

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
- American Energy Independence & Security Act 2007
 - Renewable Fuel Standards
 - Difference between 1st generation & advanced biofuels
- GHG Emissions Control
 - EPA CO2 Endangerment Finding
 - Carbon Capture & Storage

Supply & Demand

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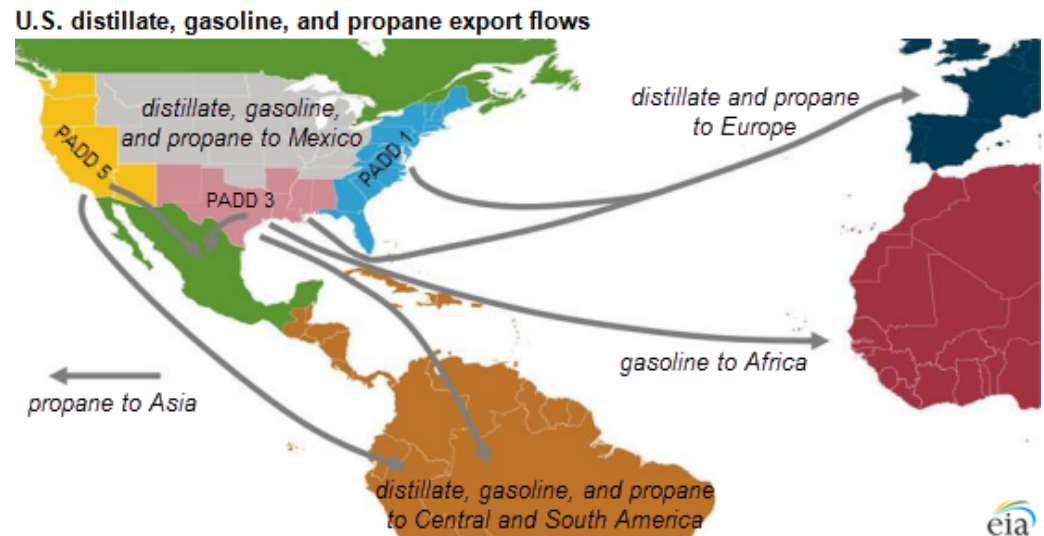
Worldwide trade of refined products

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/

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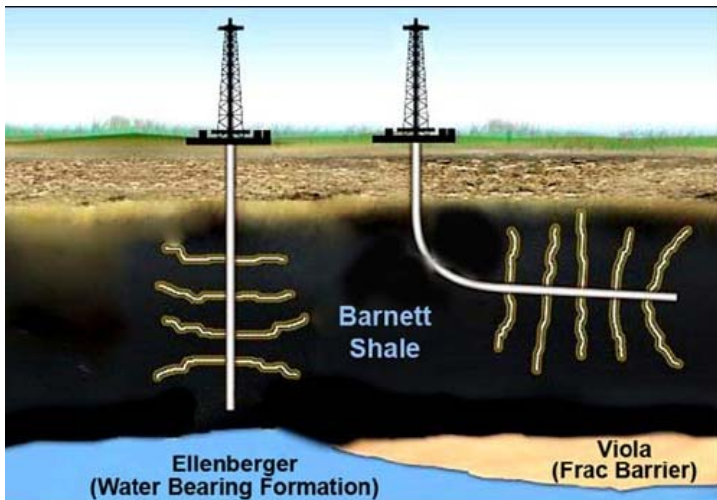
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Tight Oil from Shale Formations

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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Source: U.S. Energy Information Administration based on data from various published studies. Canada and Mexico plays from ARI. Updated: May 9, 2011

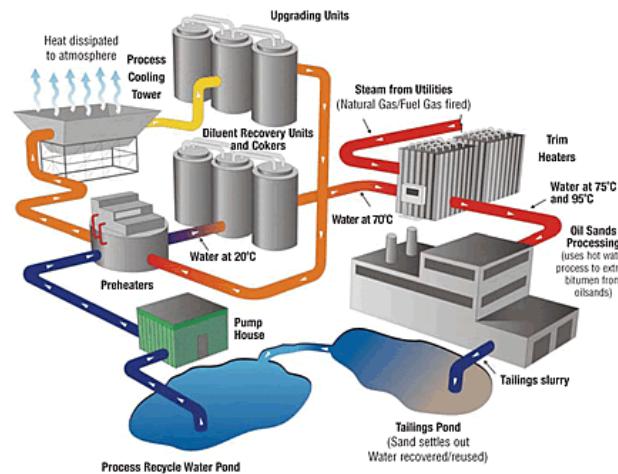
http://www.eia.gov/oil_gas/rpd/northamer_gas.jpg

<http://www.horizontaldrilling.org/>

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



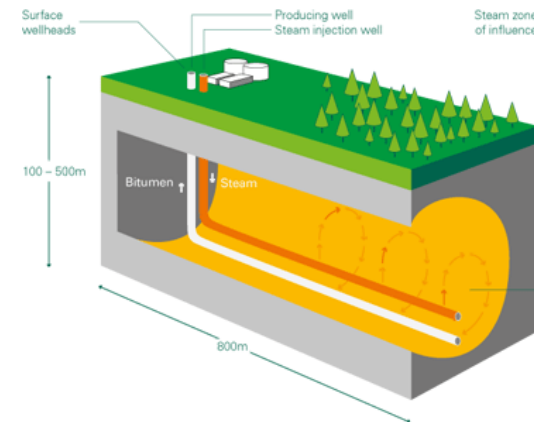
<http://newenergyandfuel.com/http://newenergyandfuel.com/2009/08/12/making-syncrude/>

Canada oil sands areas



Source: Government of Alberta Energy

<http://www.ogi.com/unconventional-resources/oil-sands.html>



<http://www.bp.com/sectiongenericarticle.do?categoryId=9036694&contentId=7067647>

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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 bbl¹

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

¹ http://www.carbontracker.org/site/wp-content/uploads/2014/08/CTI_Oil_Gas_Majors_Company_Factsheets_August_2014_FULL.pdf

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



<http://www.washingtonpost.com/wp-srv/special/nation/keystone-xl-map/>

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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



<http://www.cpr.ca/en/ship-with-cp/where-you-can-ship/bakken-shale/Documents/bakken.pdf>

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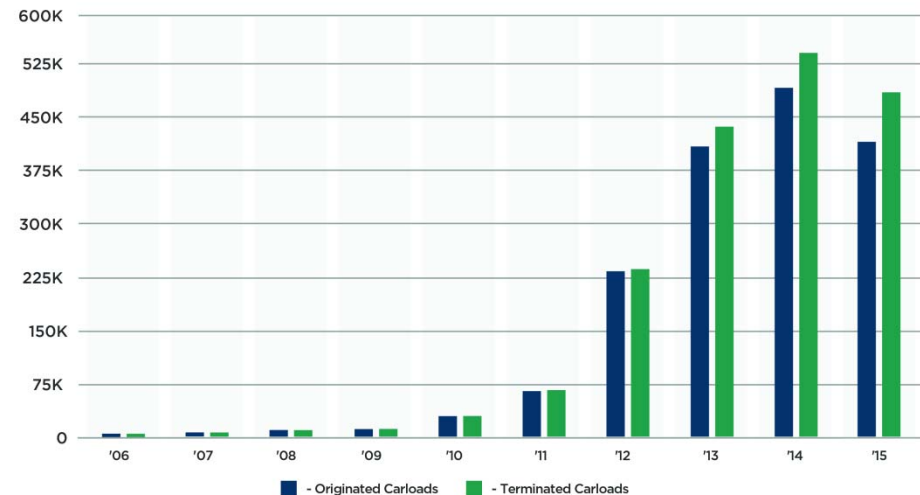
Transportation by Rail in U.S.



<https://www.aar.org/keyissues/Documents/Background-Papers/Crude-oil-by-rail.pdf>

CRUDE OIL BY RAIL

Originations vs. Terminations, 2006-2015



America's freight railroads are supporting the nation's energy renaissance by moving domestic energy resources such as crude oil. In fact, rail shipments of crude oil have skyrocketed in recent years with railroads originating 410,249 carloads in 2015. In light of increased volumes of crude oil moving by rail, freight railroads have implemented new operational protocols and advocated for stronger tank car design standards, while federal regulators have issued new regulations to help ensure this important commodity is moved safely.

