Biofuels: Unlocking the Potential & Opportunities for Catalysis

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UOP LLC

Modern Methods in Heterogeneous Catalysis Research Seminar Series
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- Leading supplier and licensor of process technology, catalysts, adsorbents, process plants, and technical services to the petroleum refining, petrochemical, and gas processing industries
- UOP technology furnishes 60% of the world's gasoline, 85% of the world's biodegradable detergents, and 60% of the world's para-xylene
- Strong relationships with leading refining and petrochemical customers worldwide
- UOP's innovations enabled lead removal from gasoline, biodegradable detergents, and the first commercial catalytic converter for automobiles

2003 US National Medal of Technology Recipient

Agenda

- Potential impact of biofuels
  - Energy supply
- Biofuels issues
  - Sustainability
    - Financial
    - Environmental
    - Social
- Biofuels potential
  - Technologies: Current and Future
  - Road-map to success

Biofuels: A Quickly Changing Landscape

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2007	2008	UOP Position
• All biofuels are good • More, faster • No criteria to measure impact of adopting biofuels • Availability of "inexpensive" bio feedstocks • Government mandates and incentives favor ethanol and biodiesel	• Not all biofuels are good • Measured biofuel adoption • Utilization of LCA analysis to "qualify": link to GHG, energy, sustainability • Bio feedstocks tracking energy prices • Government mandates and incentives increasingly technology neutral • Emphasis on "real" biofuels	• Emphasis on life cycle analysis as a way of measuring "sustainability" • Ensure technology is feedstock flexible • Focus on 2nd generation technologies • Create partnerships between bio-feedstock suppliers and fuel producers

Increasing Awareness of Impact

Macromarket Summary: 2007-2017

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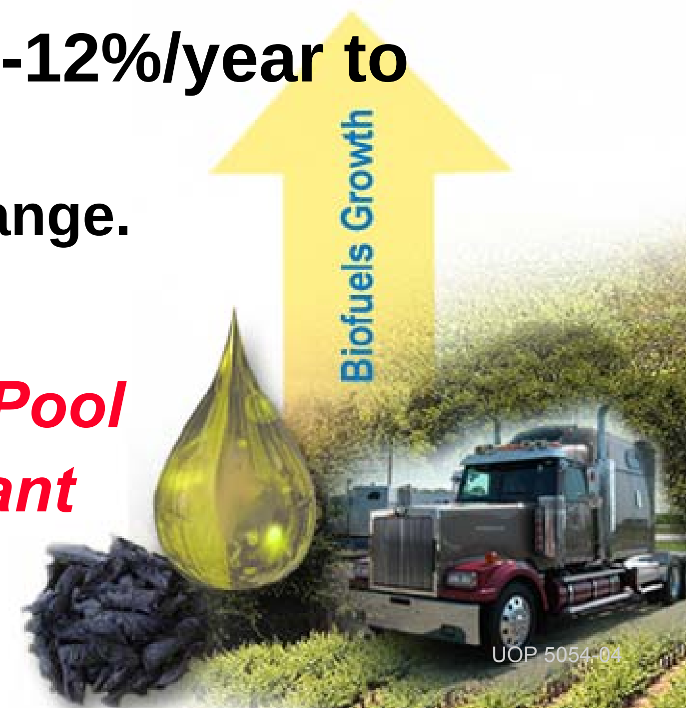
- **Global energy demand is expected to grow at CAGR 2.1%.**
  - **Primary Energy diversity will become increasingly important over this period with coal, natural gas & renewables playing bigger roles.**
- **Fossil fuels are expected to supply 83% of energy and 95% of liquid transportation needs**
- **Biofuels are expected to grow at 8-12%/year to > 3 million BPD**
  - **Main driver is to address climate change.**



Biofuels: only 5% of Global Transport Pool
But at 3 million BPD, not an Insignificant Volume

Source: IEA, 2006

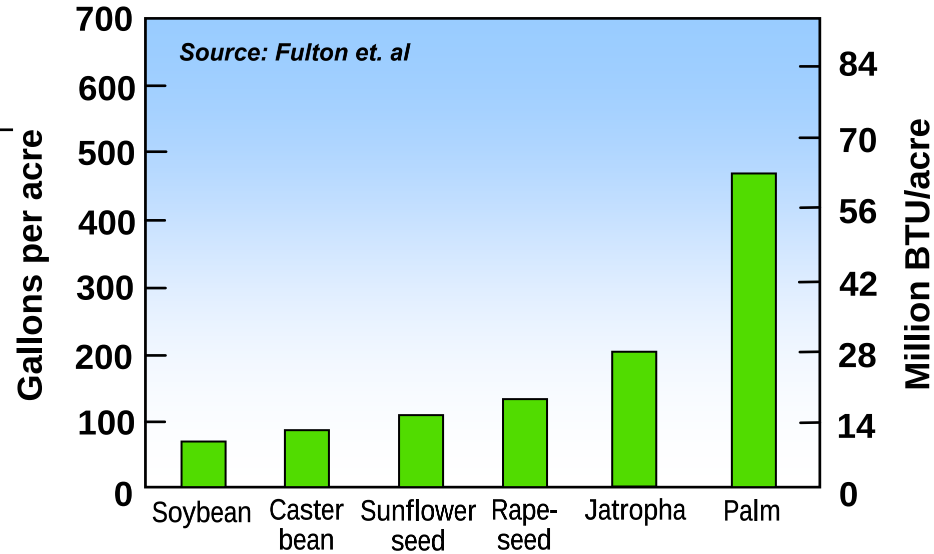
Biofuel Targets

Region	Current	Future
Brazil	25% Ethanol in gasoline 2.0% of diesel by 2008	5.0% of diesel by 2011
China	2.0% of gasoline & diesel by 2010	8.0% by 2020
Europe	5.75%* of gasoline & diesel by 2010	10%* by 2020
India	5.0% Ethanol in gasoline	*E5, B5 by 2012*
USA	*15.2 B* gal 2012	*36 B gal by 2022* *(~20% of transport pool)*

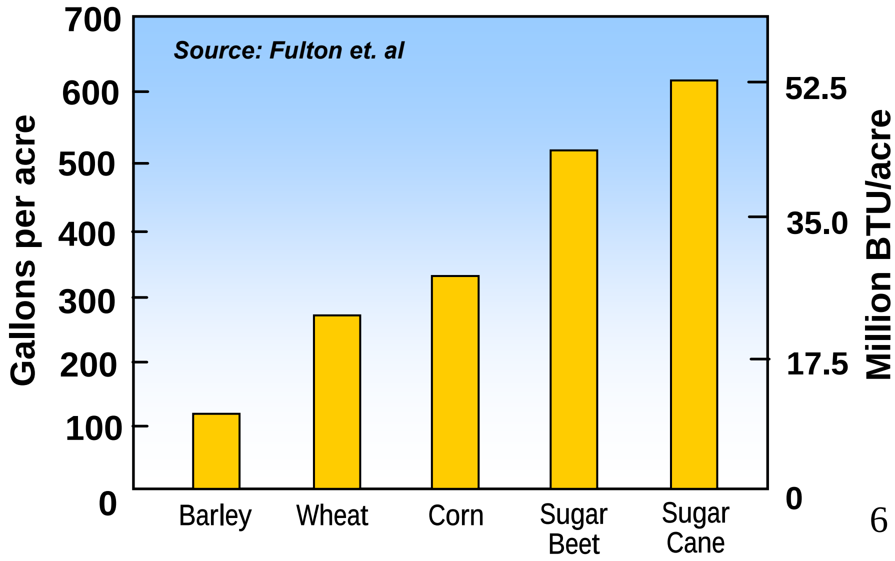
* *Energy content basis*

20% Substitution Equivalent to the Land Mass of ~Germany, Austria, Poland and Czech Republic!!

Biodiesel Production from Oils



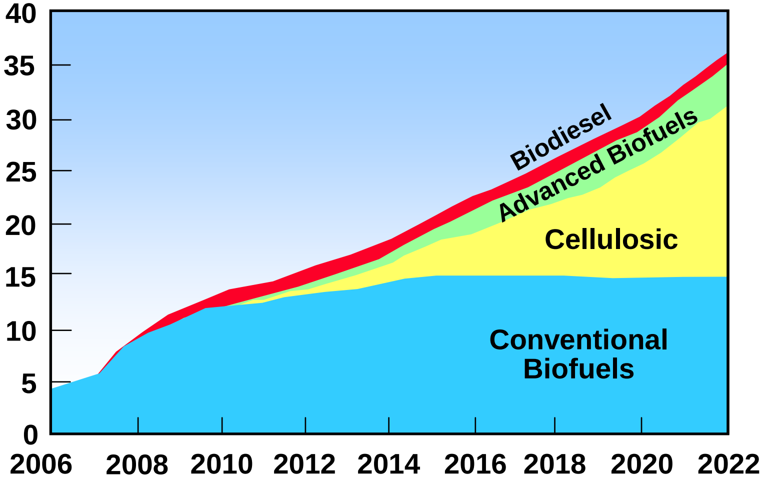
Ethanol Production from Sugars



Global Government Mandates

USA: Energy Independence & Security Act (2007)

Volume and Type of Renewable Fuel Required by the RFS



- 36 billion gallons biofuels , ~2.5M BPD by 2022 (20% of pool!)
- Corn based ethanol, capped at 15 billion gal
- Emphasis on transition to 2nd generation cellulosics
- Requires demonstration of LCA based GHG savings relative to baseline petroleum fuels

Europe: Renewable Energy & Fuel Quality Directives

- 20% of EU Primary Energy Demand from Renewable Sources by 2020
  - Transport Fuels: 10% Renewable Content by energy content
  - GHG Emissions: Fuel producers reduce 10% by 2020 relative to 2010 levels
  - Sustainability targets being put in place

Global

- Countries with B2-B10 and E5-E10 mandates include Canada, Colombia, Peru, Argentina, Thailand, China*, India*. Brazil is E25.
- *Emphasis: non-food

Increasingly Focused on Sustainability and Second Generation Feedstocks

Critical Issues

Food supply: small impact on the fuel market, yet large impact on food supply

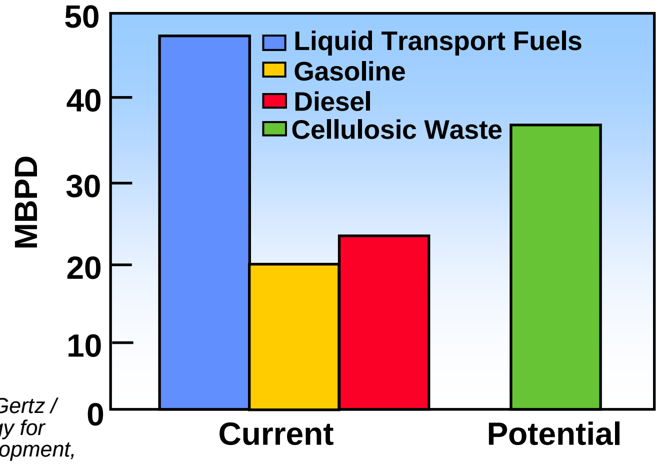
Land and water: competition for land and water resources that are already in high demand

Environmental: loss of biodiversity, soil erosion, nutrient leaching, soil and water pollution and deforestation

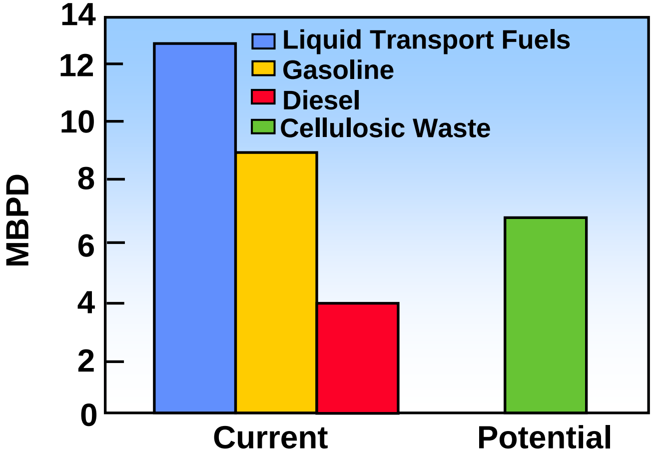
Second Generation Development Required to Ameliorate these Risks

Enablers for a Sustainable Biomass Infrastructure

Global

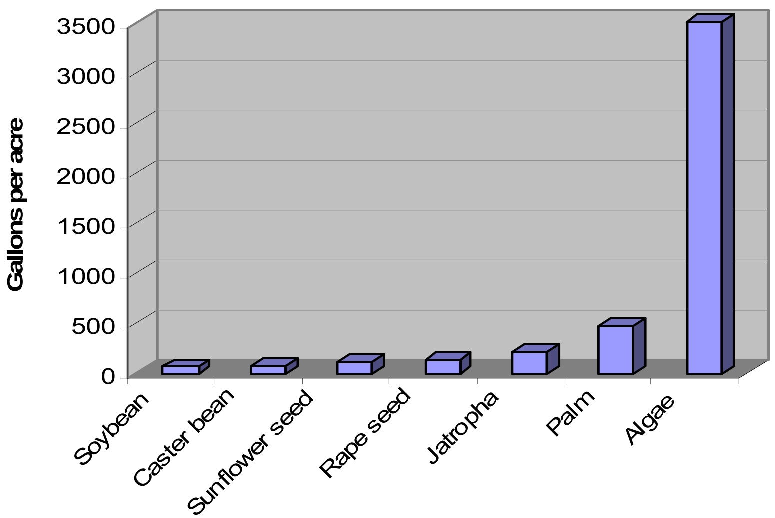


US



Source: Purvin & Gertz / Eric Larsen: Energy for Sustainable Development, 2000

Oils Productivity



- **Cellulosic waste could make a significant contribution to liquid transportation pool.**
- **Algal Oils could enable oils route to biodiesel, Green Diesel and Green Jet.**

Increases Availability, Reduces Feedstock Cost
Technology Breakthroughs Required

UOP Renewables Vision

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- Building on UOP technology and expertise
- Produce real fuels instead of fuel additives/blends
- Leverage existing refining/ transportation infrastructure to lower capital costs, minimize value chain disruptions, and reduce investment risk.
- Focus on path toward second generation feedstocks & chemicals

Oxygenated Biofuels

Ethanol | Biodiesel

Hydrocarbon Biofuels

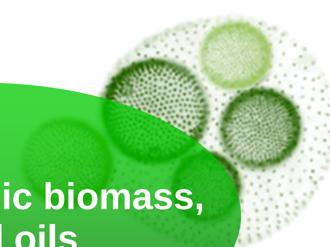
Diesel | Jet | Gasoline

First Generation

Natural oils from vegetables and greases

Inedible Oils: Camelina, Jatropha

Second Generation



Lignocellulosic biomass, algal oils

Renewable Fuels: Unlocking the Potential

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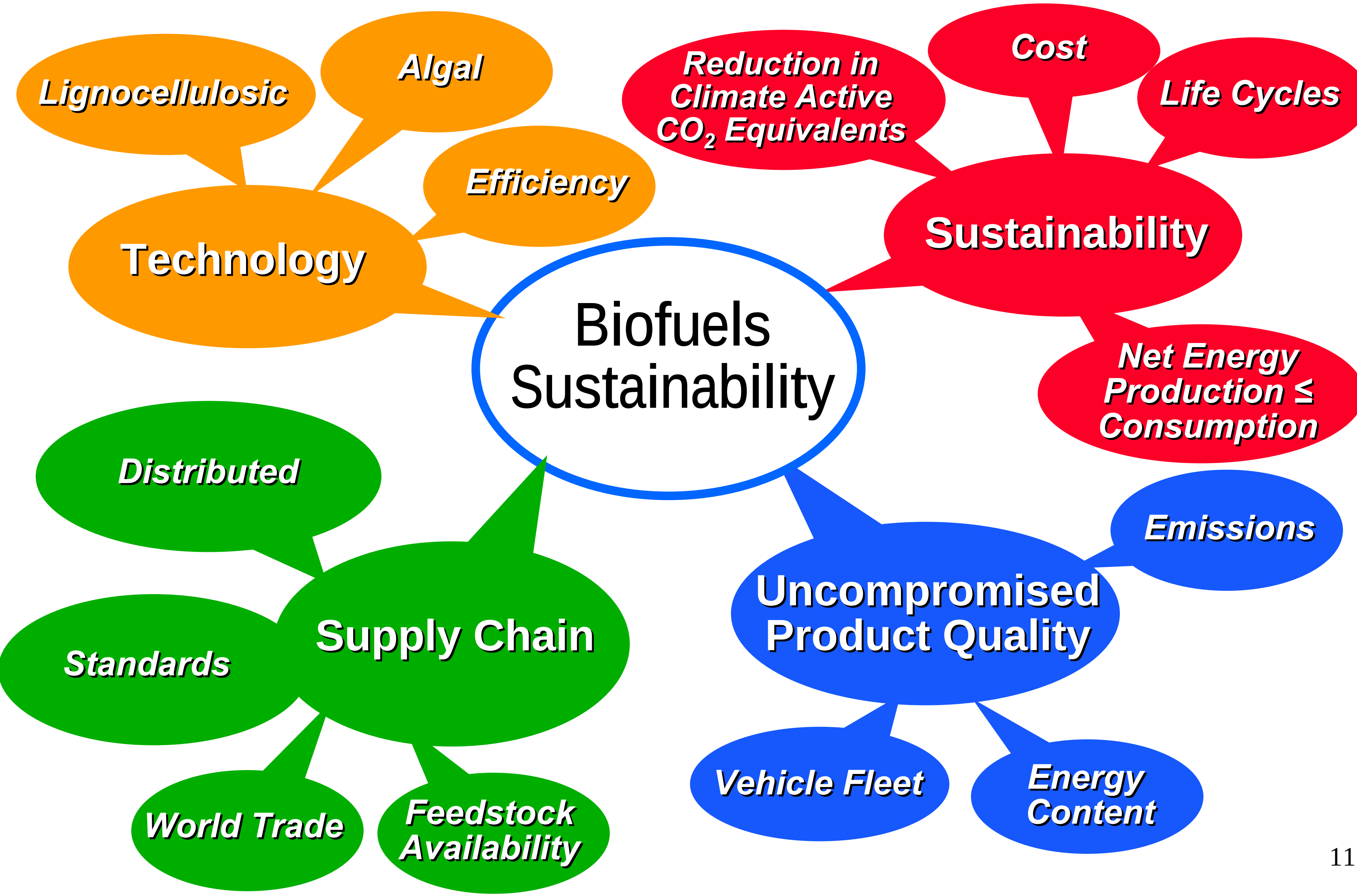
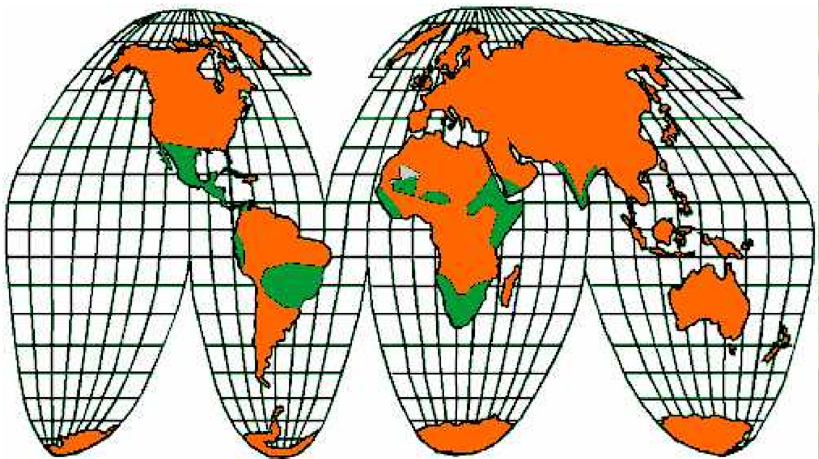


Jatropha Plant (*Jatropha curcas L*)

- Bush or small plant with irregular branches, 1-7 m height.
- Grows well in porous & infertile (marginal) soil
- Grows at rainfall of 30-238 cm/yr; Optimum rainfall 62.5 cm/yr
- Grows wild or grown as fence.
- Grows well in lowland up to 1000 m above sea level
- Required average temperature is 20-28°C
- Life 25-30 years.

