ethanol, renewable heating oil, biogas, ...</td>
<td>50%</td>
</tr>
<tr>
<td>D6 RIN</td>
<td>Renewable Fuel</td>
<td>Corn ethanol, ...</td>
<td>20%</td>
</tr>
<tr>
<td>D7 RIN</td>
<td>Cellulosic Diesel</td>
<td>Cellulosic diesel</td>
<td>60%</td>
</tr>
</tbody>
</table>

2013 Policy Developments for Advanced Biofuels
Graham Noyes, Advanced Biofuel Leadership Conference, October 11, 2013

RIN Separation

Complicated rules but RINs can be separated from actual liquid volumes
- RINs are “created” by the blender but...
- The obligation to utilize renewable fuels is carried by the refiner

RINs are separated...
- When fuel reaches obligated party
- Upon export
- When blended to produce a transportation fuel, heating oil or jet fuel
- When neat fuel is designated as or used without further blending as transportation fuel, heating oil, or jet fuel
- Upward delegation
  - RIN separated from “wet” fuel and sold separately on open market
  - Fuel sold with statement “No assigned RINs transferred”
  - Can be used by registered small blender doing less than 125,000 gal/yr renewable fuel
Typical Elemental Analyses: Fossil Fuels, Biomass, & Biofuels
1st Generation & Advanced Biofuels

1st Generation Biofuels

Ethanol
- Typically derived from fermentation of sugars & starches
  - US: Corn starch
  - Brazil: Sugar cane juice

Biodiesel – FAME (Fatty Acid Methyl Ester)
- From fats and oils
  - US: Soybean oil
  - Europe: Rapeseed oil

2nd Generation & Beyond

Cellulosic/Lignocellulosic Ethanol
- Biochemical pathway
  - Utilize sugars from cellulose & hemicellulose
- Thermochemical pathway
  - Utilize all carbon, including lignin

Butanol
- More compatible to petroleum-derived gasoline
- From fermentation (BP/DuPont)
- Gasification & catalytic synthesis

Green/Renewable Diesel/Gasoline
- Hydrocarbon, just like petroleum-derived fuels
- Hydroprocessed fats & oils
  - Integrated into existing refineries?
- Gasification & FT synthesis
  - Excellent diesel but poor gasoline
- Pyrolysis & chemical upgrading
KiOR process used a fluidized bed catalytic cracking unit to convert biomass into petroleum-like gasoline, diesel, & residual fuel oil

- Demonstration plant in Columbus, MS
  - 500 bone dry ton/day wood chips
  - 15 bpd liquid products – 13 MMgal/yr
- Next commercial facility was to have been in Natchez, MS – 1,500 bone dry ton/day feedstock

http://www.kior.com
Image: http://www.kior.com/content/?s=11&t=Technology
# Biodiesel – Fats & Oils

<table>
<thead>
<tr>
<th>Fatty Acid Fat or Oil</th>
<th>C8:0</th>
<th>C10:0</th>
<th>C12:0</th>
<th>C14:0</th>
<th>C16:0</th>
<th>C16:1</th>
<th>C18:0</th>
<th>C18:1</th>
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<th>C18:3</th>
<th>C20:0</th>
<th>C20:1</th>
<th>C22:0</th>
<th>C22:1</th>
<th>Other</th>
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<td>23</td>
<td>1</td>
<td>10</td>
<td>50</td>
<td>15</td>
<td>0.4</td>
<td>0.3</td>
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<tr>
<td>Tallow</td>
<td>2</td>
<td>2-3</td>
<td>25-30</td>
<td>21-26</td>
<td>39-42</td>
<td>39-42</td>
<td>41-51</td>
<td>4-22</td>
<td>2</td>
<td>42</td>
<td>2</td>
<td>2</td>
<td>42</td>
<td>4-22</td>
<td>2</td>
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<tr>
<td>Lard</td>
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<td>1</td>
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<td>12-16</td>
<td>42-51</td>
<td>4-22</td>
<td>42</td>
<td>2-5</td>
<td>12-16</td>
<td>25-30</td>
<td>2-5</td>
<td>12-16</td>
<td>4-22</td>
<td>42-51</td>
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<td>Coconut</td>
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<td>4-10</td>
<td>44-51</td>
<td>13-18</td>
<td>7-10</td>
<td>1-4</td>
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<tr>
<td>Palm Kernal</td>
<td>2-4</td>
<td>3-7</td>
<td>45-52</td>
<td>14-19</td>
<td>6-9</td>
<td>0-1</td>
<td>1-3</td>
<td>10-18</td>
<td>1-2</td>
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<td>16-2</td>
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<td>76-3</td>
<td>16-2</td>
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<td>Peanut</td>
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<td>3-6</td>
<td>39-66</td>
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<td>5-10</td>
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<td>Corn</td>
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<td>1-4</td>
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<td>34-56</td>
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<td>0-2</td>
<td>0-2</td>
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<td>0-2</td>
<td>0-2</td>
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<td>Soybean</td>
<td>0.3</td>
<td>7-11</td>
<td>0-1</td>
<td>3-6</td>
<td>22-34</td>
<td>60-60</td>
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<td>Tung</td>
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<td>8-15</td>
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</tbody>
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Picture of molecule from:
“Hydrotreating in the production of green diesel”
R. Egeberg, N. Michaelsen, L. Skyum, & P. Zeuthen
*Journal of Petroleum Technology, 2nd Quarter 2010*
## Biodiesel Production Example