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

Each rail car holds about 30,000 gal (714 bbls)

New rules:

<http://www.pennenergy.com/articles/pennenergy/2015/05/oil-and-gas-transportation-us-canada-unveil-rules-to-boost-oil-train-safety.html?cmpid=EnlDailyPetroMay42015>
http://www.downstreambusiness.com/global-refining-petrochemicals-fuels-processing/US-DOT-Issues-Final-Crude-Ethanol-Tank-Car-Rule_141353

Picture: http://www.nytimes.com/2015/05/02/business/energy-environment/us-sets-new-rules-for-oil-shipments-by-rail.html?_r=0

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Alternate Pipeline Projects

450 Mbpd Dakota Access line to open Q4 2016

- Will allow flow of Bakken oil to gulf coast
- Will disrupt flow of this oil to east & west coasts by rail
- Multiple owners, including Phillips 66, Marathon Petroleum, & Enbridge Energy Partners
- Reinstated January 2017

Dakota pipeline to speed crude to U.S. Gulf

The Dakota Access Pipeline, scheduled to open in the fourth quarter, will make it easier for producers to move barrels of oil to the refining-heavy U.S. Gulf Coast.



Sources: EIA; Kinder Morgan; Energy Transfer Crude Oil Company; Tallgrass Energy

C. Chan, 11/08/2016

Other major existing oil pipelines

REUTERS

<http://www.hydrocarbonprocessing.com/news/2016/08/big-dakota-pipeline-to-give-gulf-coast-refiners-another-option-for-crude-supply>

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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.

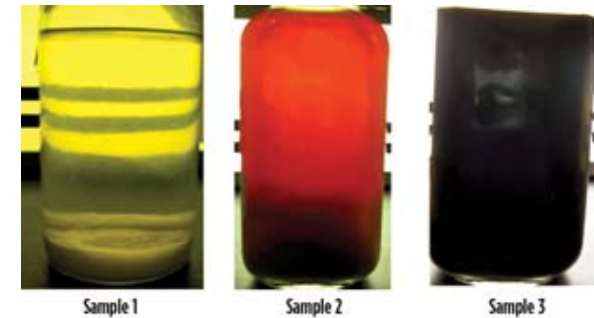
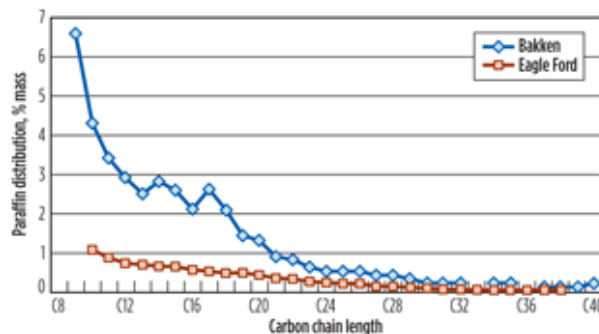


TABLE 2. Physical properties of Eagle Ford shale oil samples

Parameter	Yellow	Red	Black
API	55	44.6	52.3
TAN, g KOH/g	< 0.05	0.07	< 0.05
Sulfur, wt%	< 0.2	< 0.2	< 0.2
Na, ppm	1	1.6	1.6
K, ppm	0.3	0.4	0.5
Mg, ppm	3.4	2.9	3
Ca, ppm	2.6	2.8	3.8
Asphaltenes, wt%	0	0	0.1
Resin, wt%	0.5	3.2	1.6
Filterable solids, PTB	176	295	225



Ref: <http://www.hydrocarbonprocessing.com/Article/3223989/Channel/194955/Innovative-solutions-for-processing-shale-oils.html>

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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)

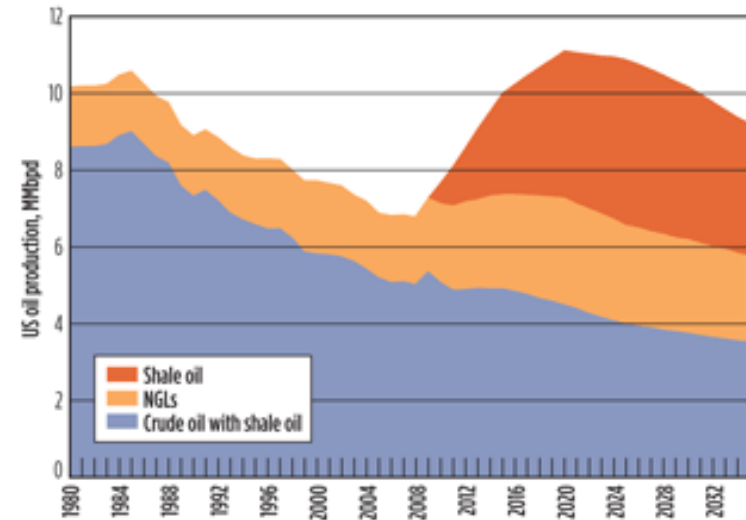
Investments to allow processing of sour crudes might limit the ability to utilize this tight oil

- Exporting tight oil while importing heavy oil is very possible

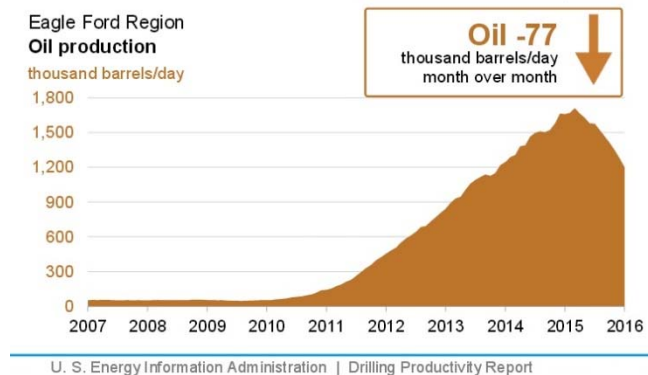
Environmental concerns could put the brakes on this production

- 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



<http://www.hydrocarbonprocessing.com/Article/3223989/Channel/194955/Innovative-solutions-for-processing-shale-oils.html>



"EIA: US shale oil output to fall 116,000 b/d in January," Dec. 7, 2015
<http://www.ogi.com/articles/2015/12/eia-us-shale-oil-output-to-fall-116-000-b-d-in-december.html?cmpid=EnLNGDecember82015&eid=288262897&bid=1251659>

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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

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Modify Existing FCC Refineries

Shift FCC operations to olefin production vs. naphtha

- ZSM-5 addition shifts C_7 - C_{10} molecules to olefinic LPG

Shift LCN production to light olefins

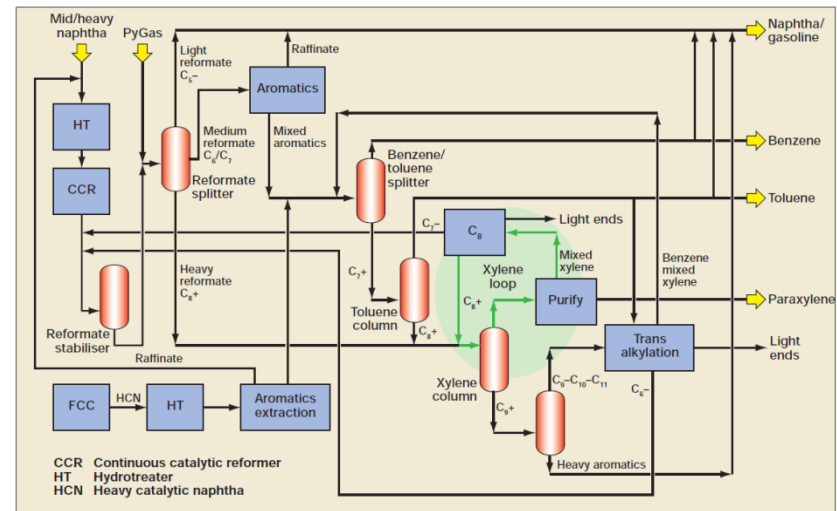
- Send LCN to 2nd FCC riser or to Steam Cracker
 - Steam cracker will produce more olefins but at a very high energy requirement

Convert MCN & HCN to aromatics

- High severity Reformer operations increase aromatic content of reformate
- Use PyGas (pyrolysis gas) from Steam Cracker

Yield comparison of naphtha cracking in FCC units versus steam cracking^{4,5}

Products	FCC, wt%	Steam cracking, wt%
Ethylene	1.5-4.5	25-30.8
Propylene	12-17	17-14
C_4 s	14.4-17	About 12
Naphthas	65.4-51.2	11.3-4.7

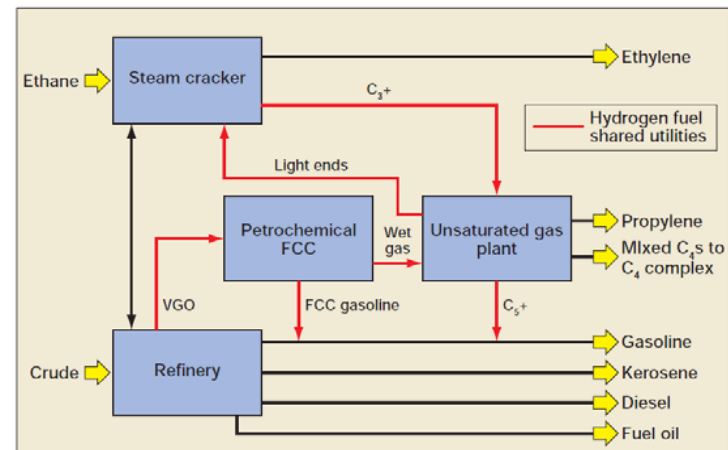


Modify Existing FCC Refineries (cont.)