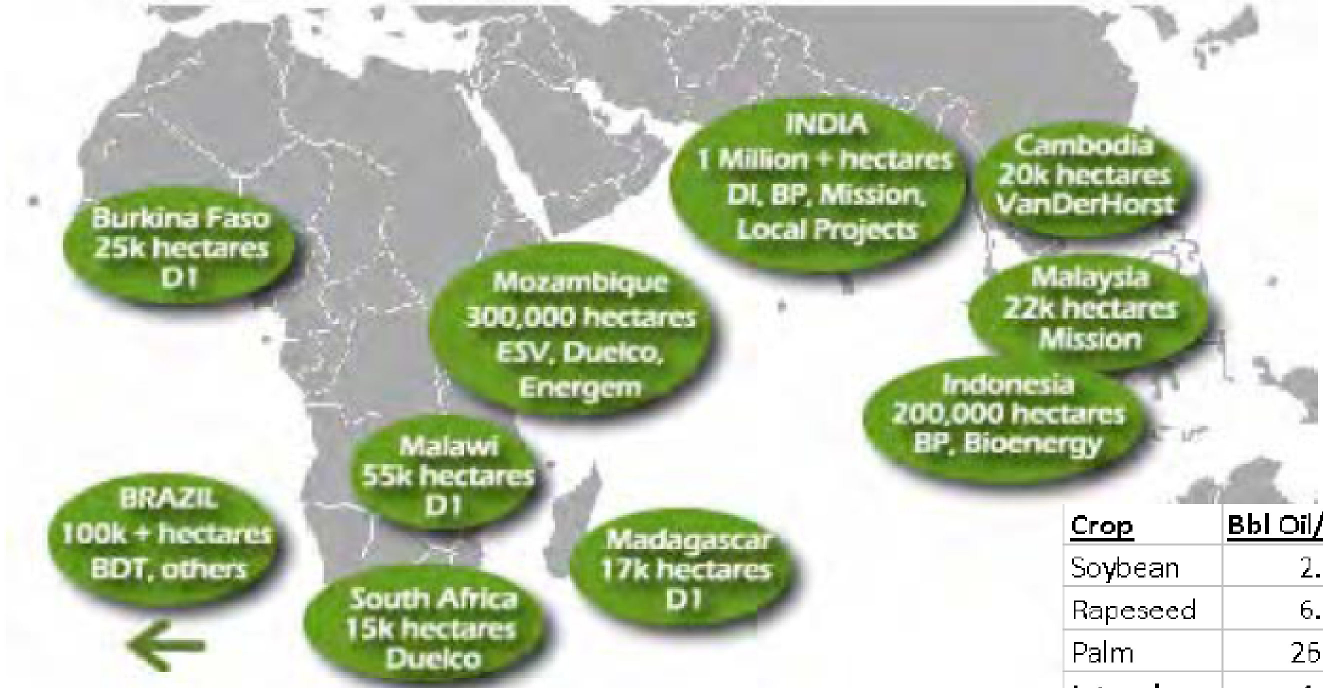


Advantages of *Jatropha* as Biofuel and Biomass Feedstock

- **Seed has high oil content (30 - 50 %)**
- **Oil is not edible → does not interfere with edible oil supply**
- **Can be grown and developed in dry and marginal lands**
- **Easy to grow and widely adaptable**

Inedible Oil Cultivation Expanding

Jatropha Commercial-Scale Projects Under Development



Crop	Bbl Oil/ha-yr
Soybean	2.6
Rapeseed	6.8
Palm	26.0
Jatropha	**4.6**

source: Emerging Markets Online

Countries are responding to the demand

UOP Biomass Processing Routes

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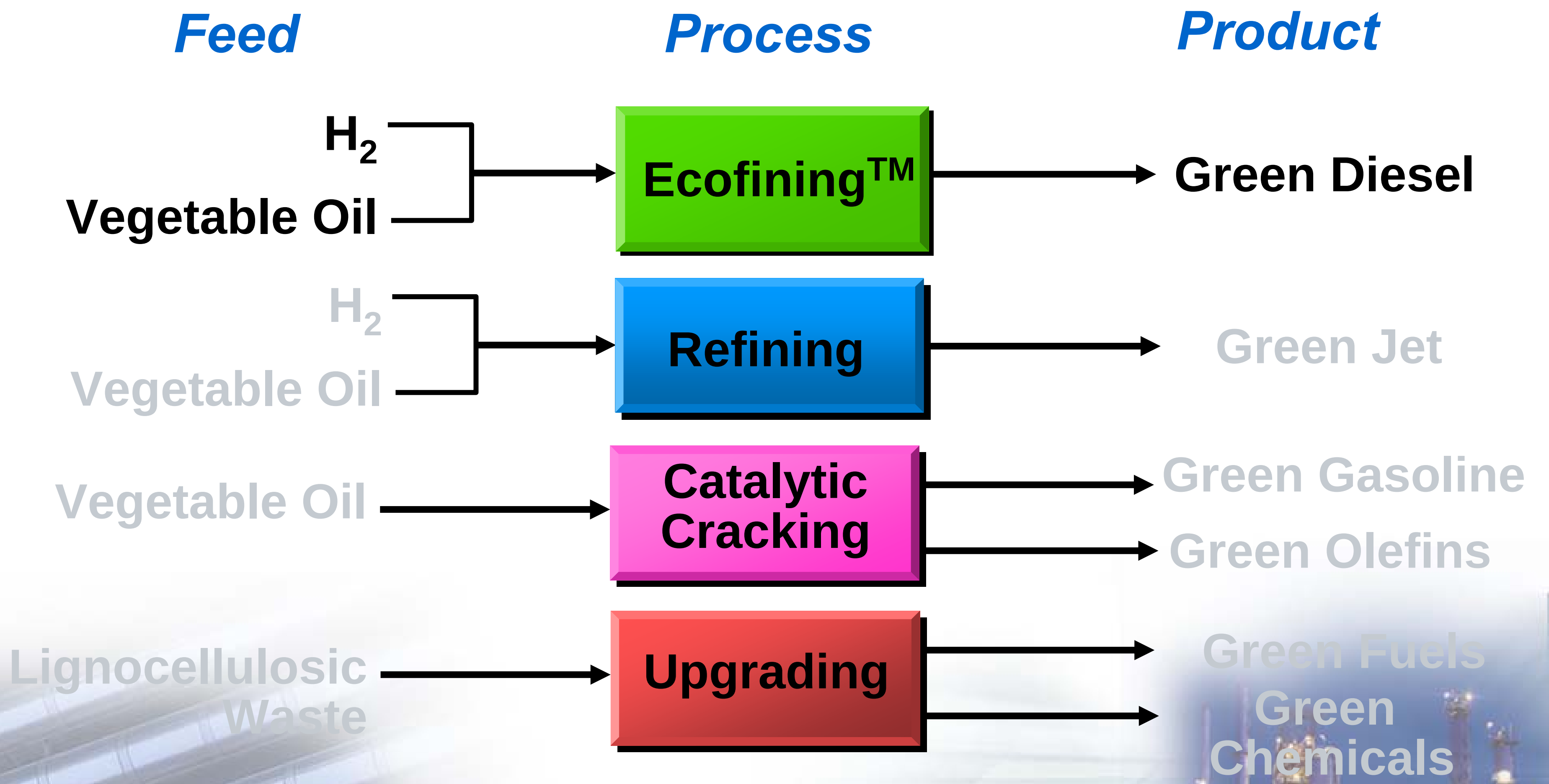
Feed	*Process*	*Product*
H_2, Vegetable Oil	Ecofining™	Green Diesel
H_2, Vegetable Oil	Refining	Green Jet
Vegetable Oil	Catalytic Cracking	Green Gasoline, Green Olefins
Lignocellulosic Waste	Upgrading	Green Fuels, Green Chemicals

UOP Biomass Processing Routes



Vegetable Oils/Greases

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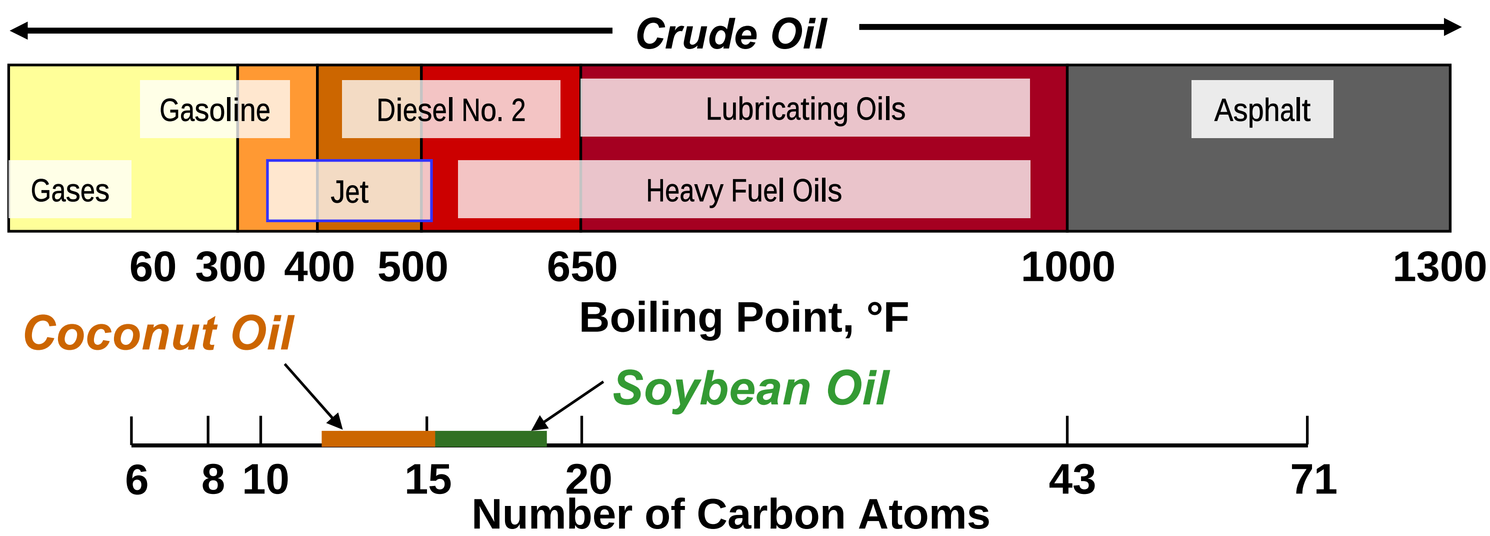
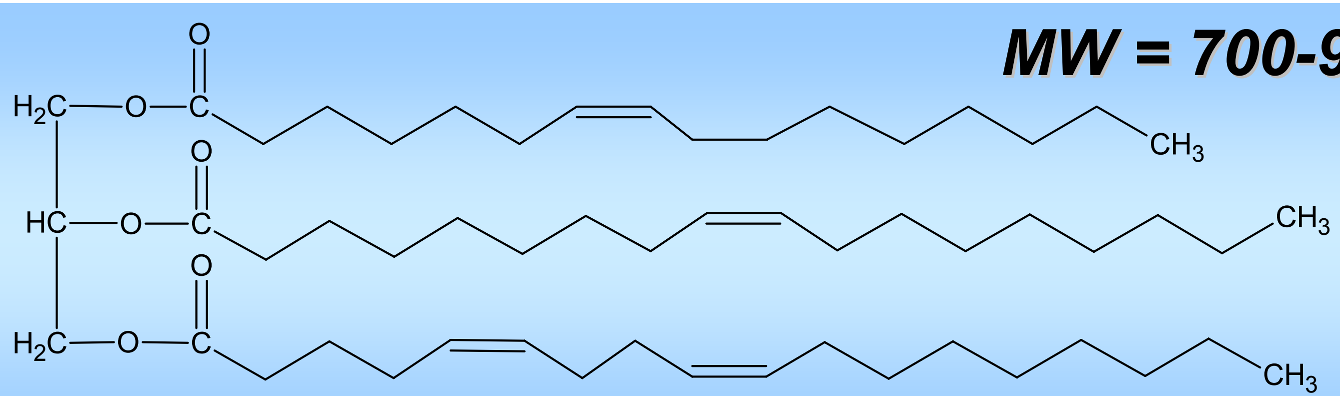
- **Boiling point and number carbon atoms hydrocarbons in vegetable oils fall in the diesel range.**



Composition of Oils and Greases
(10-12% Oxygen, Olefins, Trace Sulfur)

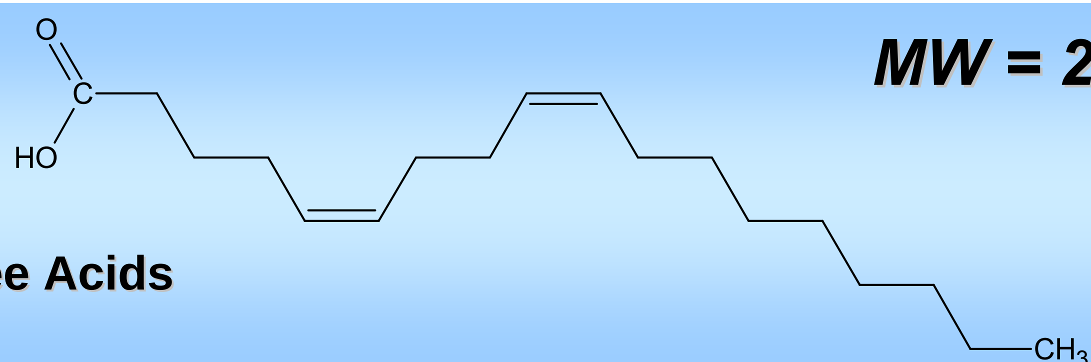
- The major component of fats/vegetable oil is triglycerides.
- Triglyceride is glycerol with a long-chain fatty acid on each of the OH groups.
- Length of the alkyl groups is 12-18 carbon atoms.