### Oleic Fatty Acid (18:1)

<table>
<thead>
<tr>
<th></th>
<th>Oil</th>
<th>Methanol</th>
<th>Glycerin</th>
<th>FAME</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$\text{C}<em>3\text{H}<em>5\text{-(OOC-C}</em>{17}\text{H}</em>{33})_3$</td>
<td>$\text{CH}_3\text{OH}$</td>
<td>$\text{C}_3\text{H}_5\text{(OH)}_3$</td>
<td>$\text{CH}<em>3\text{-OOC-C}</em>{17}\text{H}_{33}$</td>
</tr>
<tr>
<td><strong>Molar Mass</strong></td>
<td>885.4</td>
<td>32.0</td>
<td>92.1</td>
<td>296.5</td>
</tr>
<tr>
<td><strong>wt% C</strong></td>
<td>77%</td>
<td>37%</td>
<td>39%</td>
<td>77%</td>
</tr>
<tr>
<td><strong>wt% H</strong></td>
<td>12%</td>
<td>13%</td>
<td>9%</td>
<td>12%</td>
</tr>
<tr>
<td><strong>wt% O</strong></td>
<td>11%</td>
<td>50%</td>
<td>52%</td>
<td>11%</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>0.92</td>
<td>0.80</td>
<td>1.26</td>
<td>0.90</td>
</tr>
<tr>
<td><strong>Stoichiometric Coefficient</strong></td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td><strong>Mass</strong></td>
<td>885.4</td>
<td>96.1</td>
<td>92.1</td>
<td>889.5</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>962.4</td>
<td>120.2</td>
<td>73.1</td>
<td>988.3</td>
</tr>
<tr>
<td><strong>Mass Ratio</strong></td>
<td>1.00</td>
<td>0.11</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Volume Ratio</strong></td>
<td>1.00</td>
<td>0.12</td>
<td>0.08</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Soybean oil cost (August 2015 contract) = $628.75 per tonne → $2.19 per gal @ 0.92 kg/L  
Methanol cost (September 2015) = $366 per tonne → $1.10 per gal @ 332.6 gal/tonne  
Industrial-grade glycerin value (September 2015) = $700 per tonne → $3.34 per gal @ 1.26 kg/L

![Diagram of biodiesel production example](https://teachers.yale.edu/curriculum/viewer/initiative_13.05.03_u)
Algae

Better solar collector than land-based biomass

- Higher solar utilization
  - Lower land use requirements
- Can use brackish water
- Limitation is getting carbon to the organism
  - Co-locate with power plants – use CO2 in flue gas

Biofuels potential

- Kill the algae & harvest natural oils
  - Biodiesel or biocrude feedstock
- Biocatalyst to secrete desired product
  - Like yeast for fermentation
  - Hydrogen production possible

Near-term processing steps

- Cultivation
  - Open ponds
    - Low cost but high potential for contamination
  - Photo bioreactors – flat panel, tubular, column
    - Higher cost but more controlled conditions
- Harvesting
  - High water content of algae
- Oil extraction
  - Intercellular rather than intracellular
    - Usually chemical extraction
## Resource Requirements

![Map of the United States with Arizona highlighted](image)

<table>
<thead>
<tr>
<th></th>
<th>Soybean</th>
<th>Algae*</th>
</tr>
</thead>
<tbody>
<tr>
<td>gal/year</td>
<td>3 billion</td>
<td>3 billion</td>
</tr>
<tr>
<td>gal/acre</td>
<td>48</td>
<td>1200</td>
</tr>
<tr>
<td>Total acres</td>
<td>62.5 million</td>
<td>2.5 million</td>
</tr>
<tr>
<td>Water usage</td>
<td>ND</td>
<td>6 trillion gal/yr</td>
</tr>
<tr>
<td>CO₂ fixed</td>
<td>ND</td>
<td>70 million tons/yr</td>
</tr>
<tr>
<td>Price per gallon</td>
<td>$2.54</td>
<td>&gt;$9-36</td>
</tr>
</tbody>
</table>

* For algae grown in open ponds with productivity of 10 g/M²/day with 15% TAG.