Processing options for the additional C_4 s

- C_4 s 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)

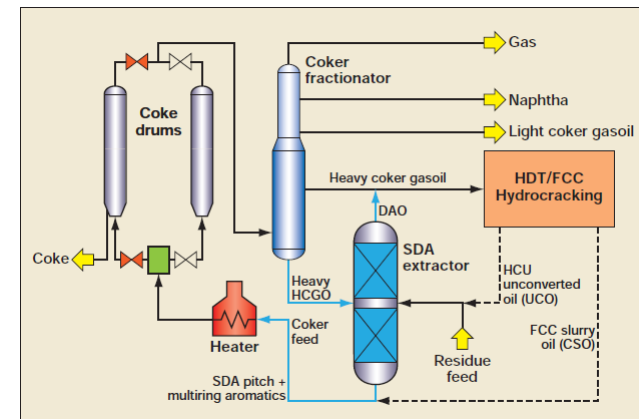
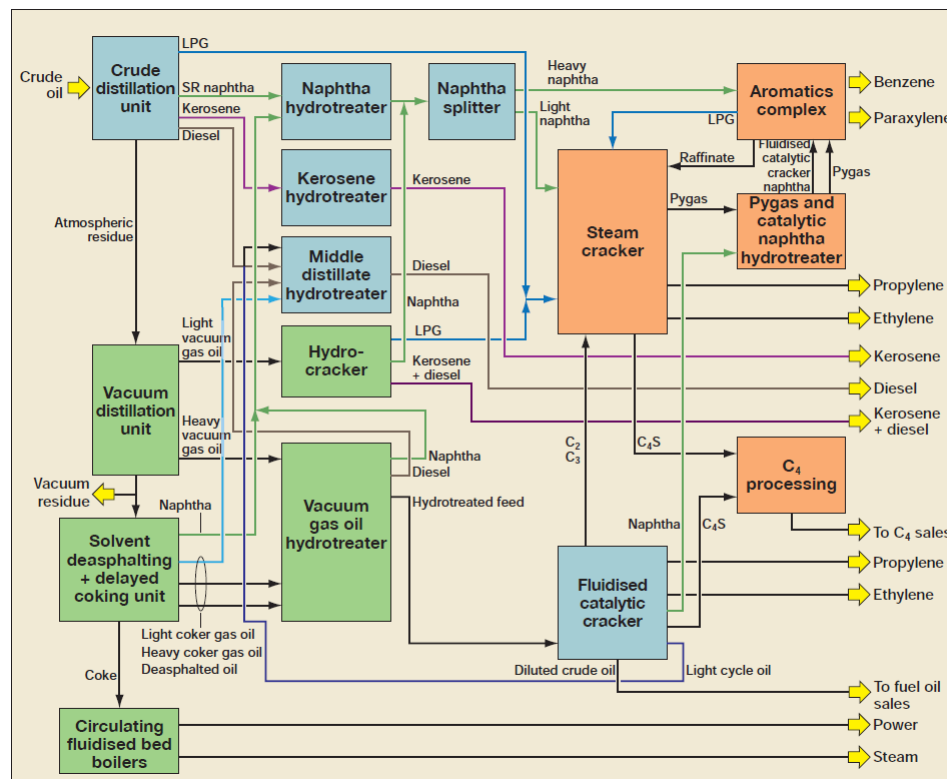
Increase petrochemical production

- 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



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U.S. Government Mandates

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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

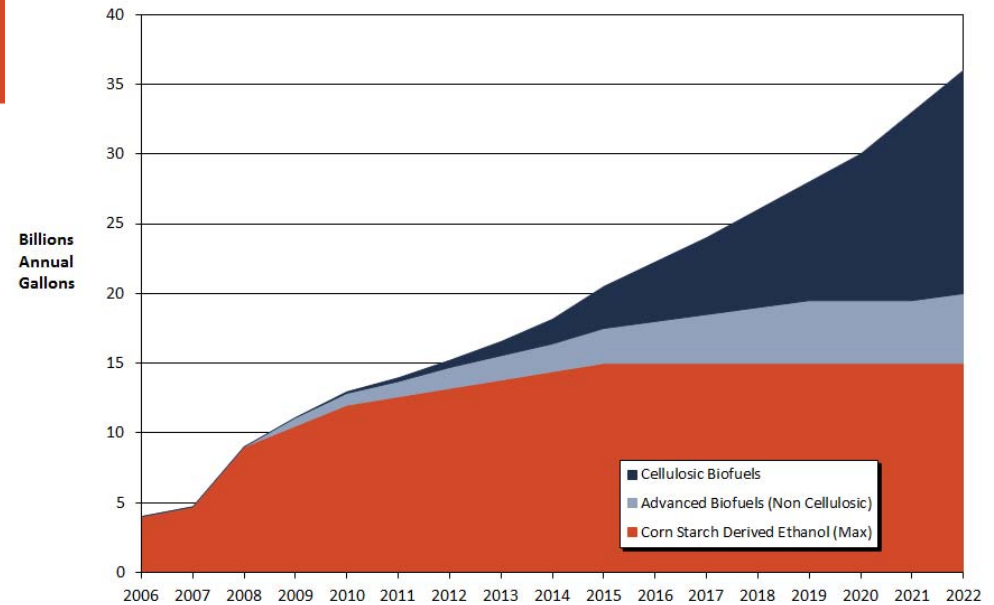
- Increased hydrotreating around the FCC
 - Increased severity in FCC feed pre-treatment
 - Remove sulfur before the olefins are formed
 - Increased H₂ consumption & decreased catalyst cycle length
 - Post treatment of FCC Naphtha
 - Required for ULS Gasoline
 - For refiners with existing post treatment, 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

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2007 Renewable Fuel Standard (RFS2)

Energy Independence & Security Act of 2007				
Year	Renewable Fuel Bgal/yr	Advanced Biofuels Bgal/yr	Cellulosic Biofuel Bgal/yr	RFS - AB Bgal/yr
2006	4.000			4.000
2007	4.700			4.700
2008	9.000			9.000
2009	11.100	0.600		10.500
2010	12.950	0.950	0.100	12.000
2011	13.950	1.350	0.250	12.600
2012	15.200	2.000	0.500	13.200
2013	16.550	2.750	1.000	13.800
2014	18.150	3.750	1.750	14.400
2015	20.500	5.500	3.000	15.000
2016	22.250	7.250	4.250	15.000
2017	24.000	9.000	5.500	15.000
2018	26.000	11.000	7.000	15.000
2019	28.000	13.000	8.500	15.000
2020	30.000	15.000	10.500	15.000
2021	33.000	18.000	13.500	15.000
2022	36.000	21.000	16.000	15.000



Replaced the RFS of the Energy Policy Act of 2005
 Administered by the Environmental Protection Agency
<http://epa.gov/otag/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 allowed biodiesel
- Have started to expand the types of allowable advanced biofuel
- Finalized November 2015, 2014, 2015, & 2016 amounts are lower than Standard – took into account “blend wall” & actual fuel sales.
- **Rules for 2017 lower than standard but higher than expected**

Year	Energy Independence & Security Act of 2007			EPA Clarifications & Adjustments			
	Renewable Fuel Bgal/yr	Advanced Biofuels Bgal/yr	Cellulosic Biofuel Bgal/yr	Renewable Fuel Bgal/yr	Advanced Biofuel Bgal/yr	Cellulosic Biofuel Bgal/yr	Biomass Based Diesel Bgal/yr
2006	4.000						
2007	4.700						
2008	9.000						
2009	11.100	0.600					
2010	12.950	0.950	0.100	12.950	0.950	0.0065	1.150
2011	13.950	1.350	0.250	13.950	1.350	0.0066	0.800
2012	15.200	2.000	0.500	15.200	2.000	0.01045	1.500
2013	16.550	2.750	1.000	16.550	2.750	0.0060	1.280
2014	18.150	3.750	1.750	16.28	2.67	0.033	1.63
2015	20.500	5.500	3.000	16.93	2.88	0.123	1.73
2016	22.250	7.250	4.250	18.11	3.61	0.230	1.90
2017	24.000	9.000	5.500	19.28	4.28	0.311	2.00
2018	26.000	11.000	7.000				2.1
2019	28.000	13.000	8.500				
2020	30.000	15.000	10.500				
2021	33.000	18.000	13.500				
2022	36.000	21.000	16.000				