MW = 700-900



Triglycerides

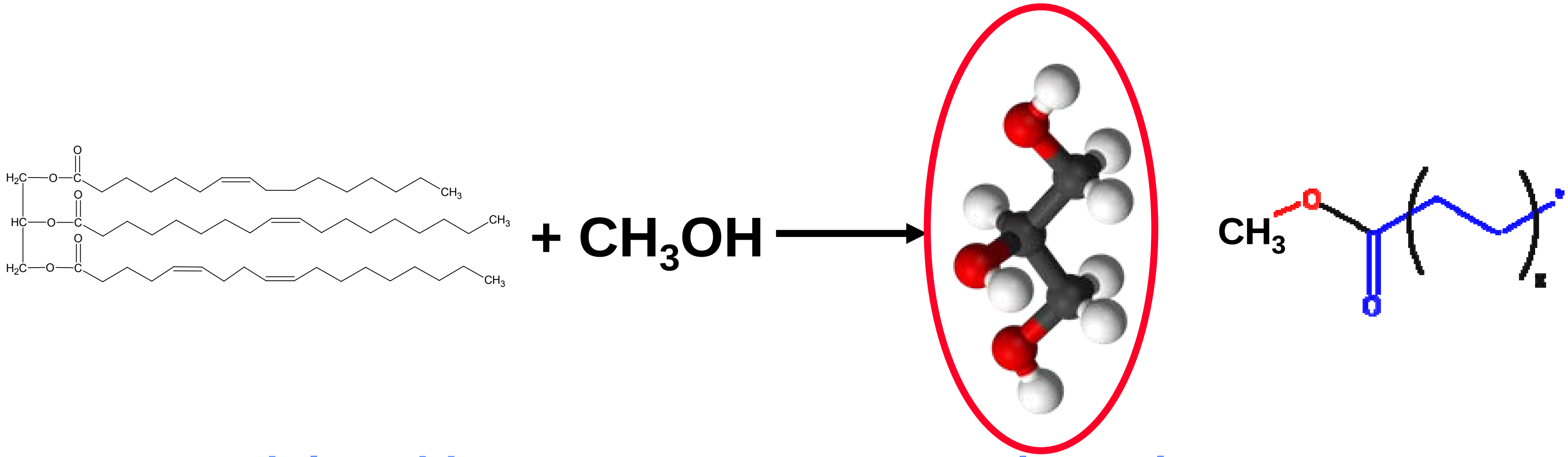
MW = 200-300



Fatty Free Acids

Biodiesel

- **Biodiesel is produced by the reaction of the triglyceride with methanol in the presence of NaOH to produce FAME – fatty acid methyl ester in a process called transesterification.**

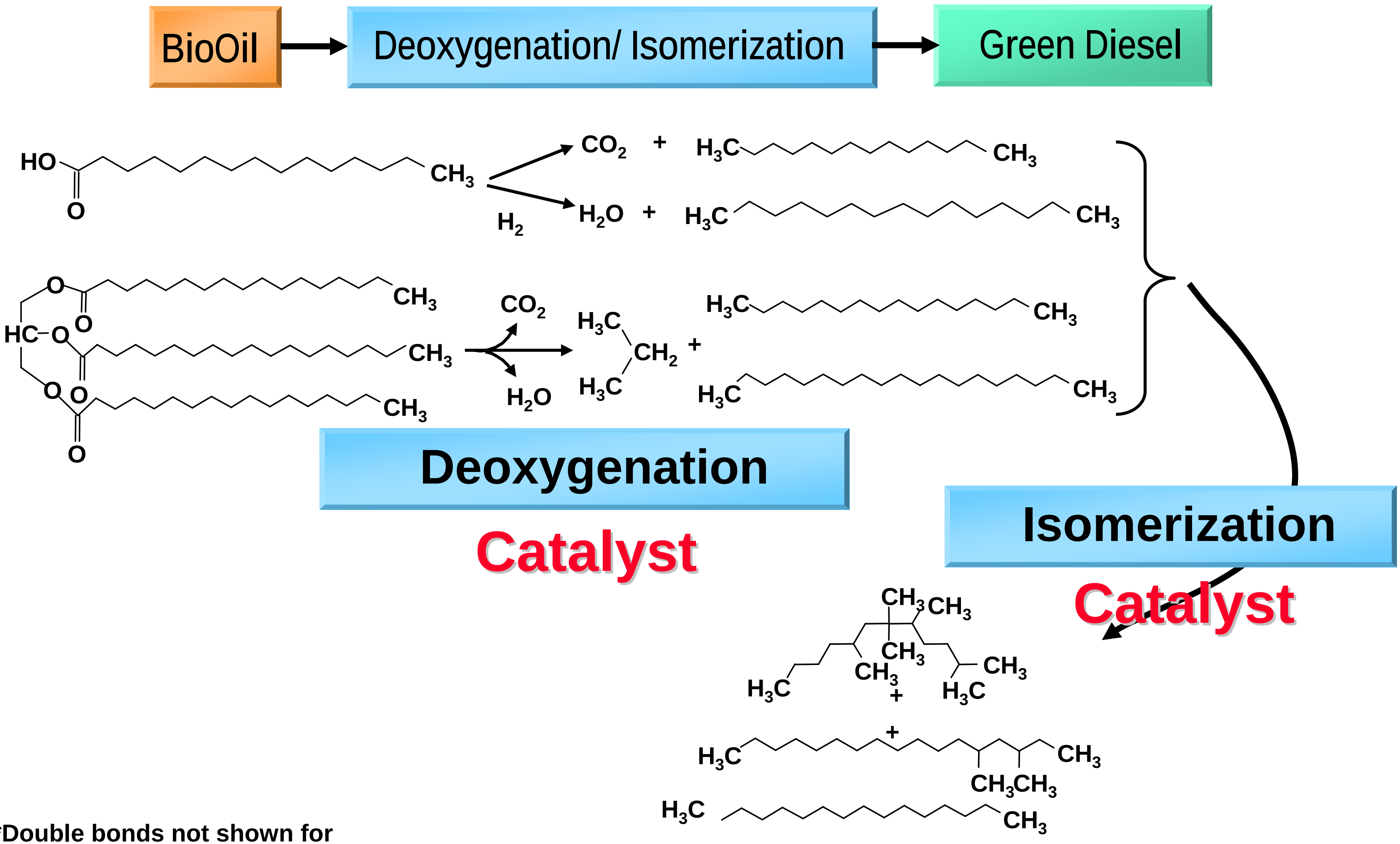


triglyceride glycerol FAME

Transesterification

Ester + alcohol $\rightarrow$ different ester + different alcohol

Green Diesel



*Double bonds not shown for simplicity

Green Diesel Reactions

- **Olefin Saturation**

- **Decarboxylation/Decarbonylation**

$$C_n\ COOH \xrightarrow{\text{Catalyst}} C_n + CO_2$$

$$C_n\ COOH + H_2 \xrightarrow{\text{Catalyst}} C_n + CO + H_2O$$

$$CO + H_2O \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} CO_2 + H_2$$ ***Water Gas Shift***

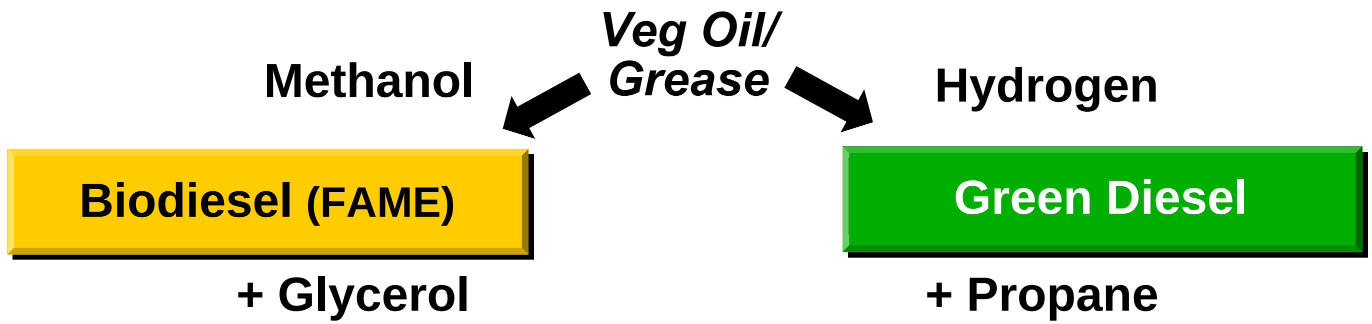
- **Hydrodeoxygenation**

$$C_n\ COOH \xrightarrow[\text{Catalyst}]{+3H_2} nC_{n+1} + 2H_2O$$

- **Hydroisomerization**

$$nC_{n+1} + nC_n \xrightarrow[\text{Catalyst}]{H_2} iC_{n+1} + iC_n$$

Green Diesel vs. Biodiesel (FAME)



	Petroleum ULSD	*Biodiesel (FAME)*	*Green Diesel*
Oxygen Content, %	0	11	0
Specific Gravity	0.84	0.88	0.78
Sulfur content, ppm	<10	<1	<1
Heating Value MJ/kg	43	38	44
Cloud Point, °C	-5	-5 to +15	-30 to -10
Cetane	40	50-65	70-90
Lubricity	Baseline	Good	Baseline
Stability	Baseline	Poor	Baseline

UOP/ENI Ecofining™ Process to Produce Green Diesel
First Unit Start-up: 2010

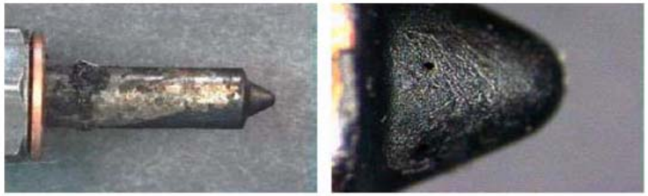
Engines OEM Experience with FAME

Biodiesel – Main Issues & Challenges to the Motor Industry

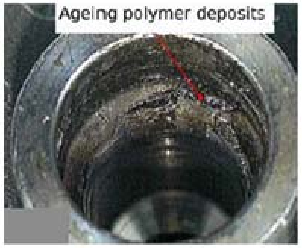
- **Stability issues - Deposits**
- **Material compatibility, Corrosion– Elastomers & polymers**
- **Cold temperature operability – Filter plugging**
- **Lubricant dilution – Impacts engine cleanliness & degrades lubricant**
- **Exhaust after-treatment systems – Long term impact not known**

Impact of a Higher Biodiesel Content in the Engine Oil

- **Negative impact on tribological system**
- **Excessive stress on additive package**
- **Deposit formation**
- **Catalyzer damage**



Fouled Injection Nozzles
(Source Bosch)



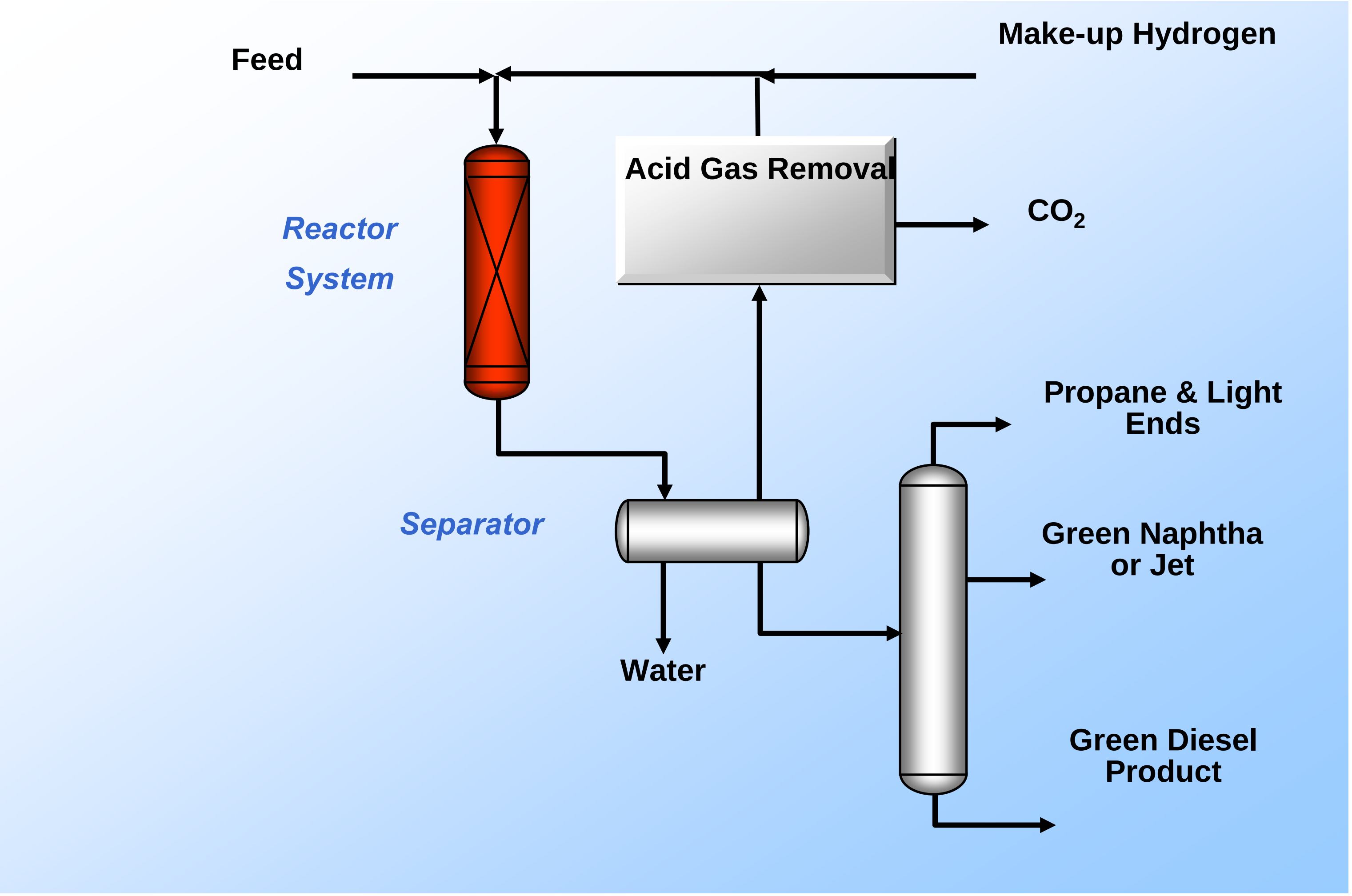
Polymer Deposits
(Source Bosch)

Gum Formation on Fuel Pump Filter
(Source Toyota)

Plugged Filter
(Source AURI)

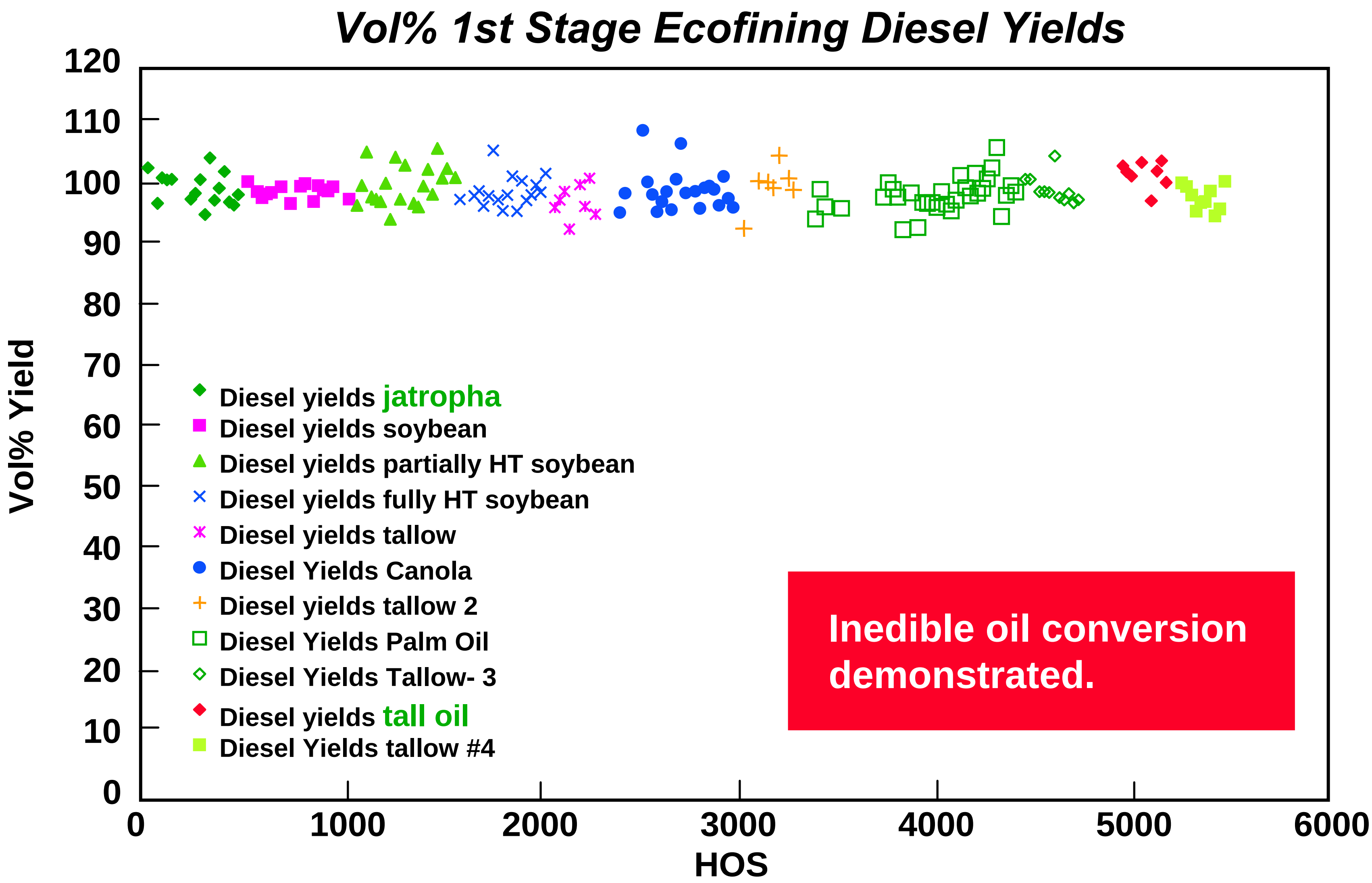
High FAME Concentrations Result in Many Undesirable Problems with Existing Engines

Ecofining Process Chemistry Details



Ecofining Feed Testing Program – Soy, Rapeseed, Palm, Jatropha, Algal, Tallow, …

Extensive Pilot Plant Testing with Various Feeds



Inedible oil conversion demonstrated.