“Algal Feedstock-Based Biofuels: Separating Myth from Reality”
A. Darzins, NREL Power Lunch Lecture Series
February 18, 2009
## Oil Company Interest in Algae

<table>
<thead>
<tr>
<th>Petroleum Company</th>
<th>Partners</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phillips 66</td>
<td>Sapphire Energy</td>
<td>Collect &amp; analyze data from co-processing algae &amp; conventional crude oil</td>
</tr>
<tr>
<td>Chevron</td>
<td>NREL, Solazyme</td>
<td>Biofuel, algae</td>
</tr>
<tr>
<td>ConocoPhillips</td>
<td>Colorado Center for Biorefining &amp; Biofuels (C2B2)</td>
<td>Biofuel - $5 million - 2008</td>
</tr>
<tr>
<td>Eni S.p.A.</td>
<td></td>
<td>Cultivation patent</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>Synthetic Genomics Inc.</td>
<td>Transportation fuels from algae</td>
</tr>
<tr>
<td>Neste Oil Corporation</td>
<td>Massey University, NZ</td>
<td>Tubular photobioreactors - $400,000 - 2008</td>
</tr>
<tr>
<td>Shell (Cellena)</td>
<td>Joint venture, Cellena Group w/ HR BioPetroleum</td>
<td>Biodiesel - 2007</td>
</tr>
</tbody>
</table>
## U.S. Commercial-Scale Cellulosic Ethanol Capacity

<table>
<thead>
<tr>
<th>Company</th>
<th>Project Location</th>
<th>Technology Pathway</th>
<th>Feedstock Category</th>
<th>Capacity [MMGY]</th>
<th>Operational Year [Anticipated]</th>
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</thead>
<tbody>
<tr>
<td>Abengoa</td>
<td>Hugoton, KS</td>
<td>Biochemical</td>
<td>Crop Residues</td>
<td>23</td>
<td>2015 (idled in 2015)</td>
</tr>
<tr>
<td>Ace Ethanol (Sweetwater Energy, Inc.)</td>
<td>Stanley, WI</td>
<td>Biochemical</td>
<td>Corn Kernel Cellulose</td>
<td>3.5</td>
<td>[2017]</td>
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<tr>
<td>Beta Renewables Inc.</td>
<td>Clinton, NC</td>
<td>Biochemical</td>
<td>Dedicated Energy Crops</td>
<td>20</td>
<td>[2017]</td>
</tr>
<tr>
<td>Canergy</td>
<td>Brawley, CA</td>
<td>Biochemical</td>
<td>Dedicated Energy Crops</td>
<td>25</td>
<td>[2017]</td>
</tr>
<tr>
<td>DuPont</td>
<td>Nevada, IA</td>
<td>Biochemical</td>
<td>Crop Residues</td>
<td>30</td>
<td>2015</td>
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<tr>
<td>Enerkom</td>
<td>Pontotoc, MS</td>
<td>Thermochemical Gasification</td>
<td>Municipal solid waste (MSW)</td>
<td>10</td>
<td>[2020]</td>
</tr>
<tr>
<td>Front Range Energy (Sweetwater Energy Inc.)</td>
<td>Windsor, CO</td>
<td>Biochemical</td>
<td>Cellulosic Sugars</td>
<td>3.6</td>
<td>[2017]</td>
</tr>
<tr>
<td>INEOS New Planet Bioenergy LLC*</td>
<td>Vero Beach, FL</td>
<td>Hybrid Biochemical/Thermochemical</td>
<td>MSW</td>
<td>8</td>
<td>[2016]</td>
</tr>
<tr>
<td>Pacific Ethanol (Sweetwater Energy Inc.)</td>
<td>Madera, CA</td>
<td>Biochemical</td>
<td>Corn Kernel Cellulose</td>
<td>3.6</td>
<td>[2017]</td>
</tr>
<tr>
<td>POET</td>
<td>Emmetsburg, IA</td>
<td>Biochemical</td>
<td>Crop Residues</td>
<td>25</td>
<td>2015</td>
</tr>
<tr>
<td>Quad County Corn</td>
<td>Galva, IA</td>
<td>Biochemical</td>
<td>Corn Kernel Cellulose</td>
<td>3.8</td>
<td>2014</td>
</tr>
<tr>
<td>ZeaChem</td>
<td>Boardman, OR</td>
<td>Biochemical</td>
<td>Woody Biomass</td>
<td>22</td>
<td>[2017]</td>
</tr>
</tbody>
</table>

*INEOS became operational in 2012 but was idled in 2015 while working on mechanical improvements and was expected to resume operations in 2016.

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2015 Survey of Non-Starch Ethanol and Renewable Hydrocarbon Biofuels Producers
Schwab, Warner, & Lewis