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/otag/fuels/renewablefuels/regulations.htm>

<http://www2.epa.gov/renewable-fuel-standard-program/final-renewable-fuel-standards-2014-2015-and-2016-and-biomass-based>

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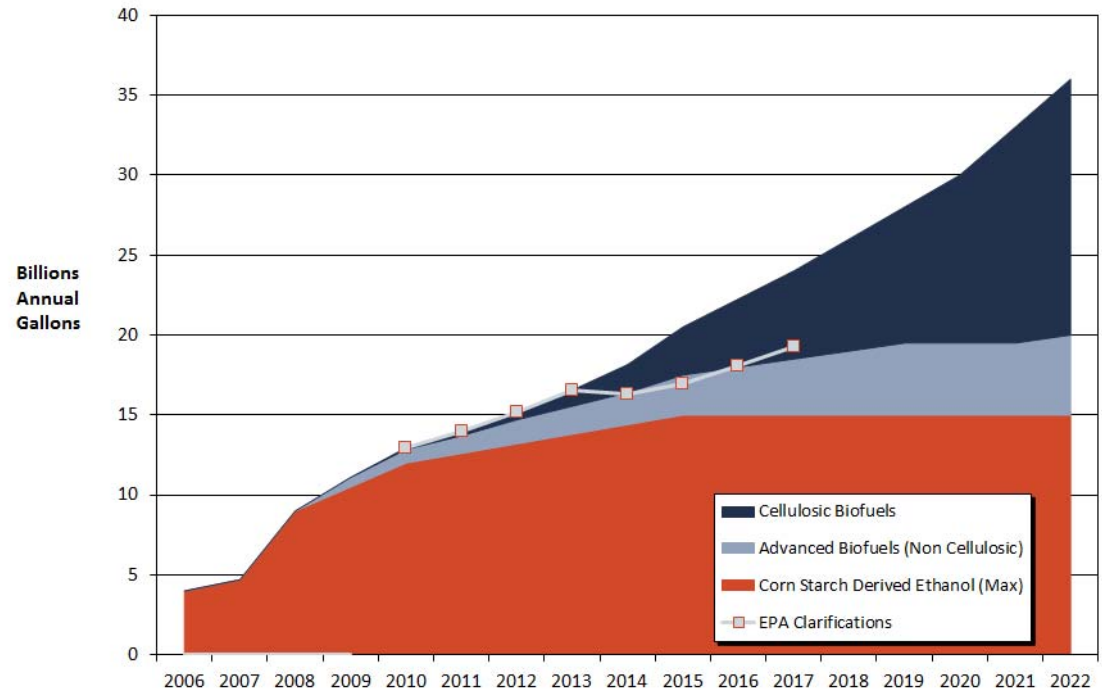
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Refs:

<http://epa.gov/otag/fuels/renewablefuels/regulations.htm>

<http://www2.epa.gov/renewable-fuel-standard-program/final-renewable-fuel-standards-2014-2015-and-2016-and-biomass-based>

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“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

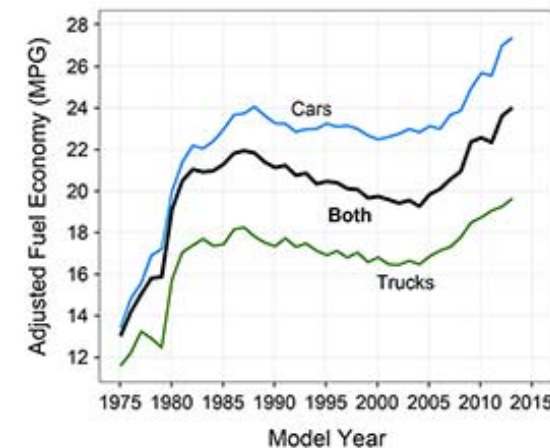
Full amount of renewable fuel will suppress amount of gasoline in the market

- 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

Adjusted Fuel Economy for MY 1975-2013¹



Ref: <http://epa.gov/otaq/fetrends.htm>

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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?

Ref: http://energynation.org/training/module/how-the-rfs-is-harming-the-environment-in-5-clicks/?utm_campaign=rfs&utm_source=smartbrief&utm_medium=email&utm_content=environment

Petroleum Company Renewable Fuels Investments

1st Generation Biofuels

Valero

- Purchased 7 corn dry mills from bankrupt VersaSun, 770 MMgal/yr capacity. Additional purchase in 2014.
- 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

Royal Dutch Shell

- Joint venture with Brazil's Cosan, the world's largest cane sugar & ethanol producer

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

- Synthetic Genomics – algae-derived biofuels. Original agreement 2009; new pact 2013.

Chevron

- Catchlight – Weyerhaeuser joint venture. Essentially no progress since 2010.

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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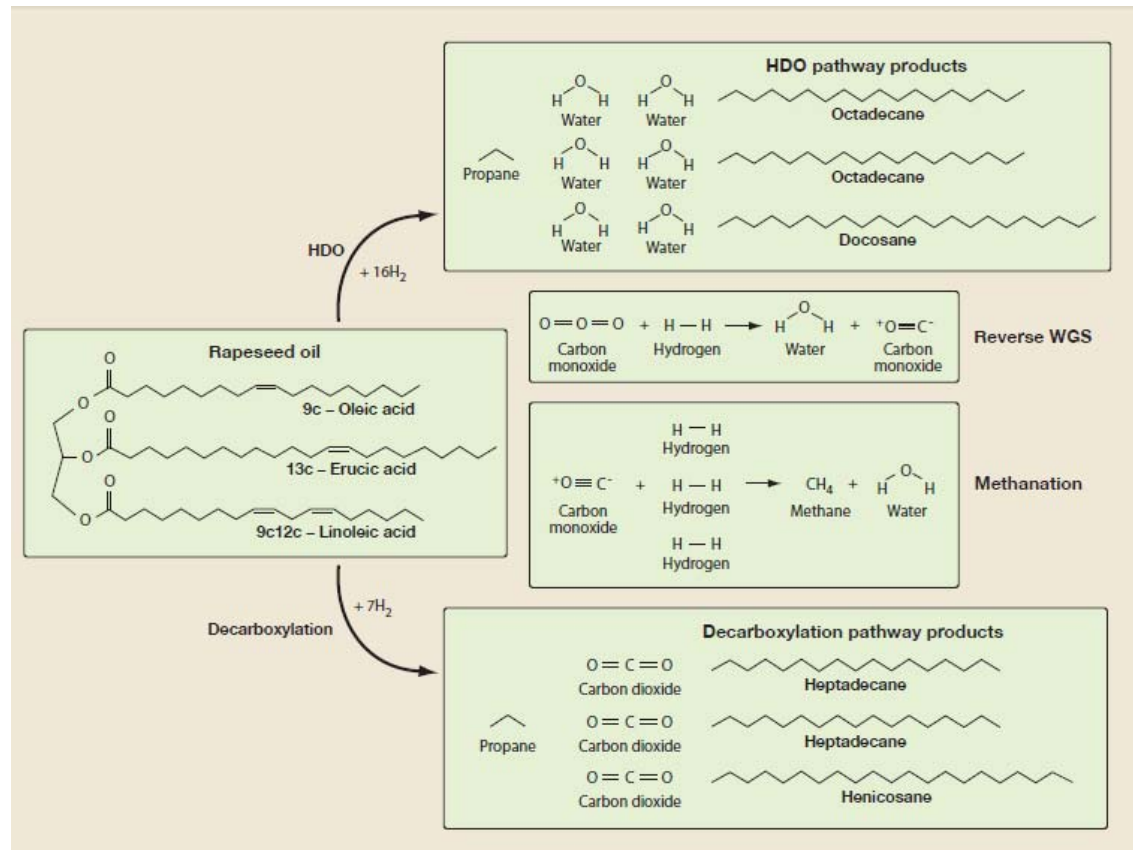
Hydrodeoxygenation of Organic Oils

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 CO_2 to maximize fuel usage of H_2



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

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Green Diesel Production Examples