Life Cycle Assessment

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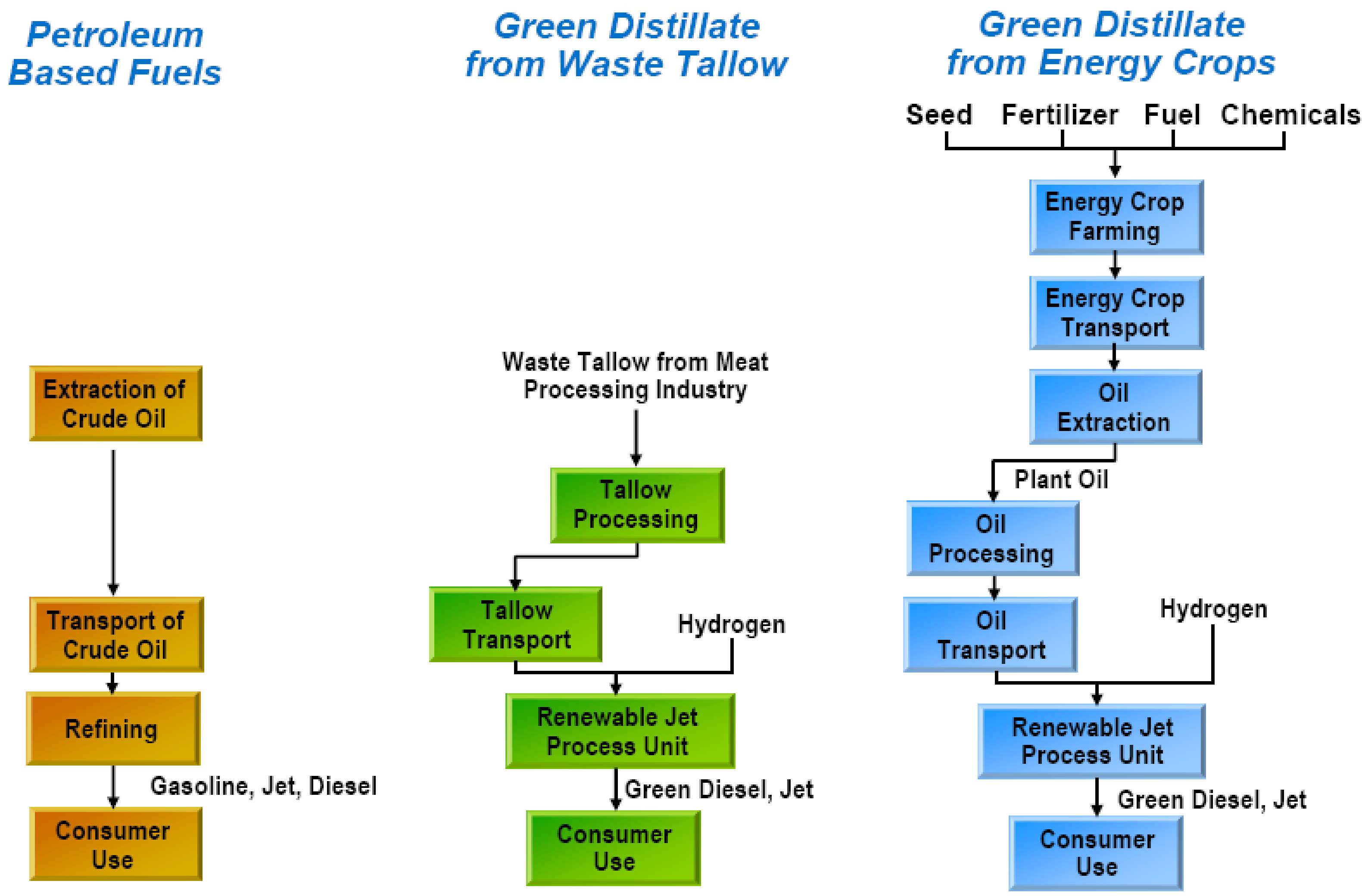
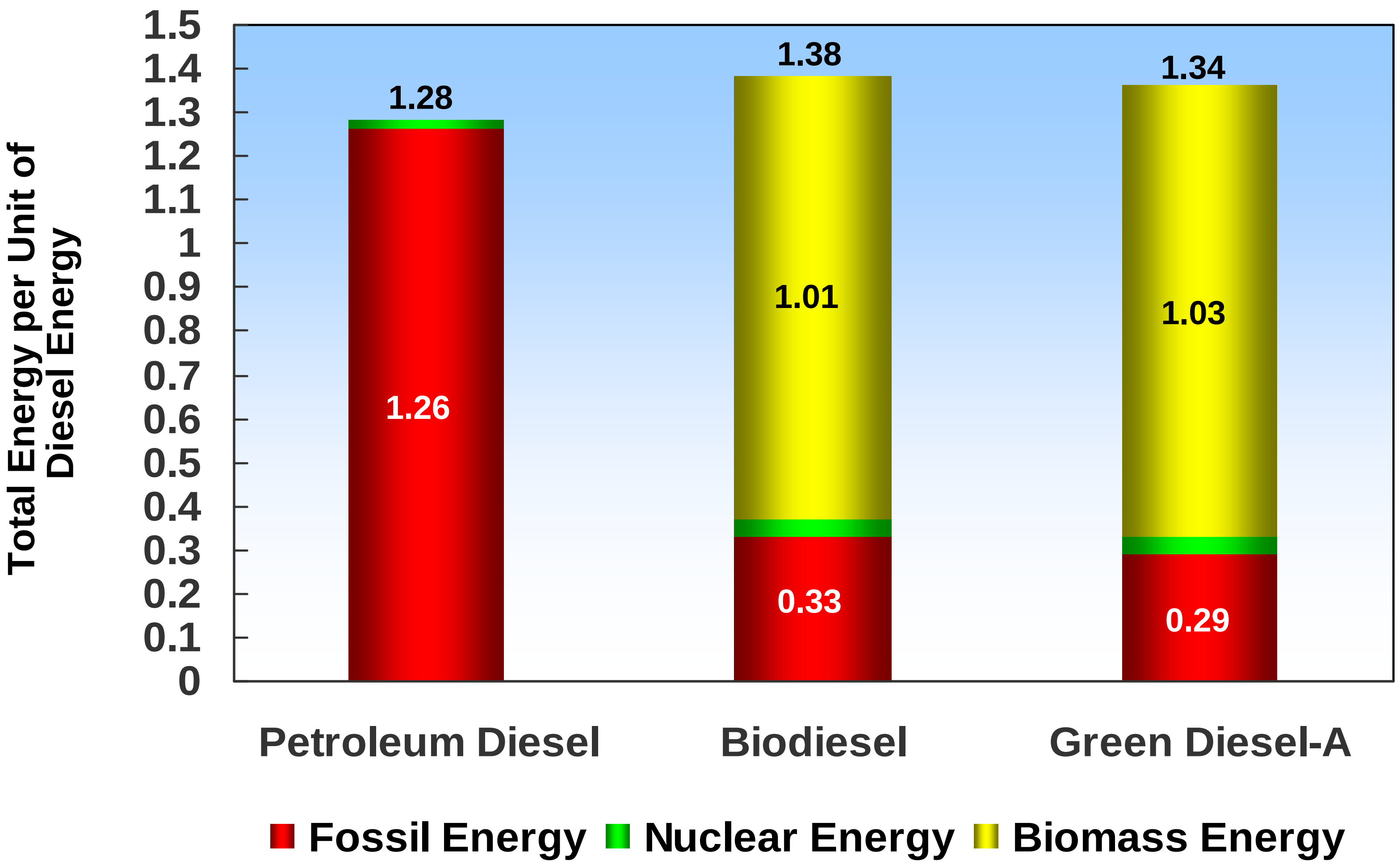
- **Method to determine and compare the environmental impact of alternative products or processes *from cradle to grave***
  - **Scope: from extraction (cultivation) through combustion (in transportation use)**
  - **Functional Unit: 1 kg of each fuel**
    - Assumption: Each fuel performs the same in transportation use
  - **Primary Focus: fossil energy consumption and emission of green house gases (GHG)**
  - **Other impact categories are included**

Scope of WTW* LCA



*well-to-wheels or well-to-wings

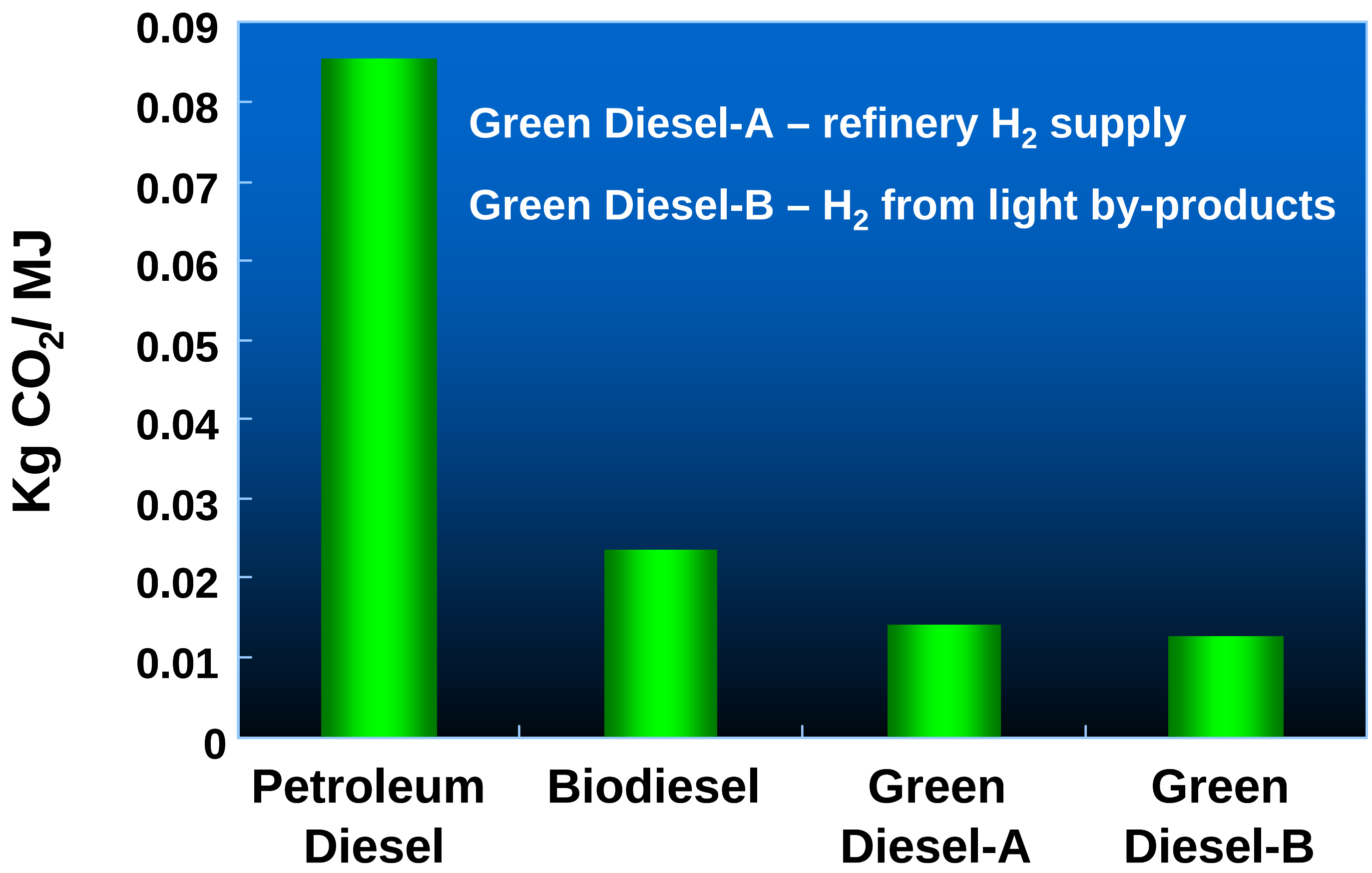
Life Cycle Analysis: Total Energy Comparison



Petroleum Fuels Production is Most Energy Efficient

Shonnard, DOE Methodology, SimaPro

Climate Active CO_2 Production



Green Diesel has the smallest CO_2 footprint

Environmental Impact

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Methodology	% Fossil Savings (relative to petroleum diesel)	
	Biodiesel	Green Diesel
DOE	74	77
CONCAWE	55	73
PNAS	72	73
	% GHG Savings (relative to petroleum diesel)	
	Biodiesel	Green Diesel
DOE	73	84
CONCAWE	37	57
PNAS	43	47

Methodology Selection is Critical

UOP Biomass Processing Routes

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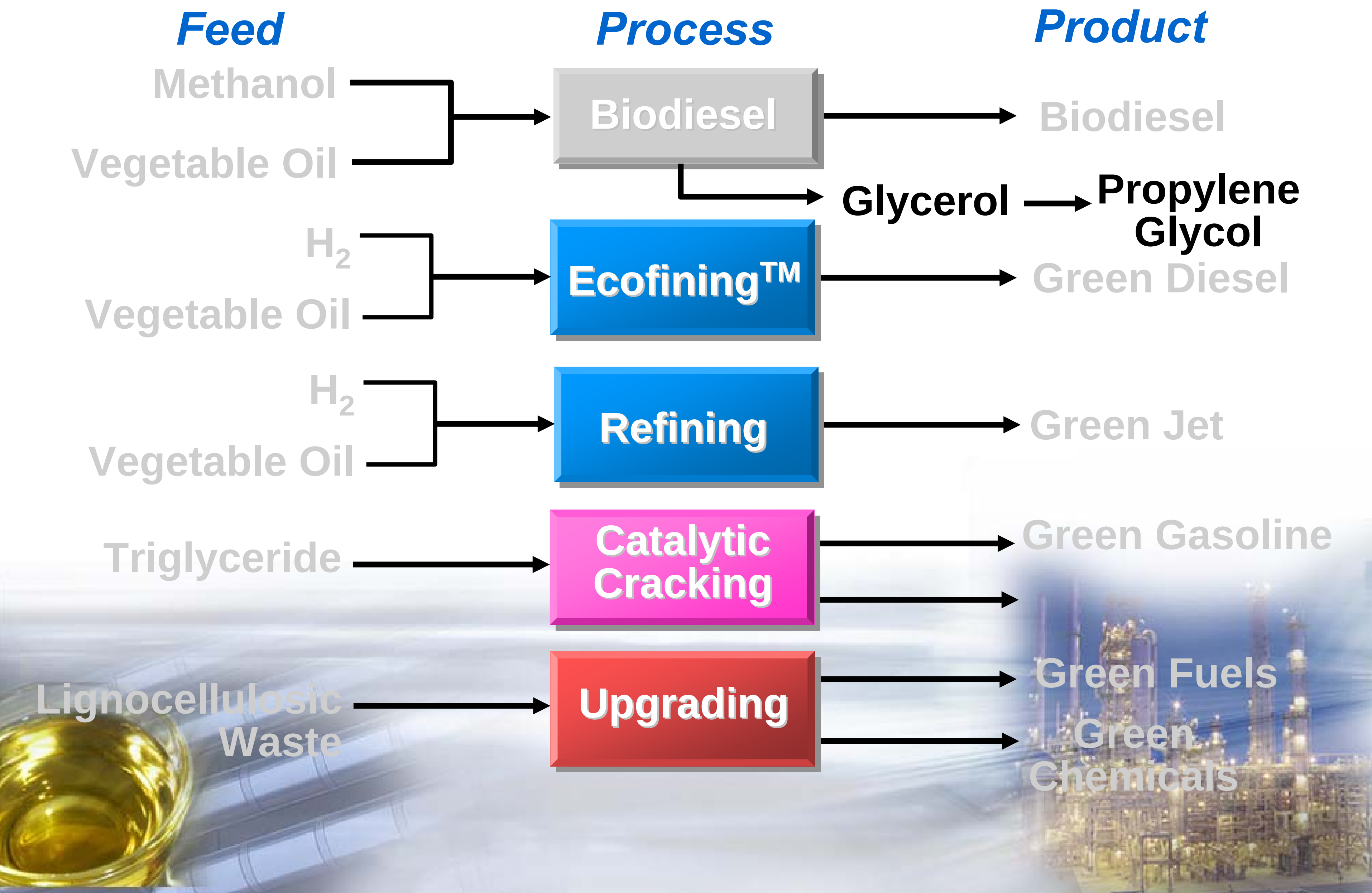
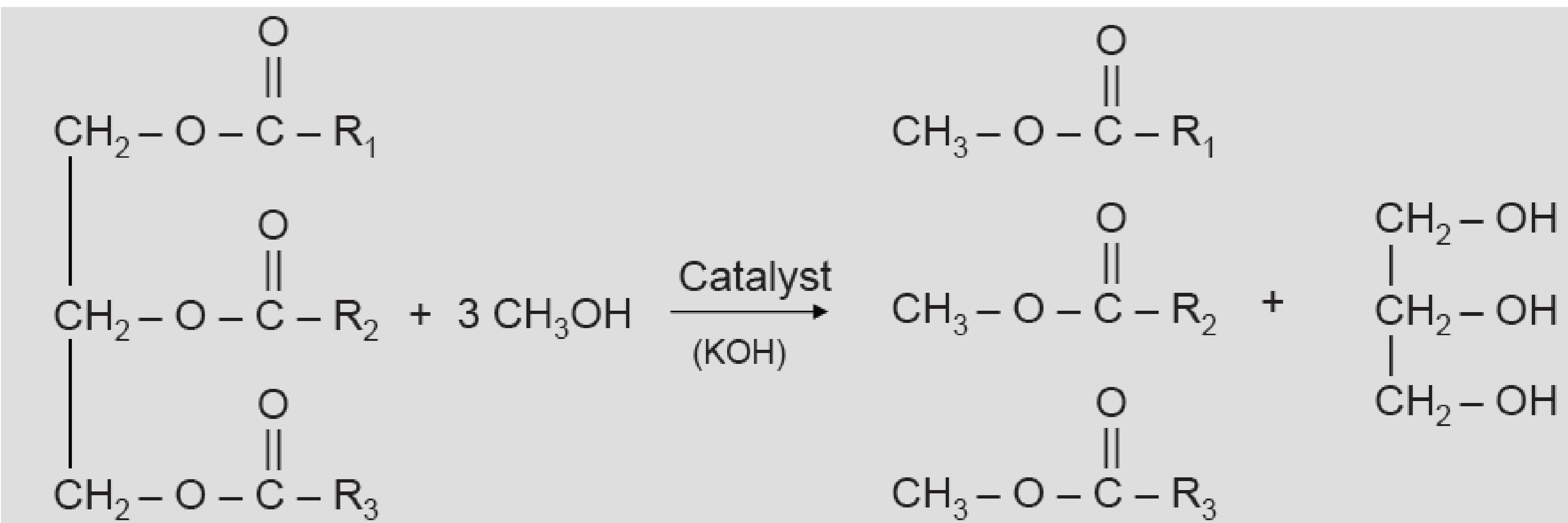