Oleic Fatty Acid (18:1)					
	Oil	Hydrogen	Water	Propane	Octadecane
Formula	$\text{C}_3\text{H}_5-(\text{OOC}-\text{C}_{17}\text{H}_{33})_3$	H_2	H_2O	C_3H_8	$\text{C}_{18}\text{H}_{38}$
Molar Mass	885.4	2.0	18.0	44.1	254.5
%C	77%	0%	0%	82%	85%
%H	12%	100%	11%	18%	15%
%O	11%	0%	89%	0%	0%
Density (g/cm^3)	0.92		1.00	0.51	0.78
Stoichiometric Coefficient	1	15	6	1	3
Mass	885.4	30.2	108.1	44.1	763.5
Volume (Liquid)	962.4		108.1	86.5	978.8
Mass Ratio	1.00	0.03	0.12	0.05	0.86
Volume Ratio	1.00		0.11	0.09	1.02
scf/bbl		2,071			

Oleic Fatty Acid (18:1)					
	Oil	Hydrogen	Carbon Dioxide	Propane	Heptadecane
Formula	$\text{C}_3\text{H}_5-(\text{OOC}-\text{C}_{17}\text{H}_{33})_3$	H_2	CO_2	C_3H_8	$\text{C}_{17}\text{H}_{36}$
Molar Mass	885.4	2.0	44.0	44.1	240.5
%C	0%	0%	0%	0%	0%
%H	0%	0%	0%	0%	0%
%O	0%	0%	0%	0%	0%
Density (g/cm^3)	0.92			0.51	0.78
Stoichiometric Coefficient	1	6	3	1	3
Mass	885.4	12.1	132.0	44.1	721.4
Volume (Liquid)	962.4			86.5	924.9
Mass Ratio	1.00	0.01	0.15	0.05	0.81
Volume Ratio	1.00			0.09	0.96
scf/bbl		828			

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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 $\text{CO}_2/\text{CO}/\text{H}_2\text{O}$
- 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

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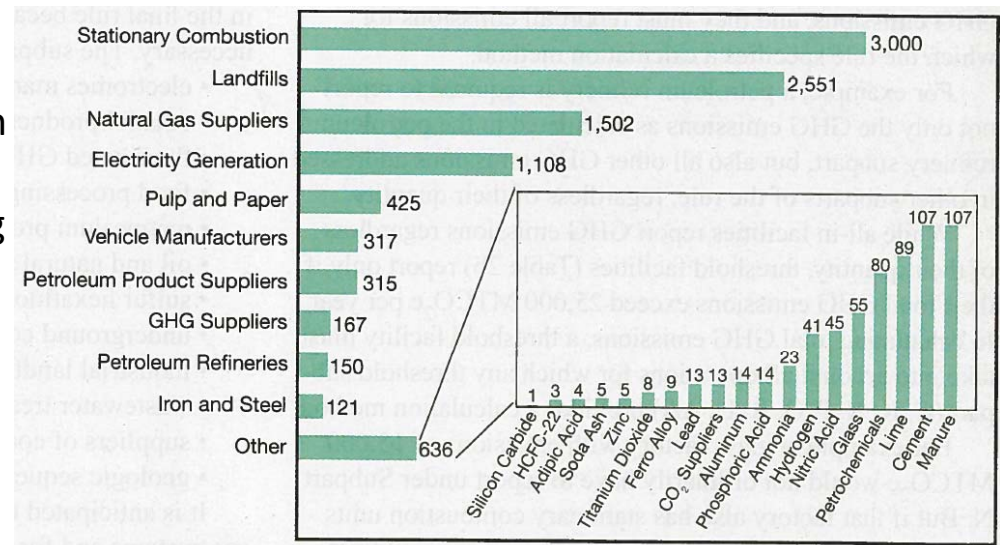
EPA CO₂ Endangerment Finding

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

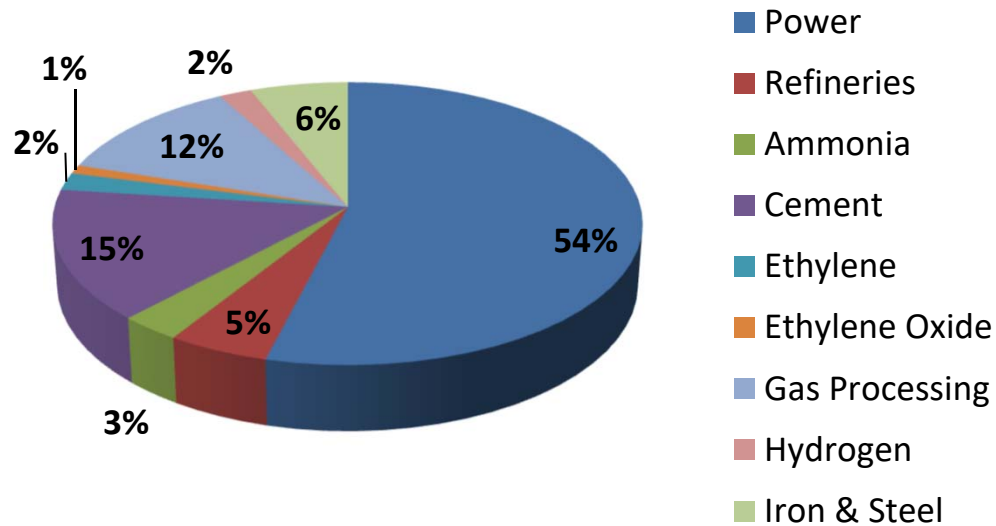
- 25,000 ton/yr CO₂(e) threshold
- Fines for reporting late, ...
 - ExxonMobil fined \$120,000 in July 2013 for late report for Torrance, CA refinery



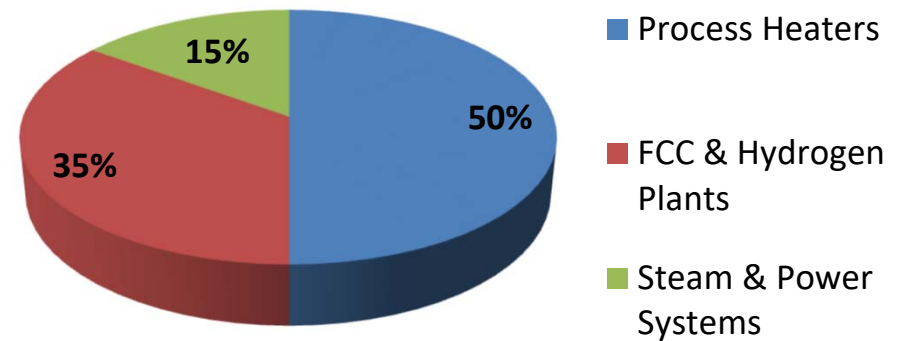
"Submitting your first GHG report"
Baranski & Ternes
Chemical Engineering Progress, March 2010