Biodiesel Math

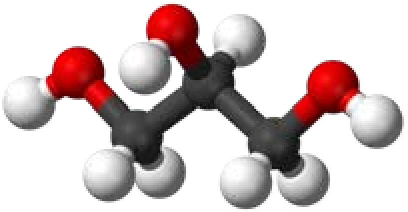
100 lbs Vegetable Oil (Triglycerides) + **10 lbs Methanol** → **100 lbs** Mixed Fatty Acid Esters **(Bio Diesel)** + **10 lbs Glycerol**

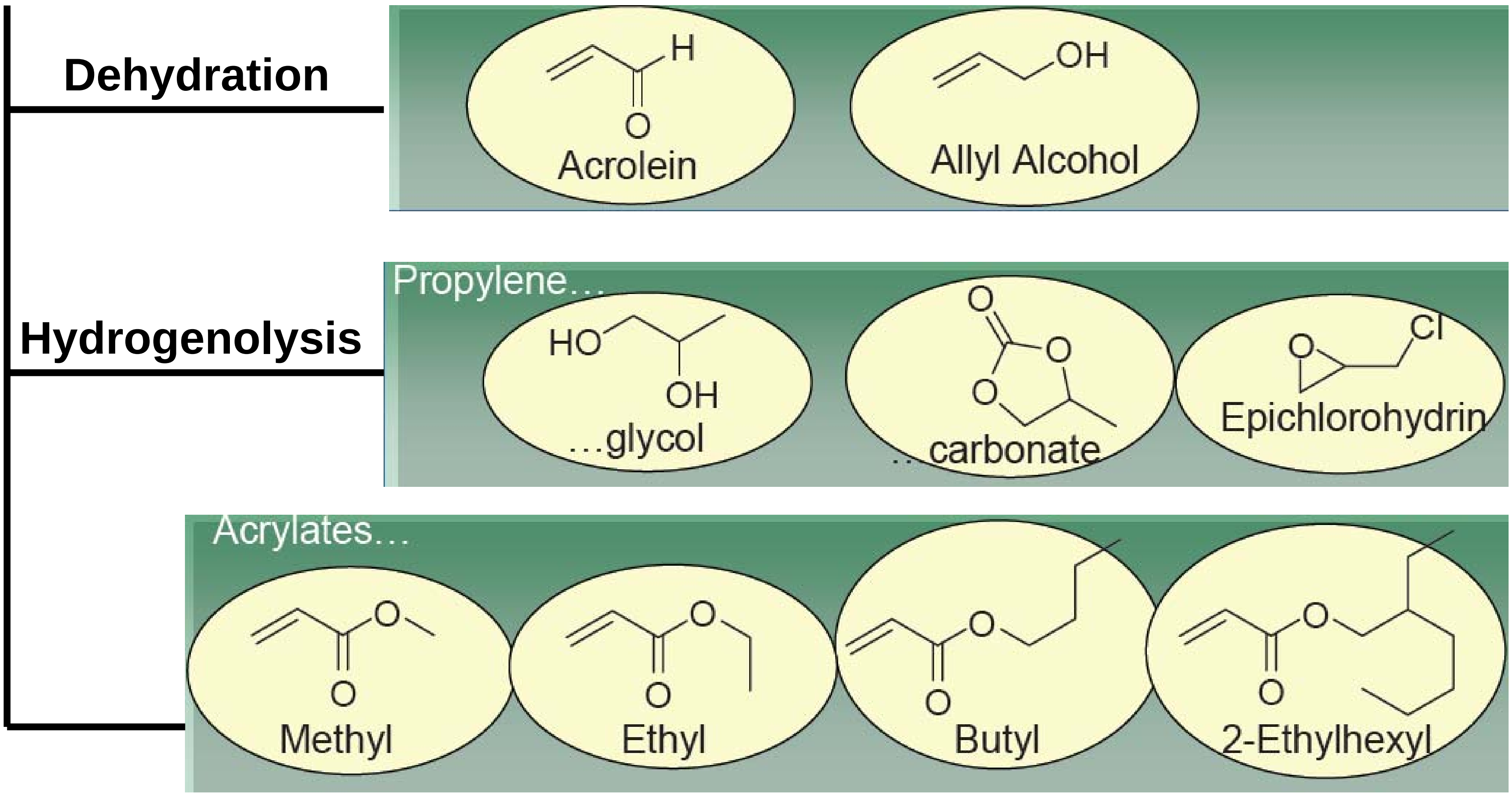


Biodiesel Math, cont.

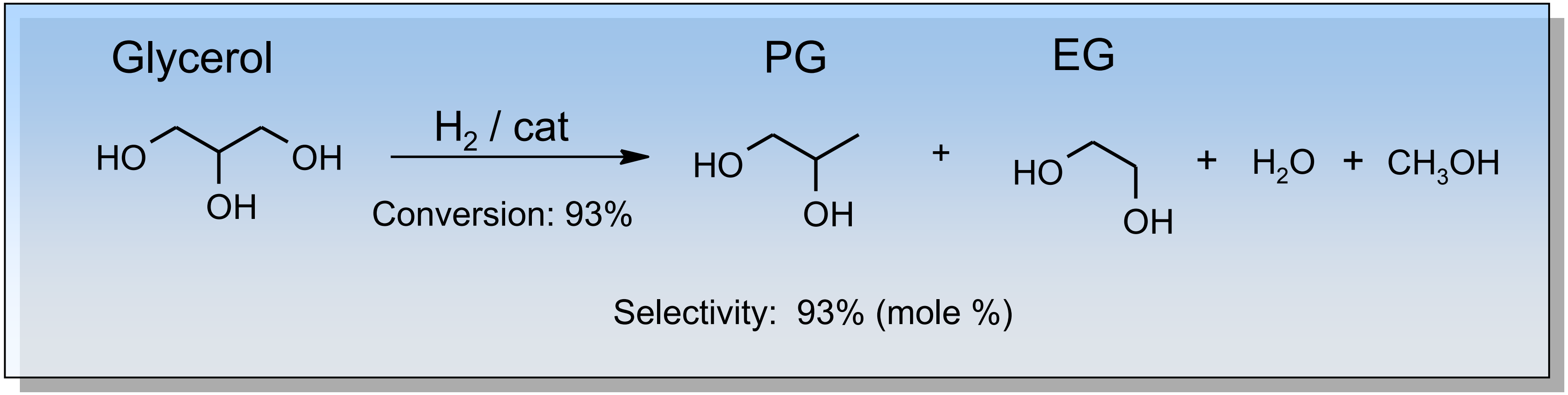
- **1 billion gallons of biodiesel would result in 770 million lbs glycerol**
  - **US glycerol market = 320 million lbs**
  - **World glycerol market = 800 million lbs**
- **Need new options for glycerol use**
- **New direct uses**
- **Glycerol as platform to other chemicals**
  - **770 million lbs of glycerol could produce 540 million lbs of propylene glycol (PG market 3.5 billion lbs)**

Products from Glycerol



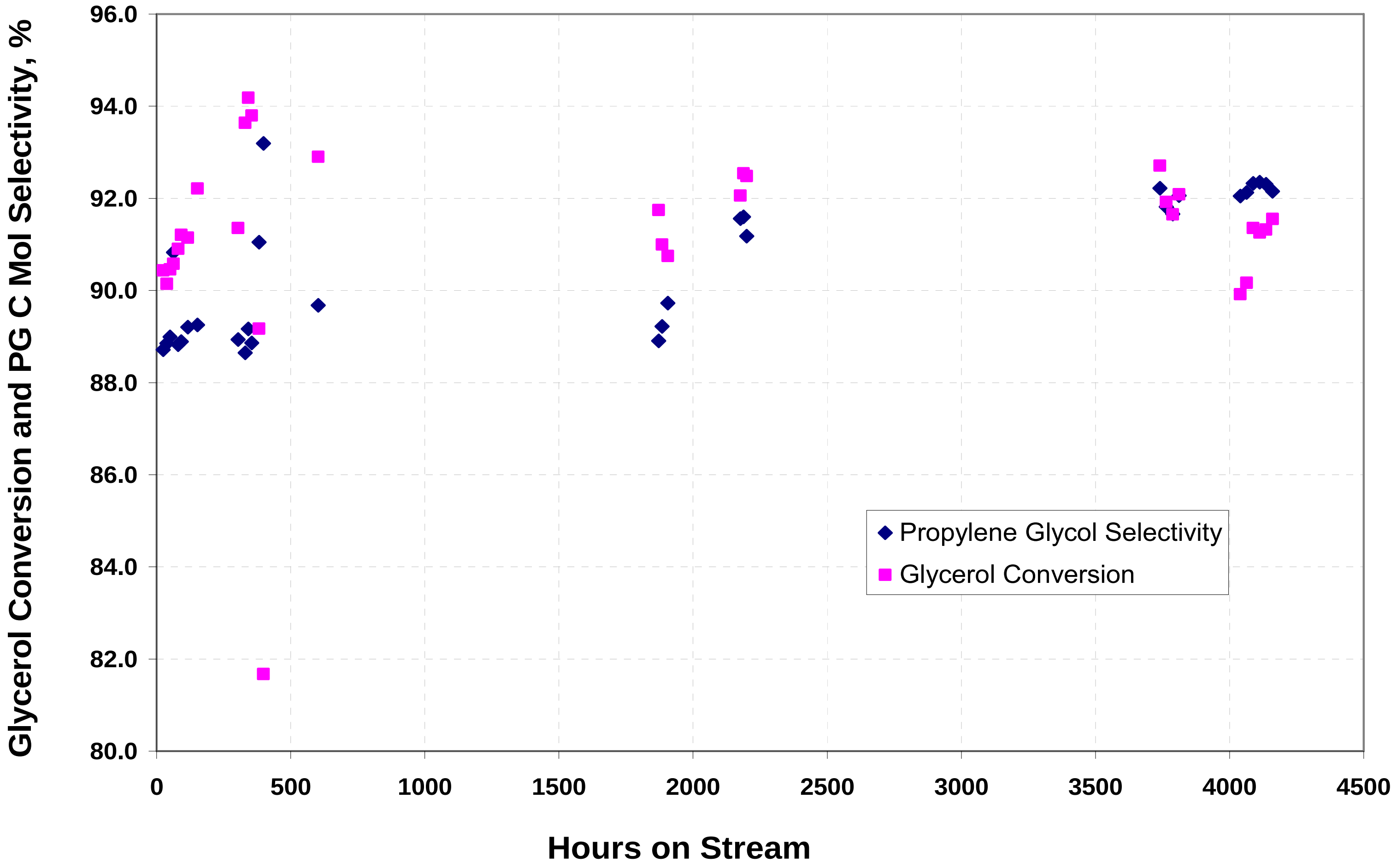


UOP Glycerol to PG Process



- **Jointly developed with Pacific Northwest National Lab**
- **High conversion of Glycerol**
- **High selectivity to PG**
  - **90+ mol% selectivity to PG**
- **Demonstrated ability to process commercial glycerol feed**
  - **Distillation of crude glycerin is not required**
  - **Methanol & water-tolerant catalyst**
  - **Feed is aqueous solution of 40-60 wt% glycerol**

Catalyst On-stream Performance



Excellent Activity and Selectivity

Hydrogenolysis Catalyst for PG Process

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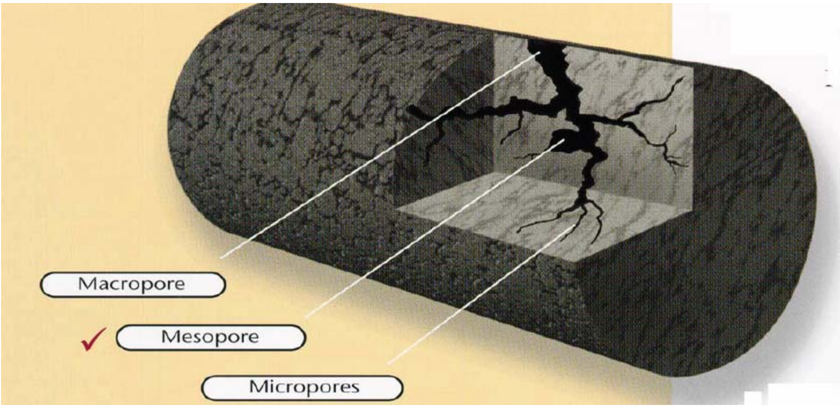
- Re-containing multi-metallic catalyst
  - Ni, Pd, Ru, Co, Ag, Au, Rh, Pt, Ir, Os and Cu
- Supports include C, ZrO_2 and TiO_2 (rutile)
- Catalyst prepared via incipient wetness technique
- Metal precursor salts prepared in single solution
  - Metal salt solution volume = support liquid pore volume
- Reduction at 210-350°C



US 6841085

Processes in Liquid Water (feed 40-60% solution)

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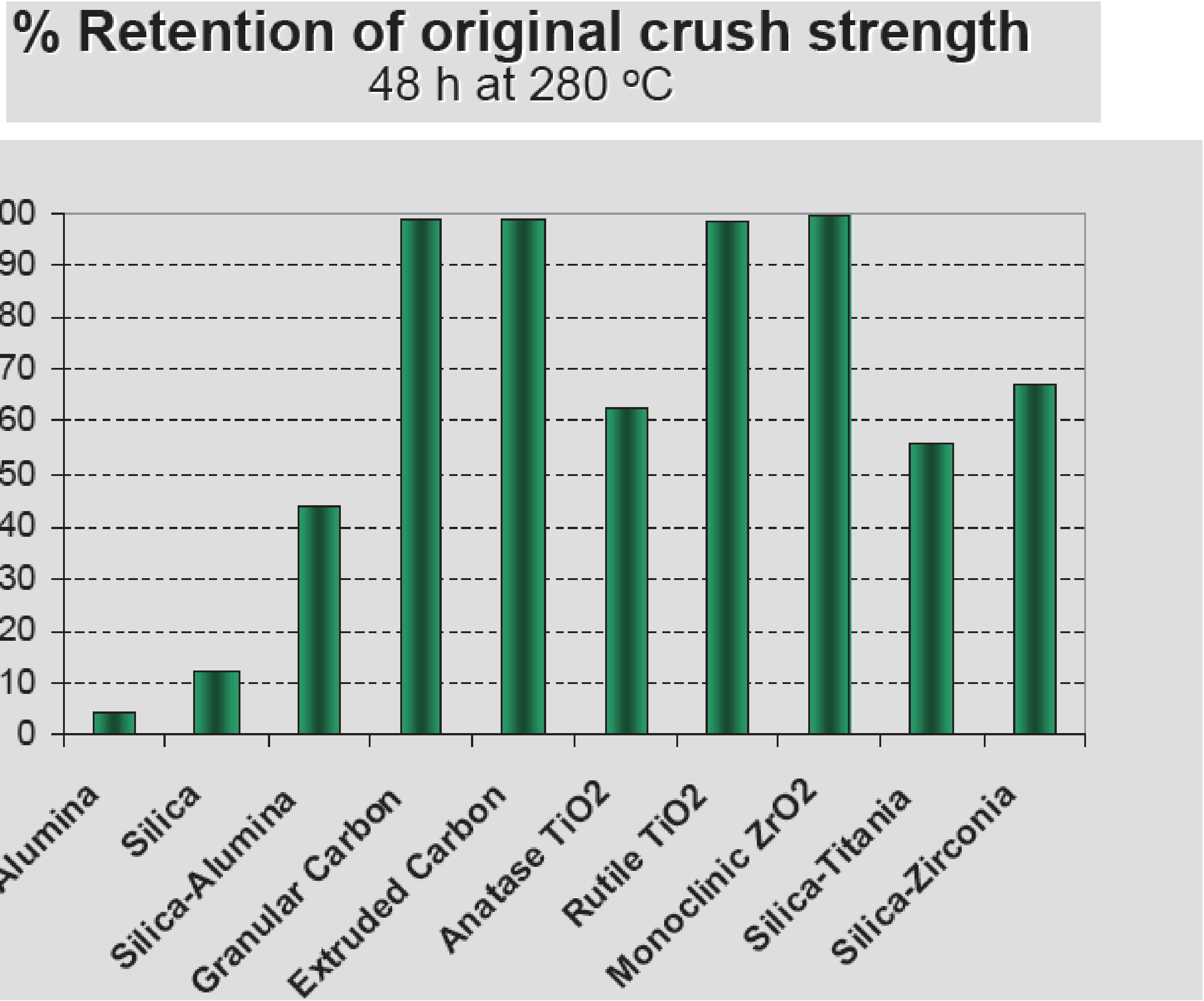
- **"Hot water is nasty stuff"**

- Dielectric and solvent properties greatly changed above 100 ºC (hot water is more "corrosive")
- Facilitates increased rates of hydration-hydrolysis

  eg: $Al_2O_3 + H_2O \longrightarrow 2\ AlO(OH)$

- Conventional supports weaken/dissolve in H_2O
- Process pH effect on support can be significant
- Hydrothermal stability is paramount criteria

Crush Strength



Support Options Limited to….