Industrial & Typical Refinery Emissions

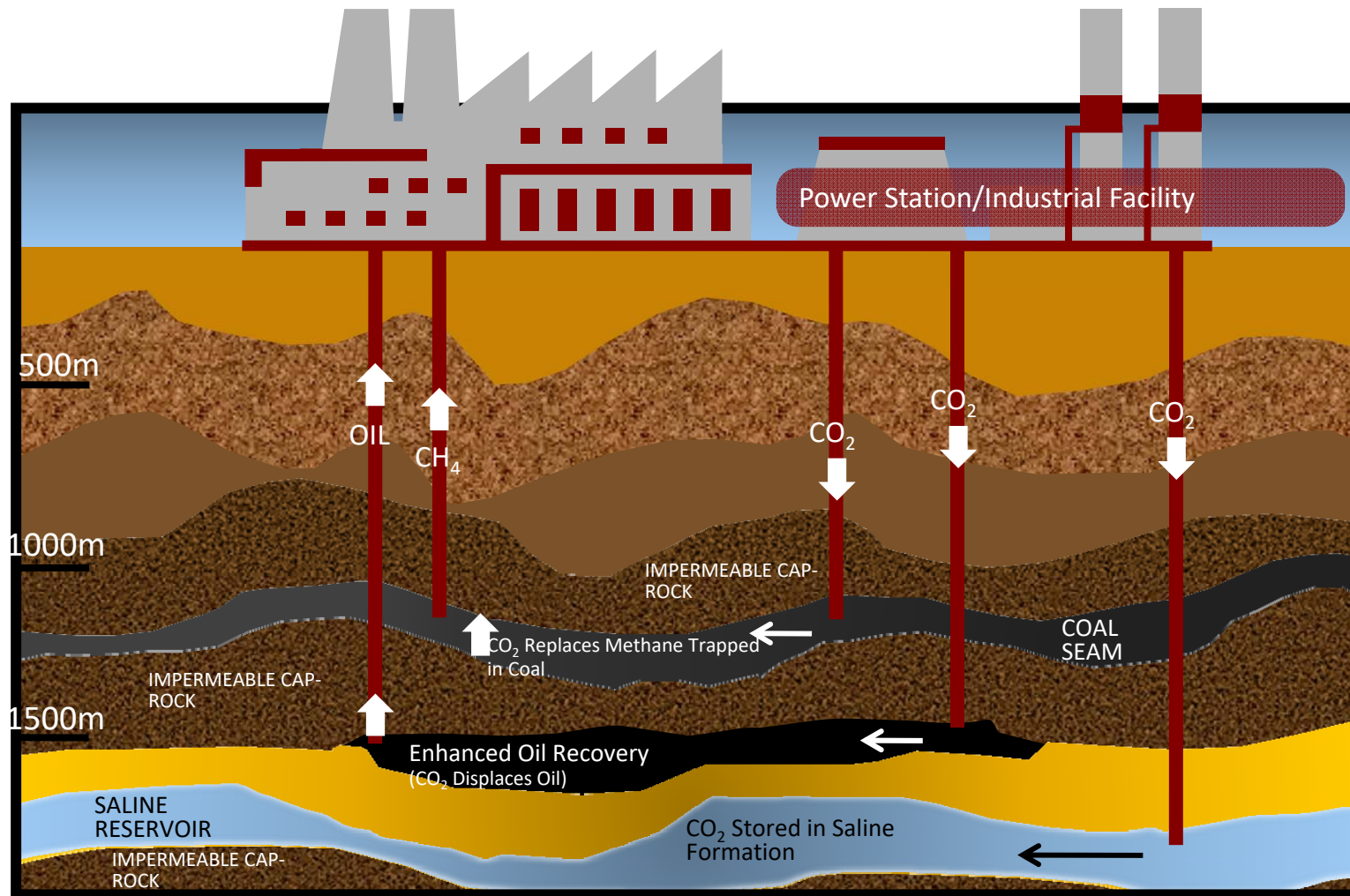
Industrial Emissions



Refinery Emissions



CO₂ Capture & Sequestration



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Carbon Capture & Storage (CCS) Technologies & Issues

	Technology	Issues
CO ₂ Capture	<ul style="list-style-type: none"> • Post-Combustion <ul style="list-style-type: none"> • Add capture to existing facilities • Pre-Combustion <ul style="list-style-type: none"> • Gasify & capture CO₂ prior to final combustion • Oxy-Combustion <ul style="list-style-type: none"> • Burn with O₂ & condense produced water 	<ul style="list-style-type: none"> • High capital cost & energy penalties • 75- 90% of the CCS cost
Transport	<ul style="list-style-type: none"> • Pipelines to final location 	<ul style="list-style-type: none"> • Infrastructure right of ways • Limited by economics of transport distance
Storage / Sequestration	<ul style="list-style-type: none"> • Sub-surface • Land possibilities 	<ul style="list-style-type: none"> • Scientific & operational basis for safe & effective long-term storage • Land & mineral access rights for geologic storage • Long-term liability
Research Focus		<ul style="list-style-type: none"> • Cost & energy penalty reductions

CO₂ Sources & Disposition Options

INDUSTRIAL CO₂ SOURCES

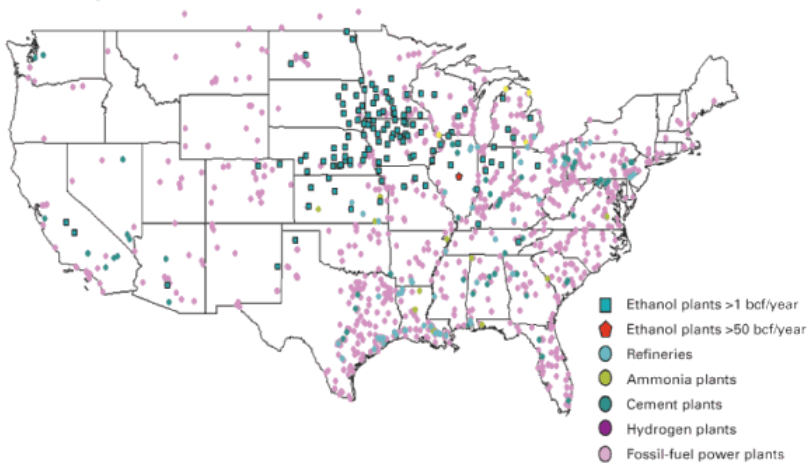


Fig. 2

CANDIDATE US CO₂ EOR FIELDS

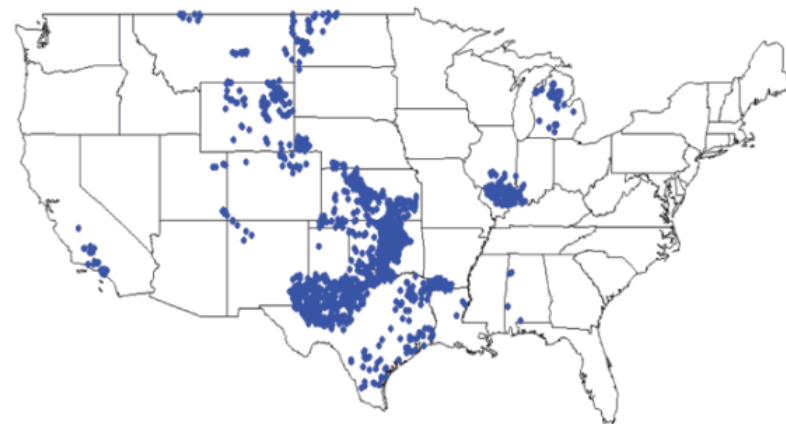
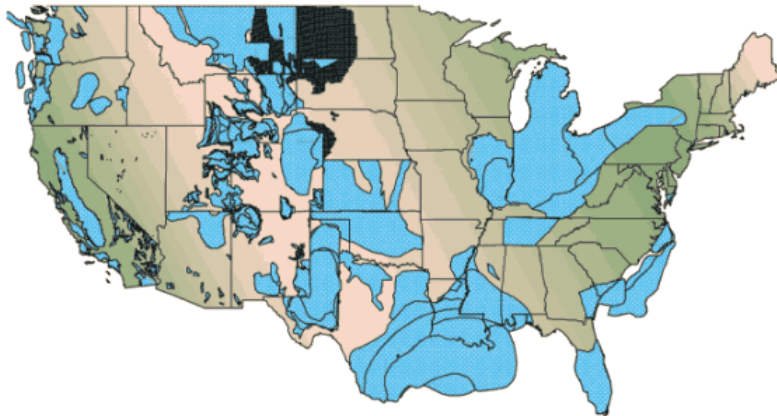


Fig. 8

DEEP SALINE AQUIFERS



Source: NatCarb

Fig. 6

UNMINABLE COAL SEAMS

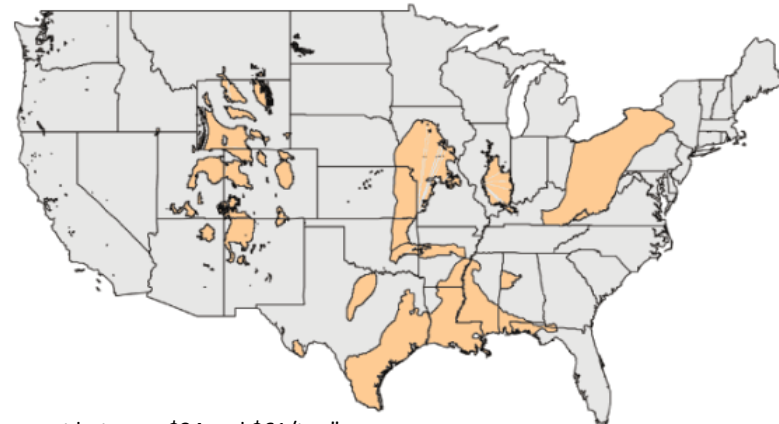


Fig. 9

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

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Summary

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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

Supplemental Slides

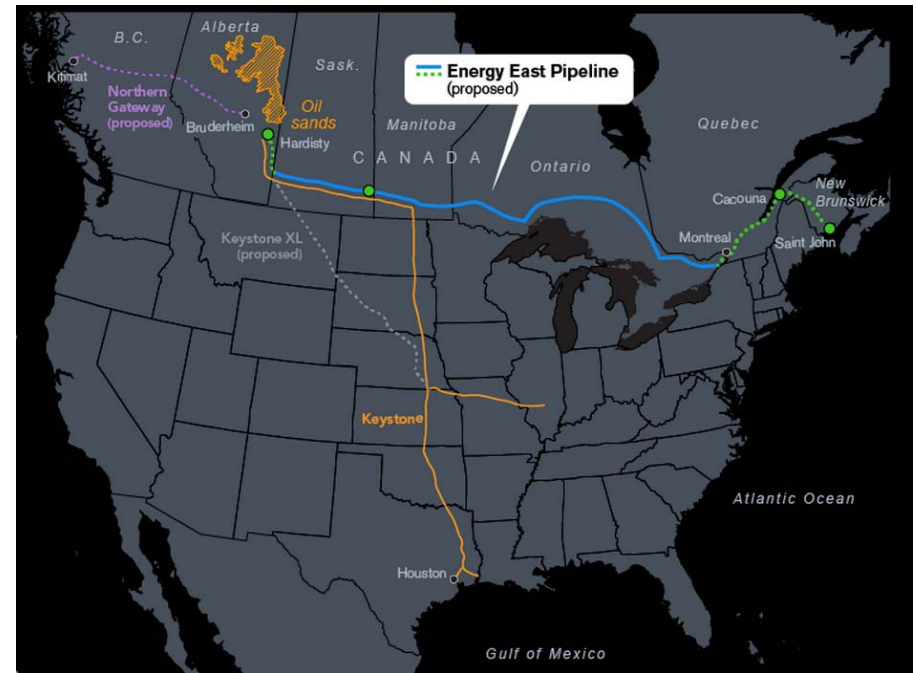
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Alternatives to Keystone XL Pipeline

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

Enbridge's Northern Gateway pipeline opposed by aboriginal groups

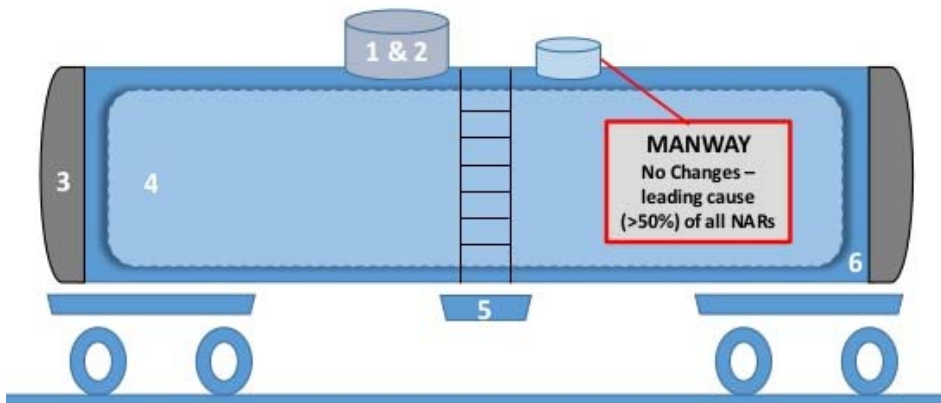


<http://www.bloomberg.com/infographics/2014-10-07/canada-oil-pipeline-to-the-atlantic.html>

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Proposed AAR DOT-111 Railway Tank Car Upgrades



Copyright Parker Hannifin 2014

		Current Standard	Latest Proposal
1	HIGH CAPACITY PRESSURE RELIEF VALVE	No Requirement	Requires a high capacity relief valve protect against a rise in internal pressure resulting from fire and to then quickly release product
2	TOP FITTINGS PROTECTION	Protect integrity of valves and fittings used in loading in event of accident	No change
3	HEAD SHIELDS	½ inch thick/ half height head shields on either end to improve puncture resistance	½ inch thick/ full-height on either end
4	STEEL TANK	½ inch thickness for unjacketed cars 7/16 inch thickness for jacketed cars	Minimum 9/16 inch thick steel tank
5	BOTTOM OUTLET HANDLES	No requirement	Reconfigured to prevent handle from opening outlet valves in event of accident
6	JACKET AND THERMAL PROTECTION	Minimum ½ inch thick steel tank OR 1/8 inch thick steel jacket	Minimum 9/16 inch thick steel tank

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

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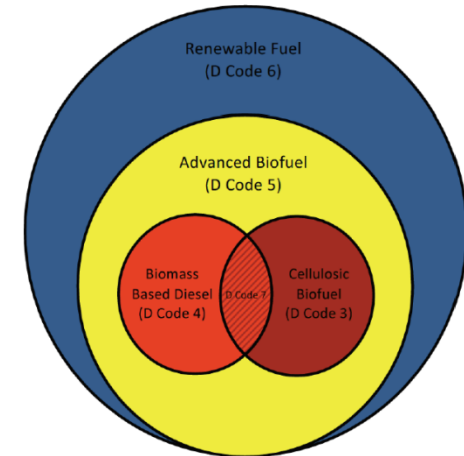
Renewable Identification Number (RIN)

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)



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

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

Ref: http://www.energy.ca.gov/altfuels/notices/2013-01-11_workshop/presentations/04_Shashi_Menon-Ecoengineers.pdf

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RIN Separation

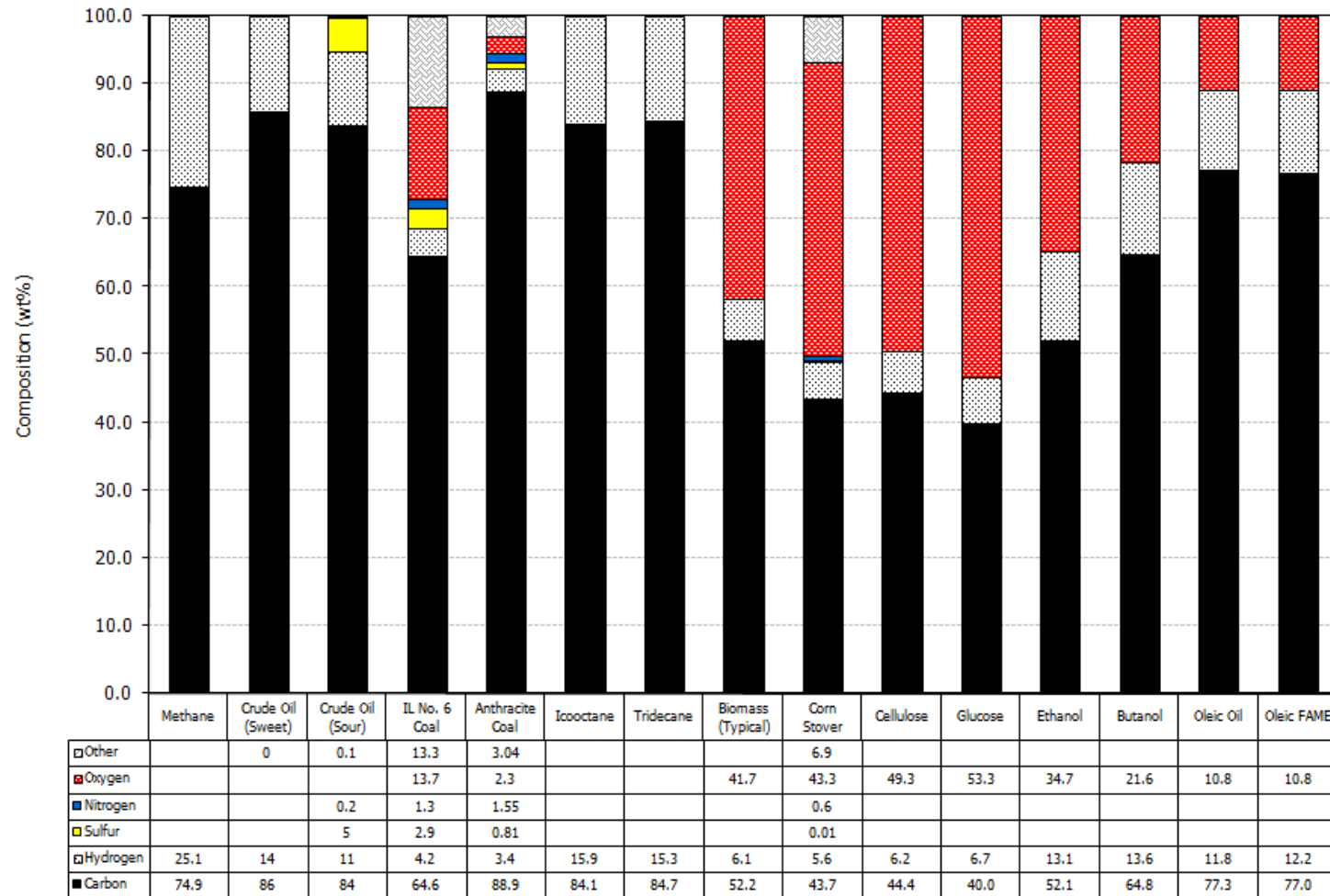
Complicated rules but RINs can be separated from actual liquid volumes