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- "Hot water is nasty stuff"

- Carbon (<10 – > 2000)
- rutile TiO_2 (1 – 40)
- Monoclinic ZrO_2 (15 – 60)
- perhaps
  - SnO_2
  - Nb_2O_5
  - $BaSO_4$

- Carbon
  - Excellent chemical stability
  - Higher porosity & surface area than most oxides
  - Mechanically robust
  - Easy recovery of catalyst metals
  - Activity often higher than oxides

( ) = surface area (m^2/g)

Hydrogenation Comparison

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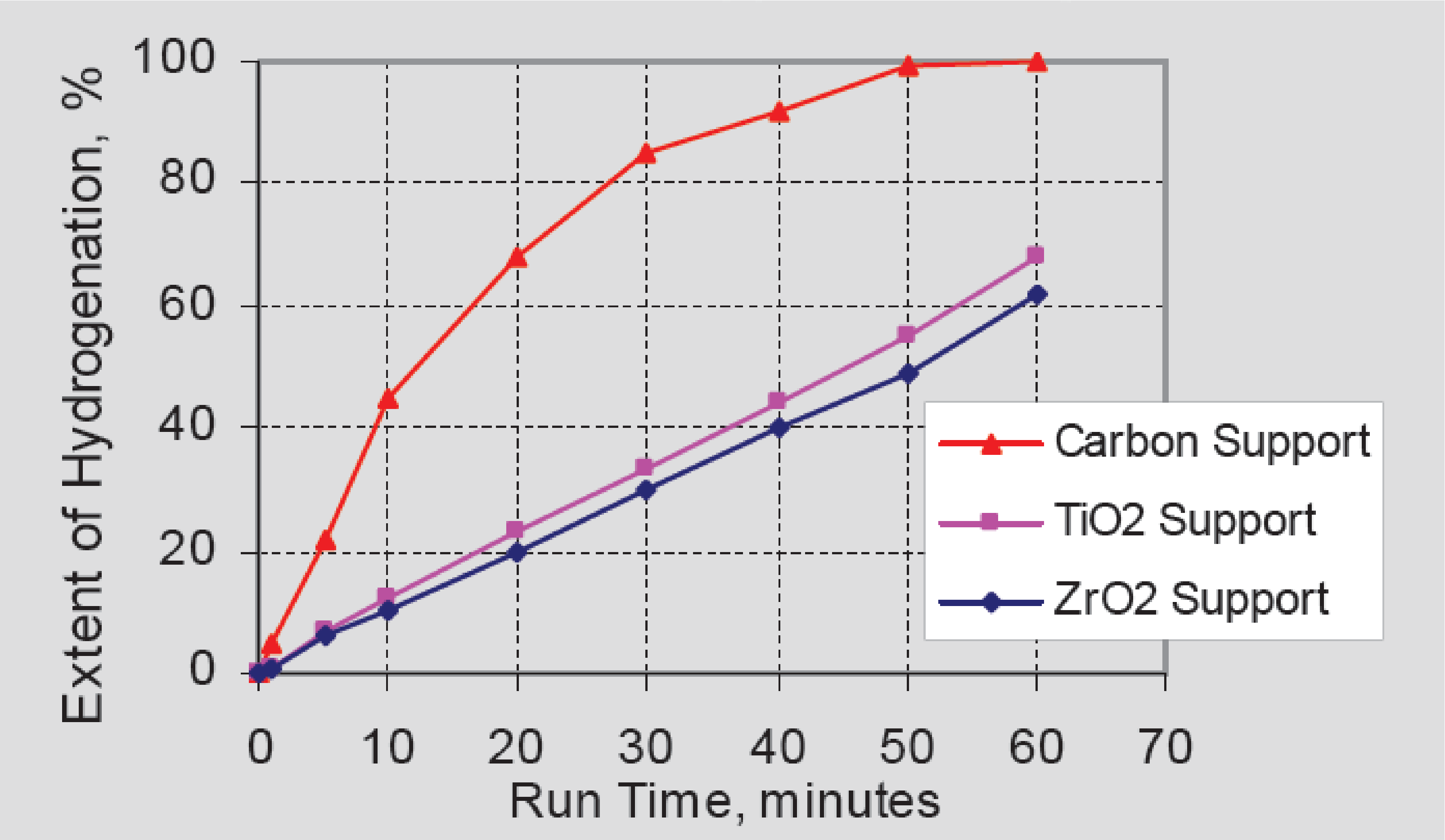

Likely result of high porosity and surface area of carbon

The Metals….

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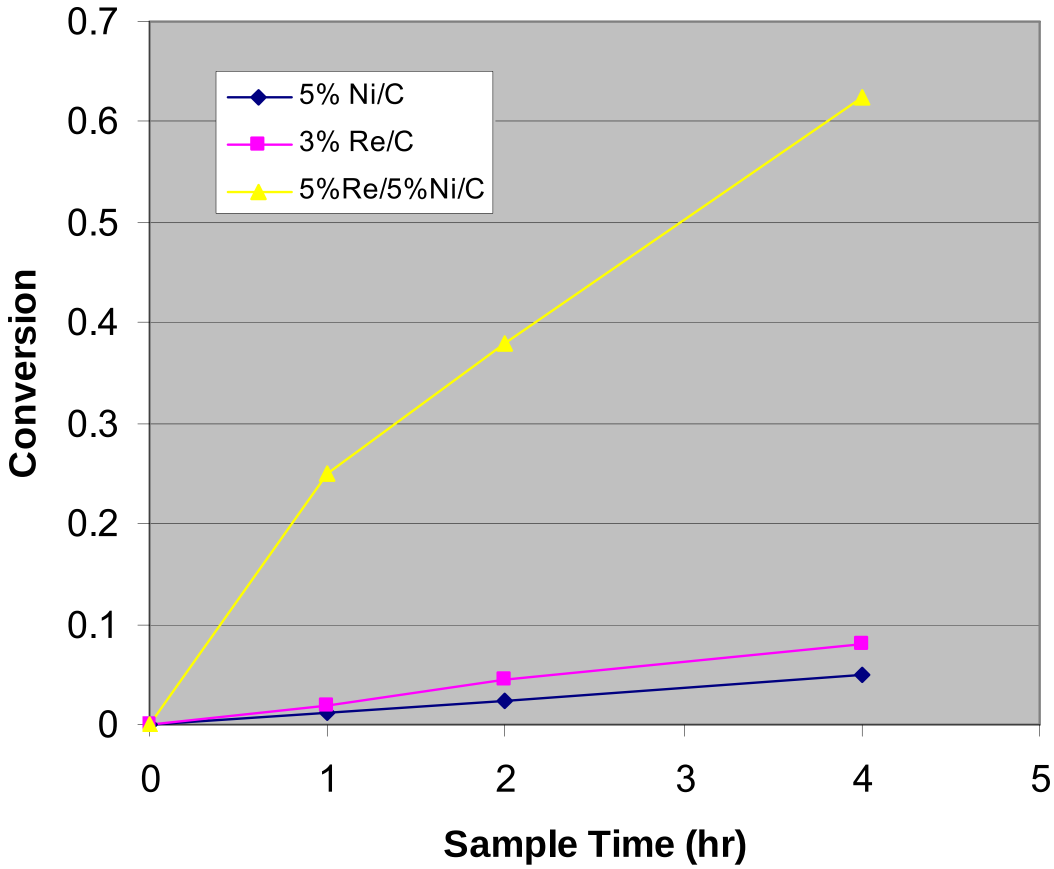
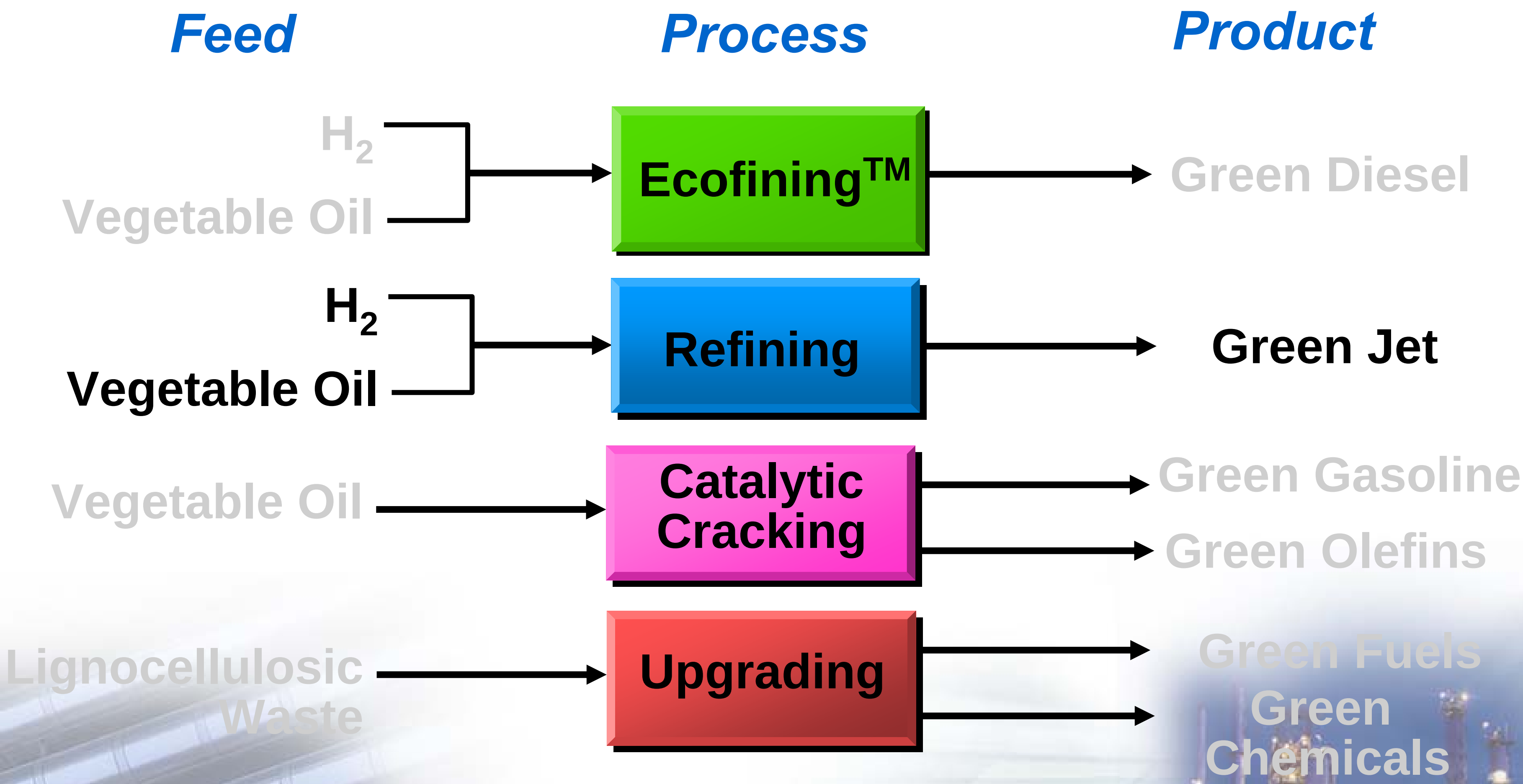
- **Conversions of Ni-Re catalyst >> Ni-only or Re-only: Interaction between Ni and Re.**



Glycerol to PG Summary

- **Potential outlet for the glycerol produced in biodeisel process.**
- **Robust catalyst system developed**
  - **High selectivity and activity**
  - **Catalyst stable to process conditions**
- **Economically competitive to the petroleum based process**

UOP Biomass Processing Routes



Biofuel Sources to Jet Fuel

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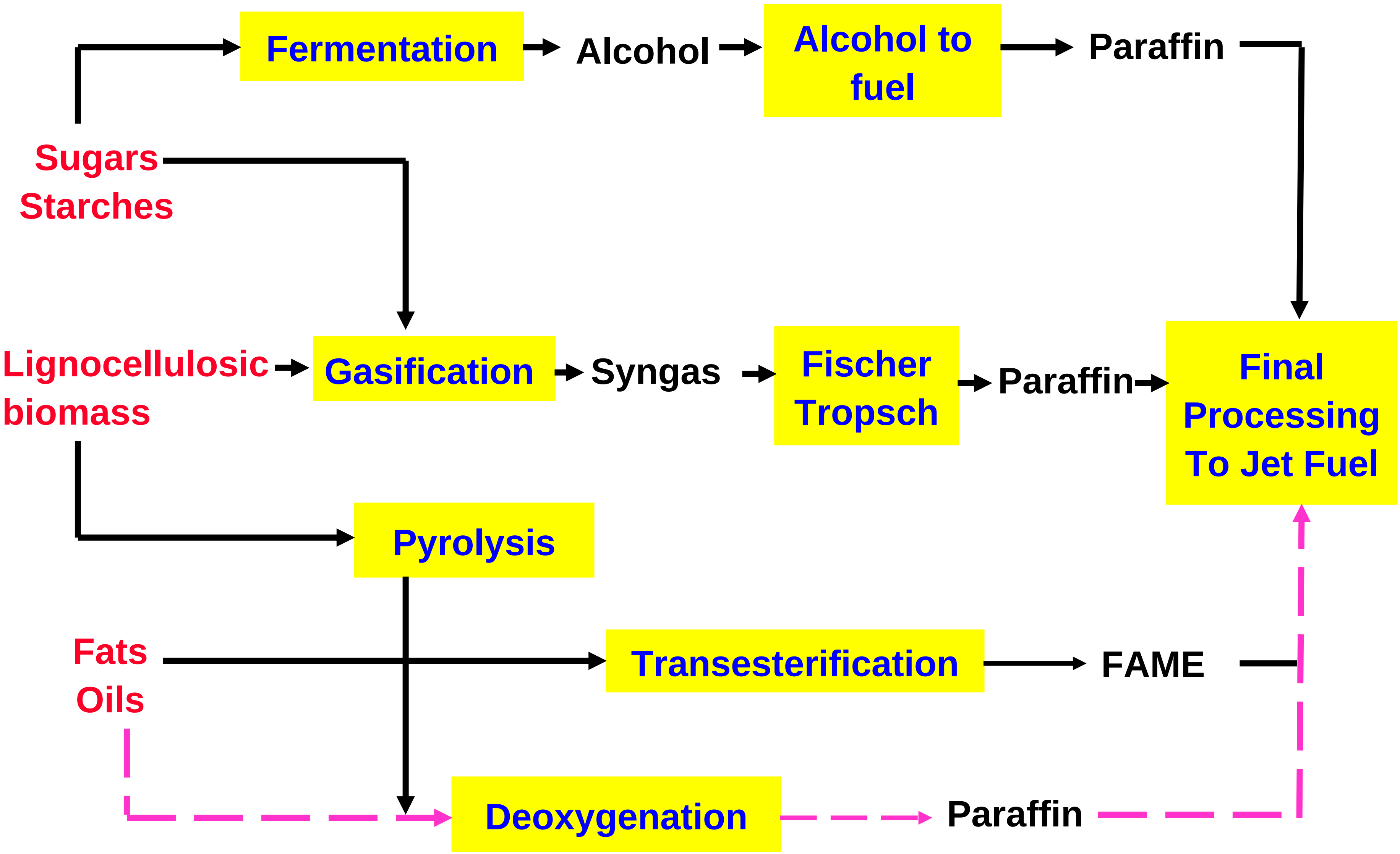
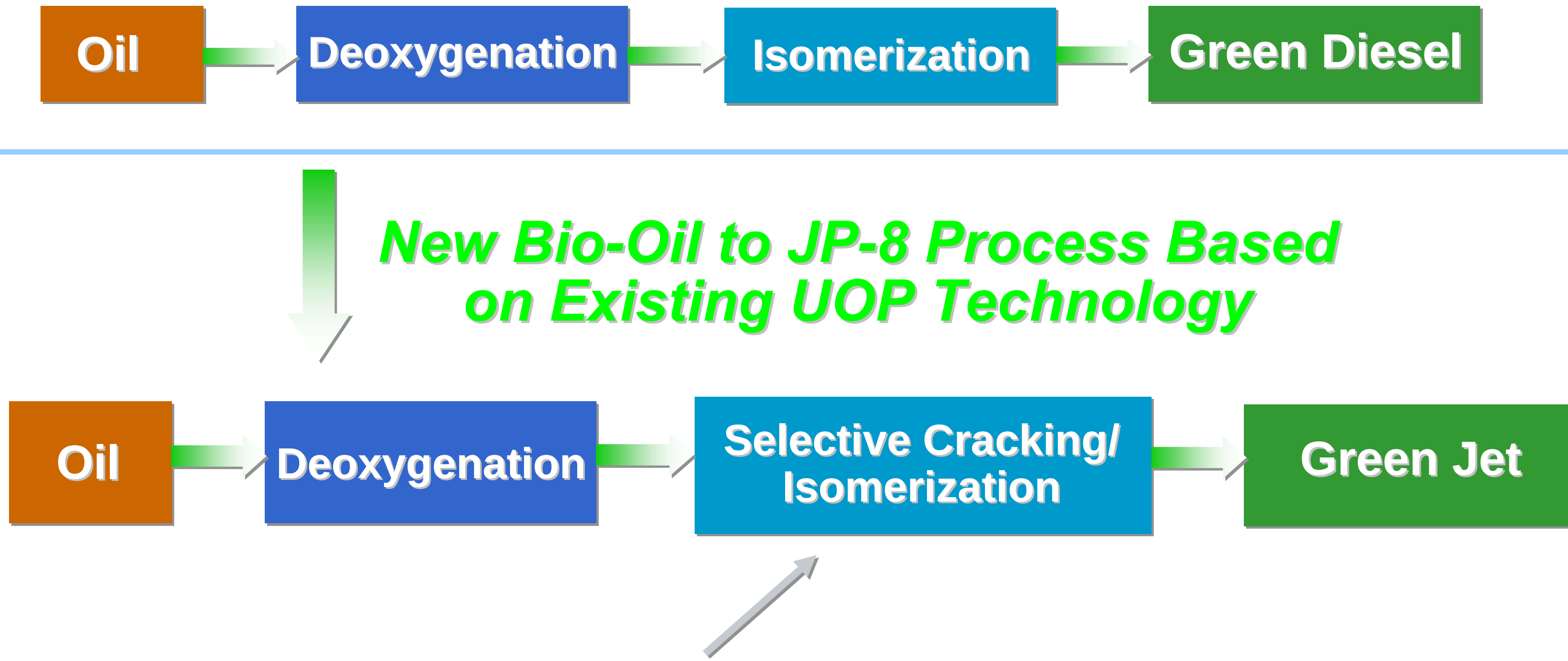


Production of Jet Fuel

Ecofining



Selective cracking: Process and catalyst development to maximize economic production of higher yields of jet-range paraffins

Production of Jet Fuel

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UOP/ENI Ecofining^{TM}

BioOil → Deoxygenation/ Isomerization → Green Diesel

New Bio-Oil to Jet Process Based on Ecofining

BioOil → Deoxygenation/ Selective Cracking/ Isomerization → Green Jet

DARPA

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Honeywell

Cargill

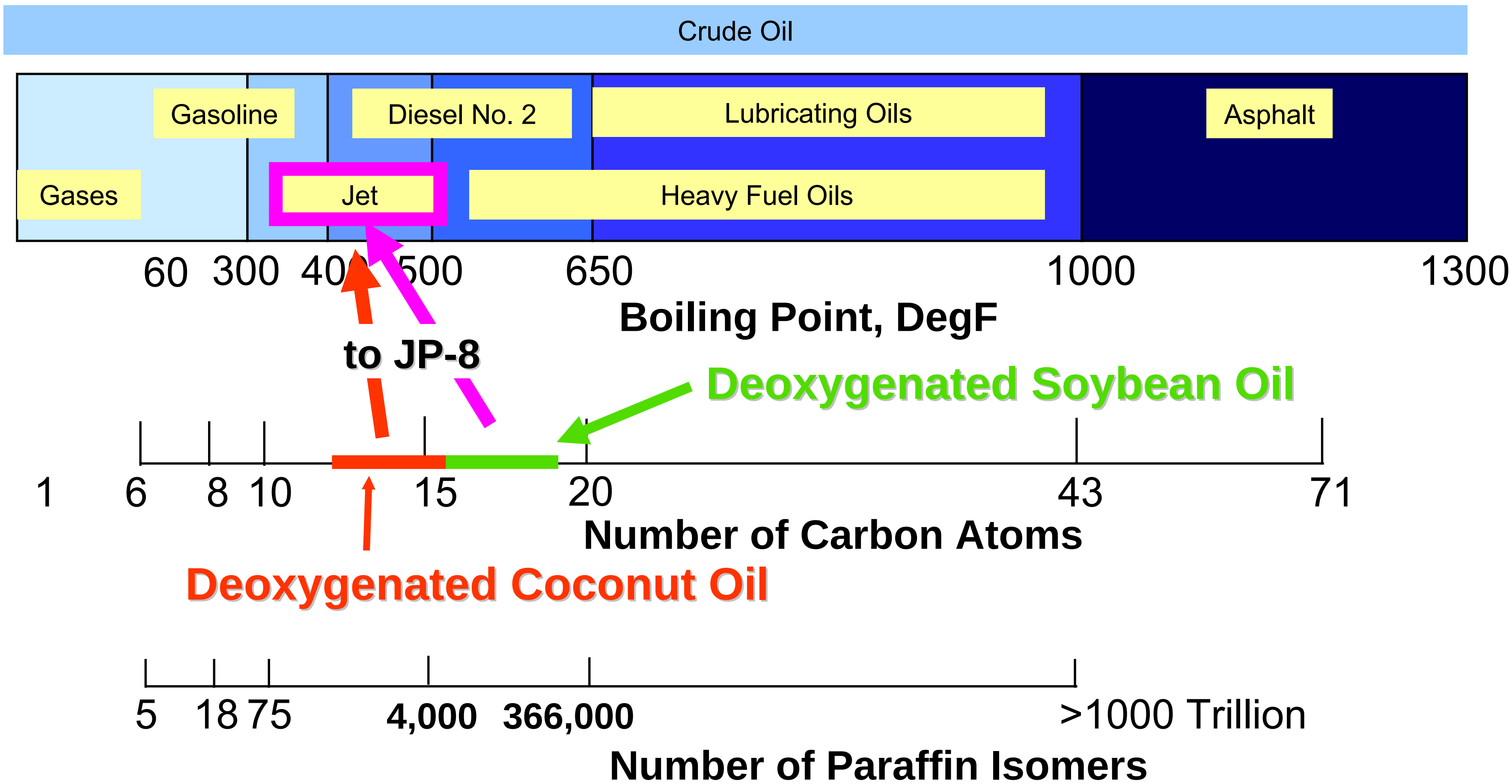
ASU Arizona State University

Southwest Research Institute

Sandia National Laboratories

Integrated Biofuels Production

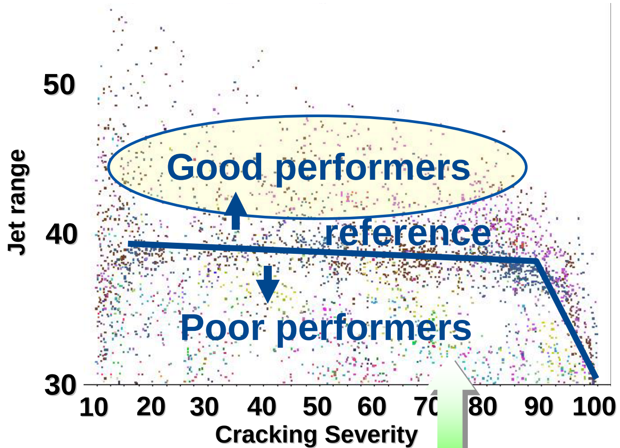
Producing jet-range fuel from deoxygenated natural oils and fats



	Carbon Chain Length									
	5-10	11	12	13	14	15	16	17	18	19+
Coconut Oil	15		49		18		8		11	0
Soybean Oil	0		0		0		11		88	0
Deoxygenated Coconut oil	15	19	29	7	11	3	5	4	6	0
Deoxygenated Soybean oil	0	0	0	0	0	4	7	35	53	0

Maximizing Jet Fuel Production

Identifying Best Catalyst Through Combinatorial Chemistry



Variables screened:
- **Acid supports**
- **Metal type/concentration**
- **Process Variables**

Pilot plant screening: Yield confirmations/ short term stability

DeOx natural oil feed

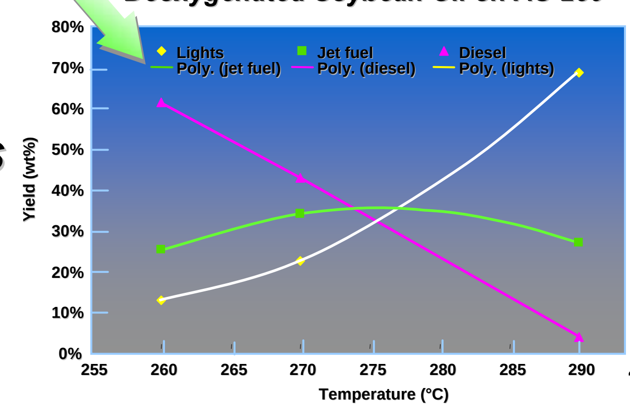
Combi Catalyst Preparation → Combi Testing → Lab Scale Preparation → Lab Plant Test Confirmation of Combi Results → Candidates for Development

g scale | ***Model feed*** | ***500g scale***

Many catalysts — *9 months* → ***6-8 candidates***

- **>70 supports**
- **>400 final catalysts (with metals)**

Deoxygenated Soybean Oil on AS-250



Combinatorial Chemistry

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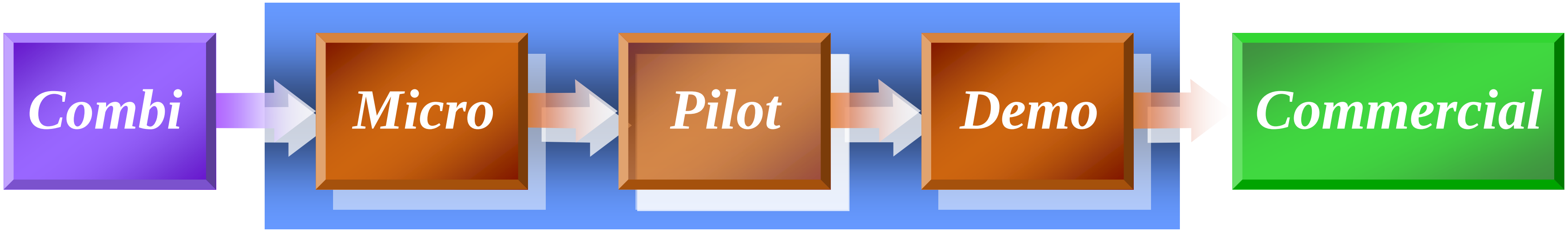
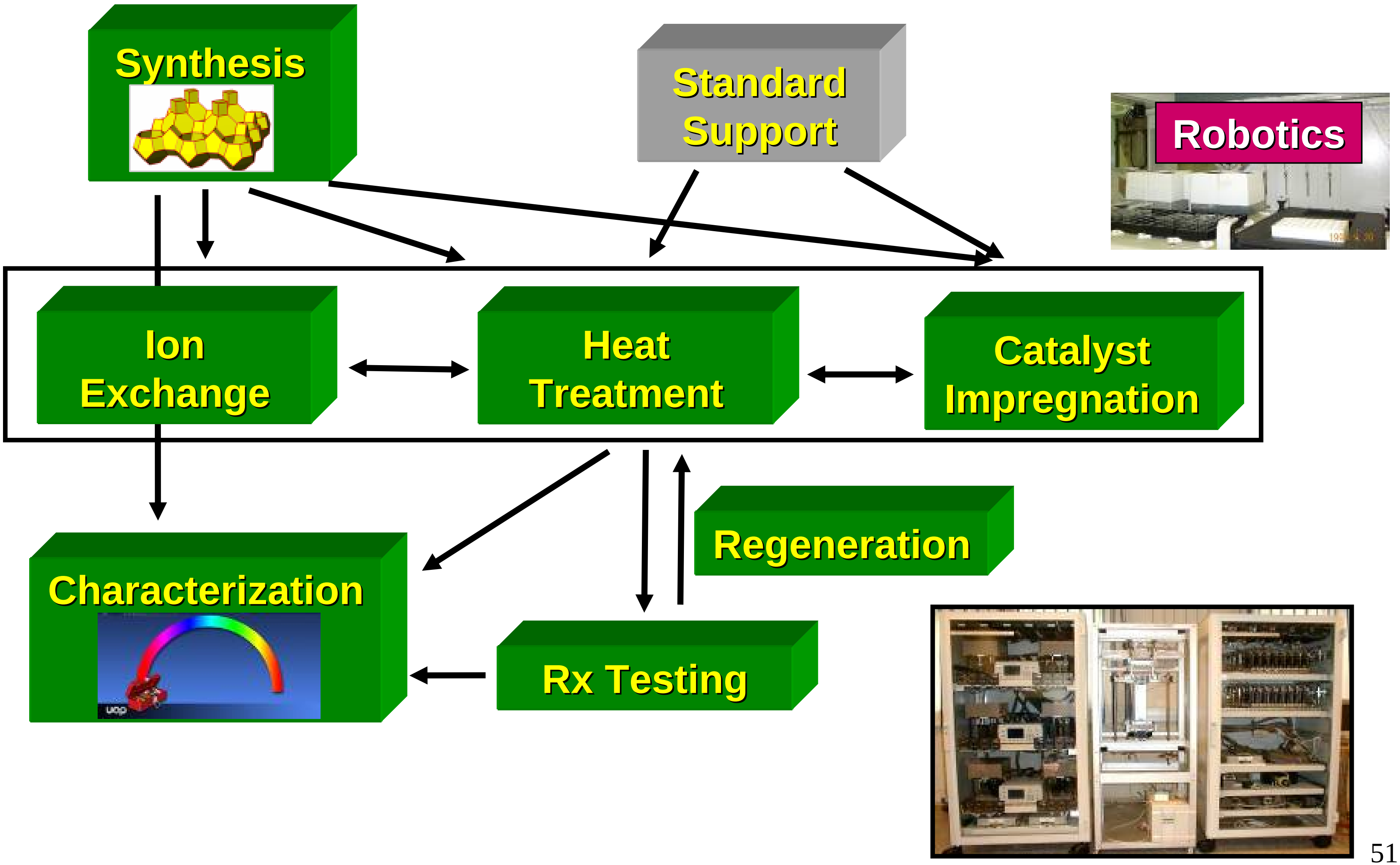
- ***Vision:*** **Utilize combinatorial tools and methods to reduce cycle time for new product invention *and* commercialization.**
- ***Implication:*** **Invent and implement combinatorial tools and methods that effectively link combi scale to pilot and commercial scales**
  - **Sample preparation is representative**
  - **Screening tests are predictive**



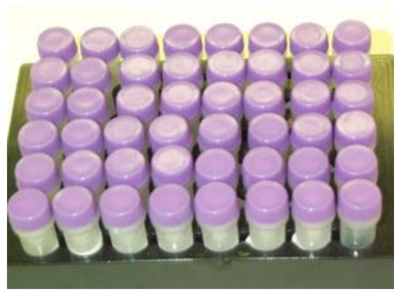
Scalable
Predictive

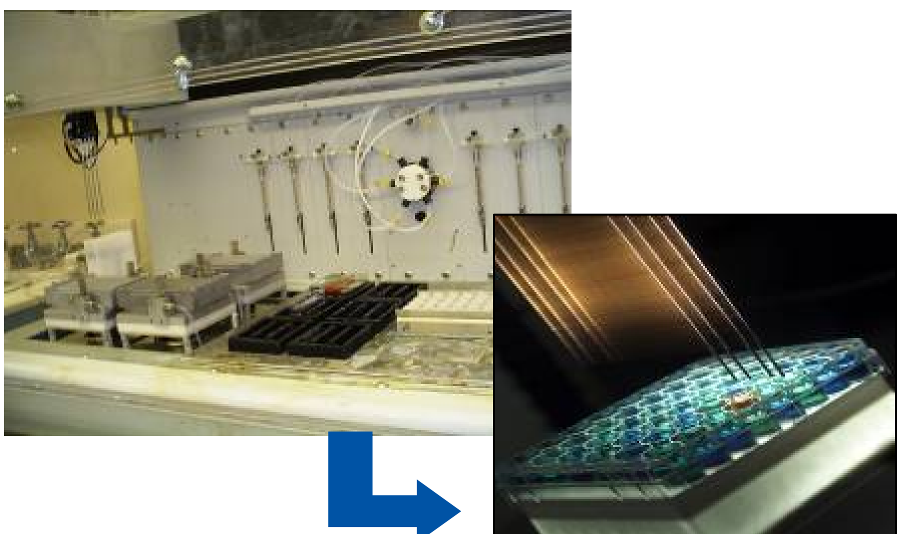
Combi Tools – Overview



Combi Tools: Catalysts Preparation

- **Standard Unit Operations:**
  - Solid dosing
  - Liquid dosing
  - Ion Exchange
  - Drying





Combi Tools: Heat Treatment

Multi-Temperature

Multi-Temperature

Multi-Flow

48

Controlled gas

Liqu

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am

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ice

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Combi Tools: Catalysts Testing

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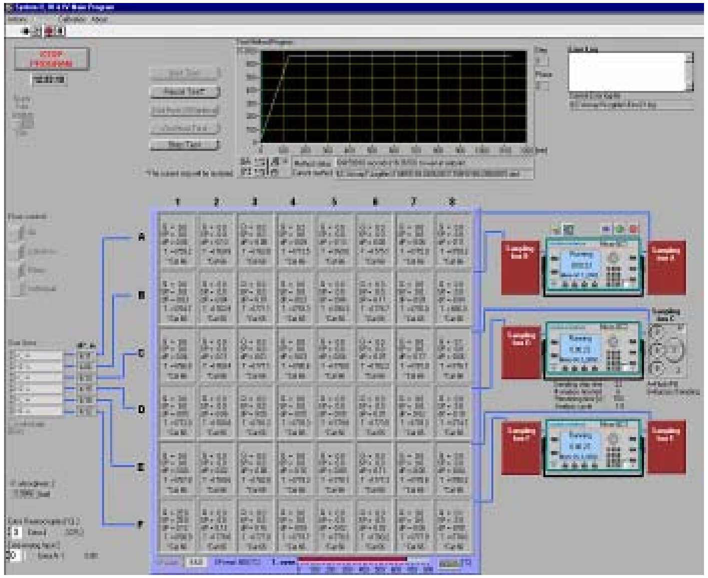
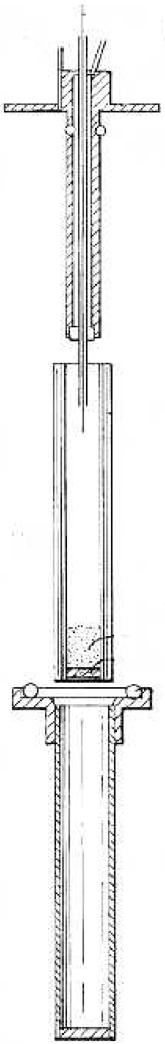
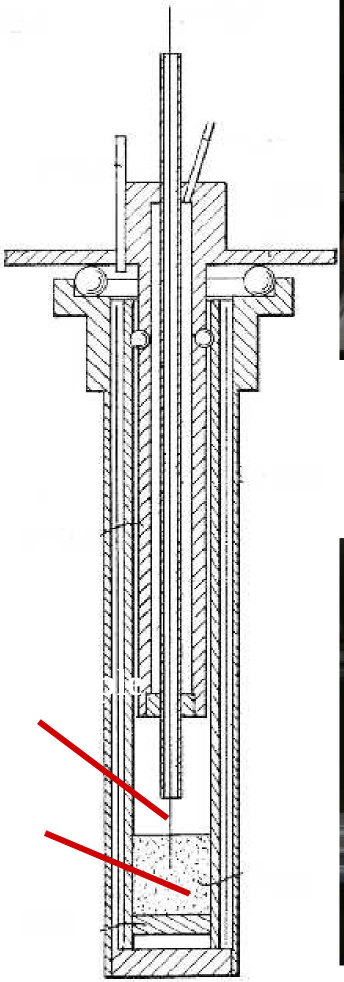
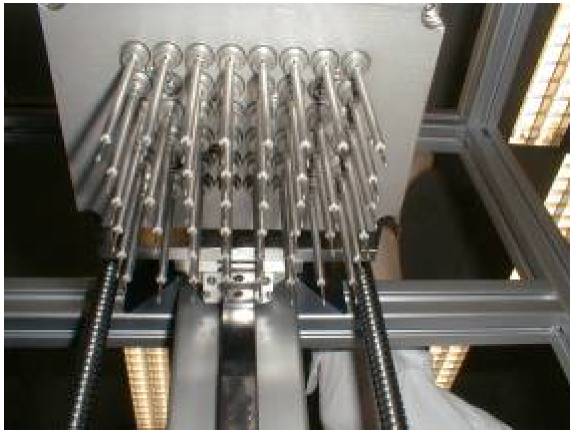
- ☑ **Realistic Conditions**
  - **Successful Miniaturization**
- ☑ **Independent Control of Variables**
  - **Temperature**
  - **Flow**
  - **Reactant Composition**
  - **Pressure**
- ☑ **Modular**
  - **Variety of Reactor Types**
  - **Inlet/Outlet Manifold**
  - **Versatile Analytical**
- ☑ **Parallel Test Design, Set-up, Control**
- ☑ **Automated On-line Monitoring**