- 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



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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

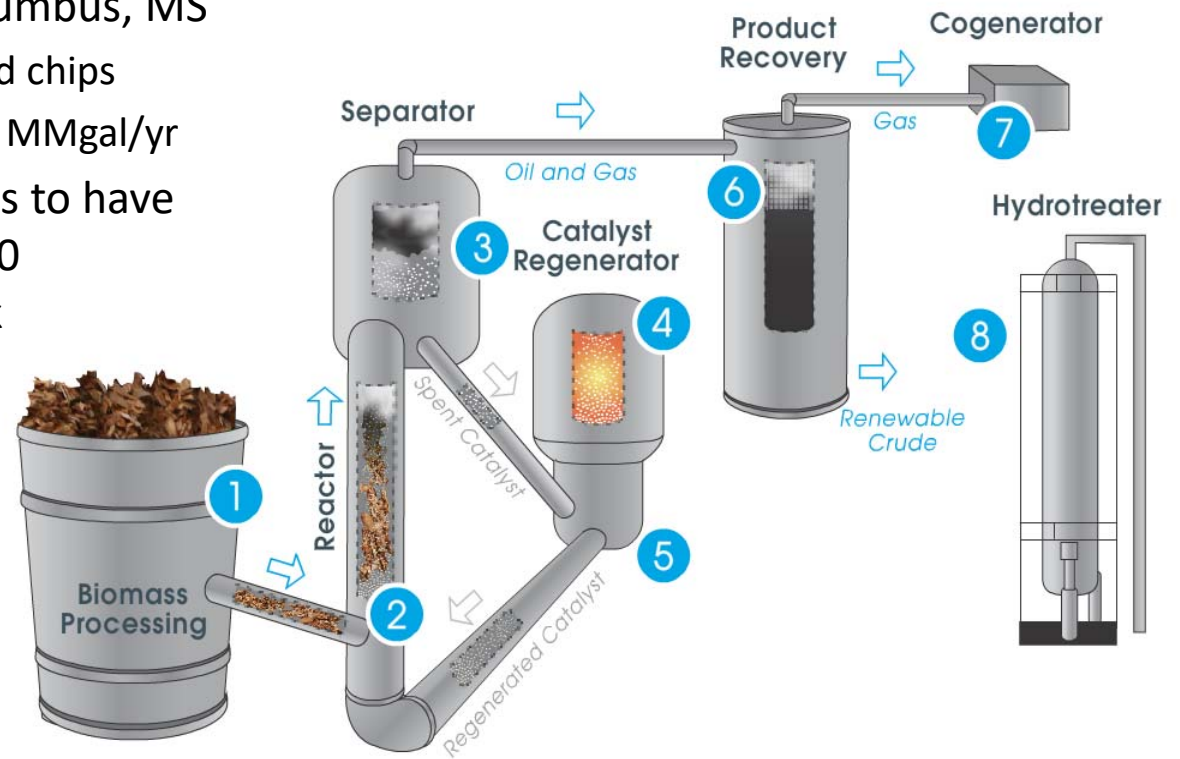
Green/Renewable Diesel/Gasoline

- Hydrocarbon, just like petroleum-derived fuels
- Hydroprocessed fats & oils
 - Integrated into existing refineries?
- Gasification & FT synthesis
 - Excellent diesel but poor gasoline
- Pyrolysis & chemical upgrading

Other conversions analogous to petroleum refining

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>

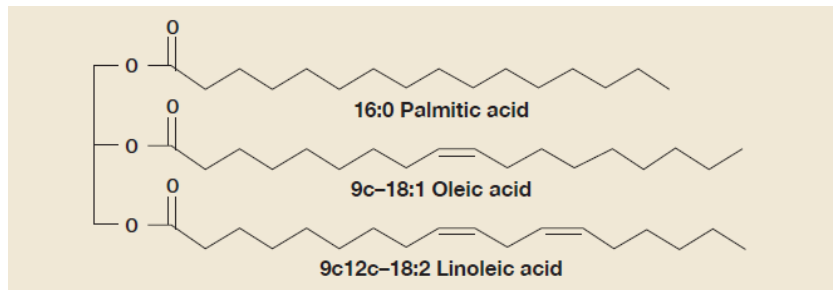
Image: <http://www.kior.com/content/?s=11&t=Technology>

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Biodiesel – Fats & Oils

Fatty Acid Fat or Oil	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0 C22:0	C20:1 C22:1	Other
Yellow Grease	--	--	--	1	23	1	10	50	15				
Tallow	--	--	0.2	2-3	25-30	2-3	21-26	39-42	2	--	0.4-1	0.3	0.5
Lard	--	--	--	1	25-30	2-5	12-16	41-51	4-22	--	-	2-3	0.2
Butter	1-2	2-3	1-4	8-13	25-32	2-5	25-32	22-29	3	--	0.4-2	.2-1.5	1-2
Coconut	5-9	4-10	44-51	13-18	7-10	--	1-4	5-8	1-3	--	--	--	--
Palm Kernal	2-4	3-7	45-52	14-19	6-9	0-1	1-3	10-18	1-2	--	1-2	--	--
Palm	--	--	--	1-6	32-47	--	1-6	40-52	2-11	--	--	--	--
Safflower	--	--	--	--	5.2	--	2.2	76.3	16.2	--	--	--	--
Peanut	--	--	--	0.5	6-11	1-2	3-6	39-66	17-38	--	5-10	--	--
Cottonseed	--	--	--	0-3	17-23	--	1-3	23-41	34-55	--	--	2-3	--
Corn	--	--	--	0-2	8-10	1-2	1-4	30-50	34-56	--	--	0-2	--
Sunflower	--	--	--	--	6.0	--	4.2	18.7	69.3	0.3	1.4	--	--
Soybean	--	--	--	0.3	7-11	0-1	3-6	22-34	50-60	2-10	5-10	--	--
Rapeseed	--	--	--	--	2-5	0.2	1-2	10-15	10-20	5-10	.9	50-60	--
Linseed	--	--	--	0.2	5-9	--	0-1	9-29	8-29	45-67	--	--	--
Tung	--	--	--	--	--	--	--	4-13	8-15	72-88	--	--	--



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)				
	Oil	Methanol	Glycerin	FAME
Formula	$C_3H_5-(OOC-C_{17}H_{33})_3$	CH_3OH	$C_3H_5(OH)_3$	$CH_3-OOC-C_{17}H_{33}$
Molar Mass	885.4	32.0	92.1	296.5
wt% C	77%	37%	39%	77%
wt% H	12%	13%	9%	12%
wt% O	11%	50%	52%	11%
Density (g/cm ³)	0.92	0.80	1.26	0.90
Stoichiometric Coefficient	1	3	1	3
Mass	885.4	96.1	92.1	889.5
Volume	962.4	120.2	73.1	988.3
Mass Ratio	1.00	0.11	0.10	1.00
Volume Ratio	1.00	0.12	0.08	1.03

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

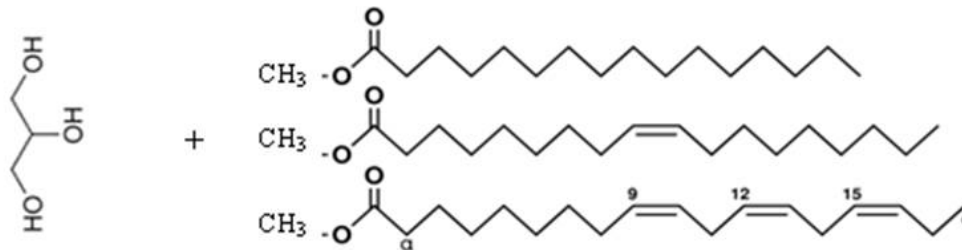


Image: https://teachers.yale.edu/curriculum/viewer/initiative_13.05.03_u

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



	Soybean	Algae*
gal/year	3 billion	3 billion
gal/acre	48	1200
Total acres	62.5 million	2.5 million
Water usage	ND	6 trillion gal/yr
CO ₂ fixed	ND	70 million tons/yr
Price per gallon	\$2.54	>\$9-36

* 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

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

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U.S. Commercial-Scale Cellulosic Ethanol Capacity

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

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

2015 Survey of Non-Starch Ethanol and Renewable Hydrocarbon Biofuels Producers
Schwab, Warner, & Lewis
NREL Technical Report NREL/TP-6A10-65519, January 2016

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