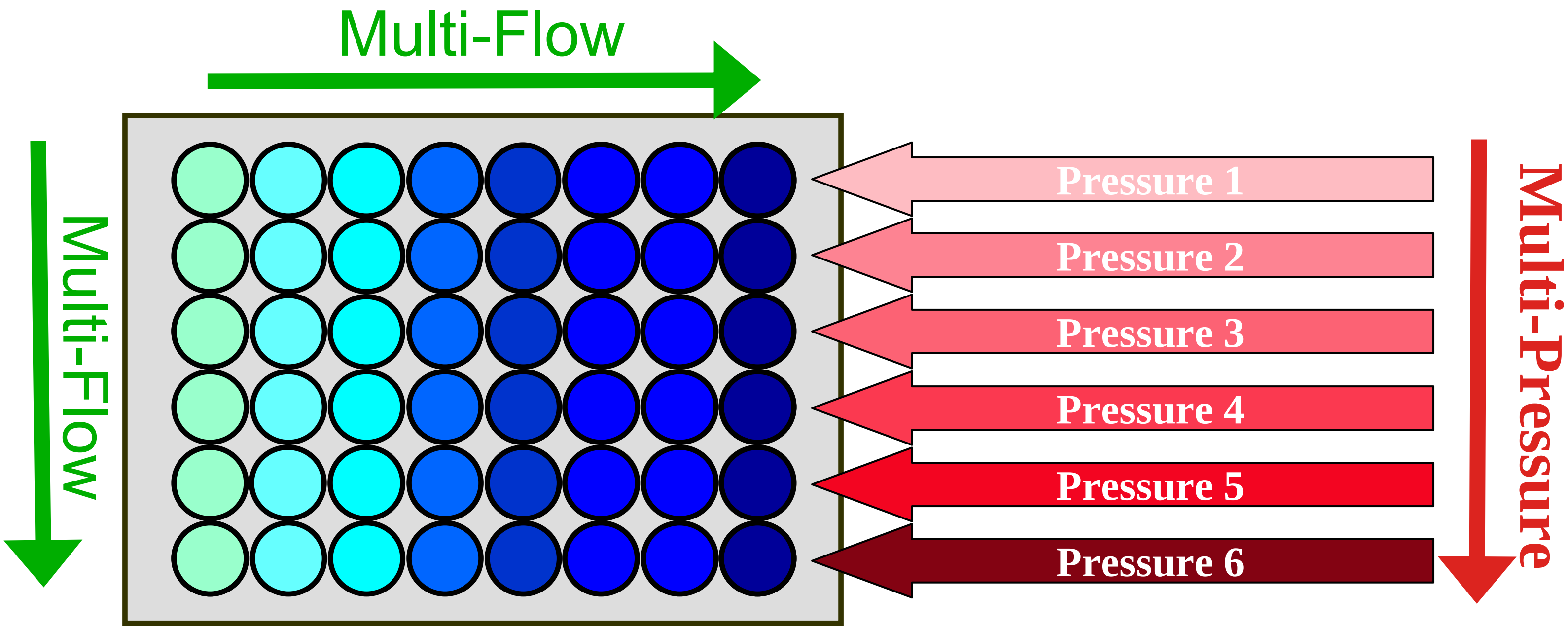








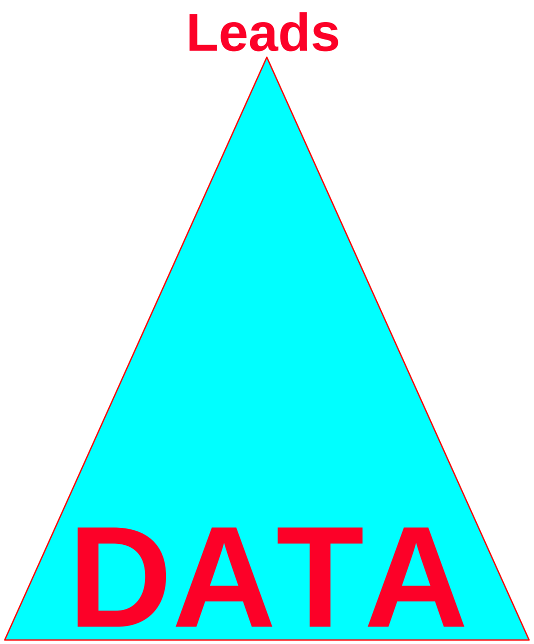
Combi Tools: Catalysts Testing, *cont*

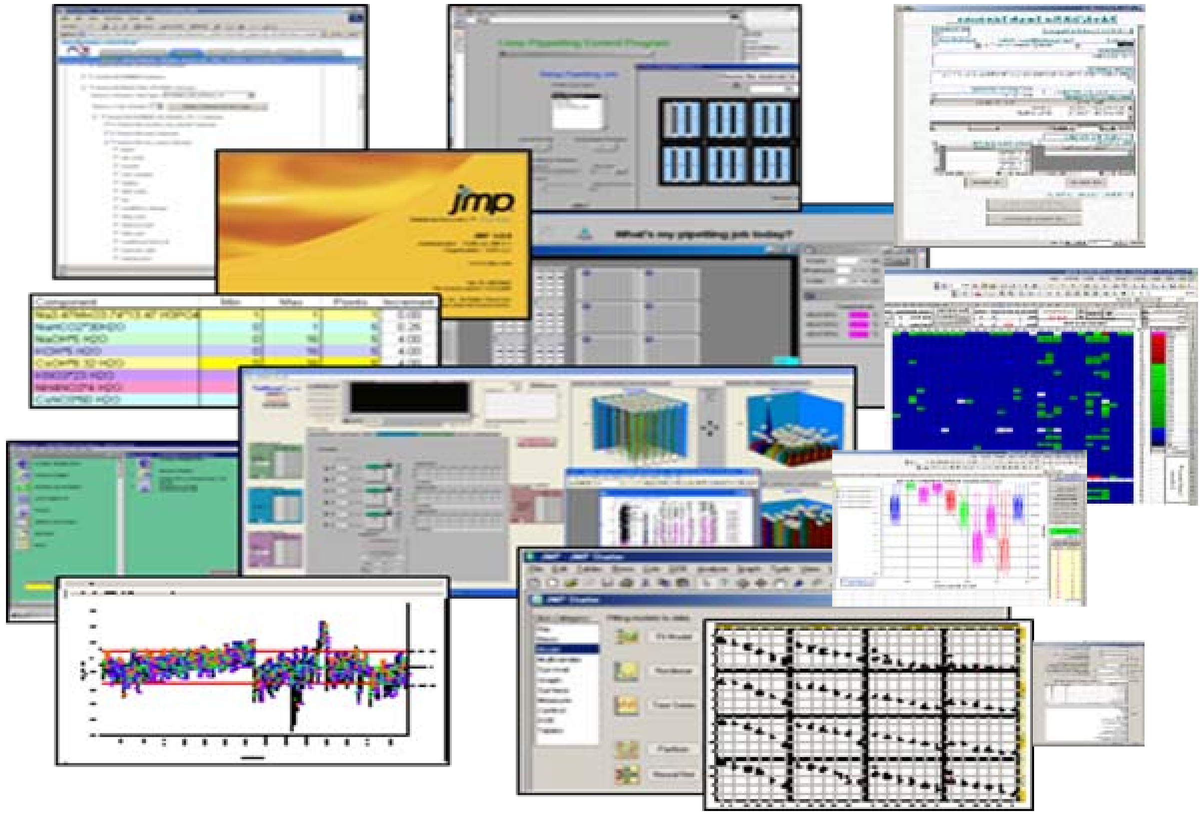


Capability	Atm Rx	High-P Rx
Vapor Phase, Plug Flow	Yes	Yes
48-Rx In-Situ Temp. Measurement	Yes	Yes
48 Independent Gas Flows	Yes	Yes
48 Independent Liquid Flows	-	Yes
In-Situ Liquid Vaporization	-	Yes
6 Independent Pressures	-	Yes

Combi Tools – Informatics

- **Combi Data**
  - Lots of it
  - Wide diversity
  - Trusted quality
- **Informatics Tools**
  - For every task
  - Manage info flow
  - Expandable
- **Integrated Workflow**
  - Multiple users
  - Multiple unit ops
  - Exercised daily





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Maximizing Jet Fuel Production

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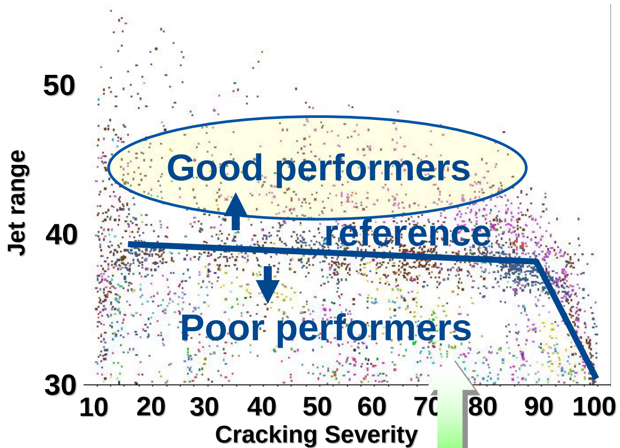
Identifying Best Catalyst Through Combinatorial Chemistry



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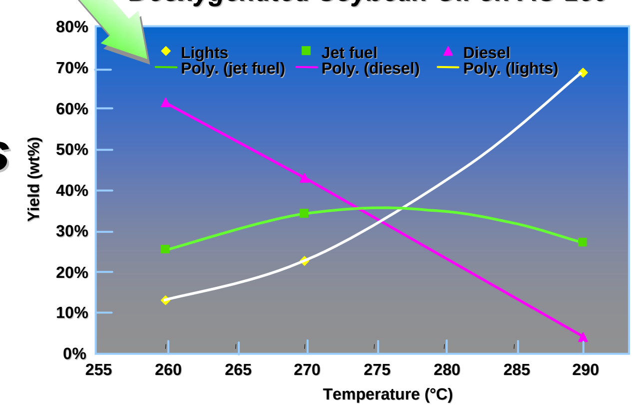
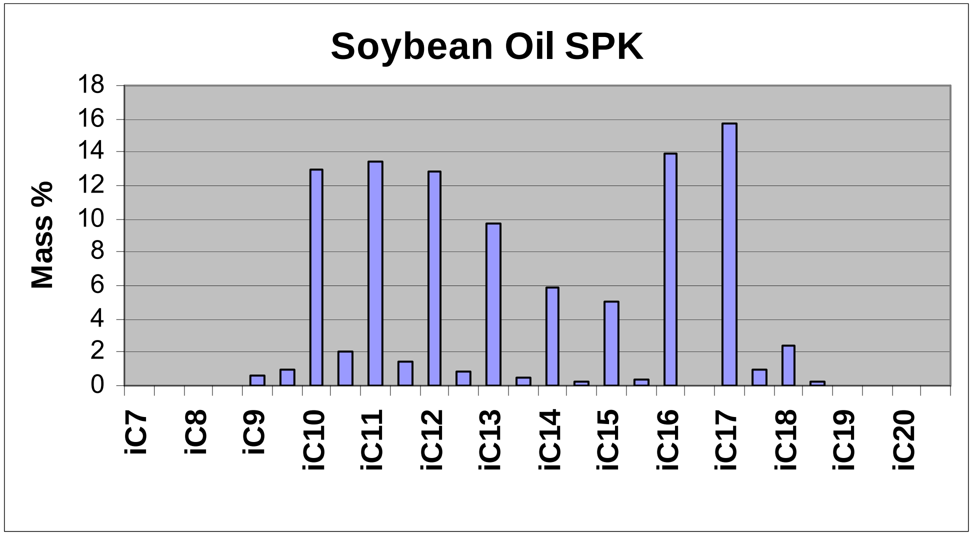
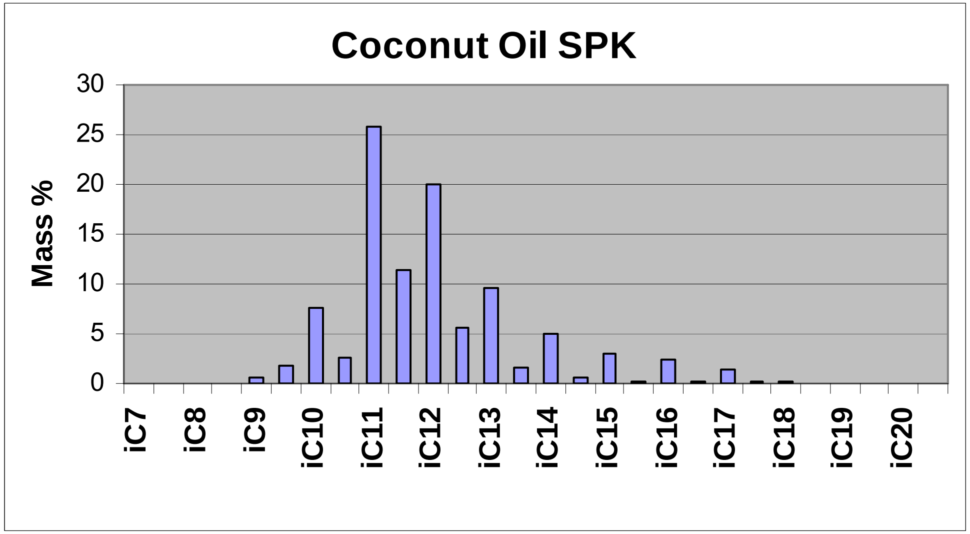
Deoxygenated Soybean Oil on AS-250



Hydrocarbon Compositions

- **Isoparaffins and normal paraffins in the jet boiling range**
- **Exact carbon number distribution varies between oil sources but can be controlled by processing targets**
- **This and FT derived synthetic paraffinic kerosines (SPK) exhibit the same characteristics; both SPK's have varied hydrocarbon compositions**





Meeting JP-8 Specifications: Aromatics to Meet Density Specs

Oil → Deoxygenation → Selective Cracking/ Isomerization → Green Jet-range Paraffins → Renewable JP-8

Aromatics (<25%) → Renewable JP-8

Sources of Aromatics

- Refinery sources
  - Aromatics complexes
  - Platforming

Properties of UOP's Bio-Based JP-8

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Property		*Jet A or Jet A-1*	*ASTM Test Method*	*Composition of JP-8 Fuel*					
				Jatropha	*Soybean*	*Coconut*	*Soybean/ Py Oil*	*Canola*	*Petroleum JP-8*
Acidity, total mg KOH/g	max	0.1	D 3242						
1. Aromatics, vol %	max	25	D 1319	24.3	15.1	22.2		22.2	18.8
	min	8	D 1319						
2. Aromatics, vol %	max	26.5	D 6379		14.9	21.2		20.5	19.6
	min	8.4	D 6379				3.2		
Volatility									
1. Physical Distillation			D 86						
Distillation temp, °C:									
10% recovered, temp (T10)	max	205		168	176	177	188	174	182
50% recovered, temp (T50)		report		182	199	188	216	196	208
90% recovered, temp (T90)		report		219	268	226	262	248	244
Final boiling point, temp	max	300		241	279	262	282	267	265
T50-T10, °C	min	15		14	23	11	28	22	26
T90-T10, °C	min	40		51	92	49	74	74	62
Distillation residue, %	max	1.5		1.1	1.4	1.4	1.4	1.4	1.3
Distillation loss, %	max	1.5		0.4	0.8	0.7	0.6	0.6	0.8
2. Simulated Distillation			D 2887						
Distillation temperature, °C									
10% recovered, temp	max	185		156.2	162.4	162	166.2	158.8	
50% recovered, temp		report		180.6	200.8	190.8	210.8	195.2	
90% recovered, temp		report		231.2	286	238	284.6	266.4	
Final boiling point, temp	max	340		273.2	302.3	292.2	308	287.6	
Flash point, °C	min	38	D 56 or D 3828	48	54	56	56	48	51
Density at 15°C, kg/m^3		775 to 840	D 1298 or D 4052	778	779	780	781	783	804
Fluidity									
Freezing point, °C	max	–40 Jet A	D 5972, D 7153, D 7154, or D 2386						
		–47 Jet A-1		-69	-50	-62	-59	-55	-51
Combustion									
Net heat of combustion, MJ/kg	min	42.8	D 4529, D 3338, or D 4809	43.5	43.2	43.2	43.7	43.2	43.2

Enablers for a Sustainable Biomass Infrastructure

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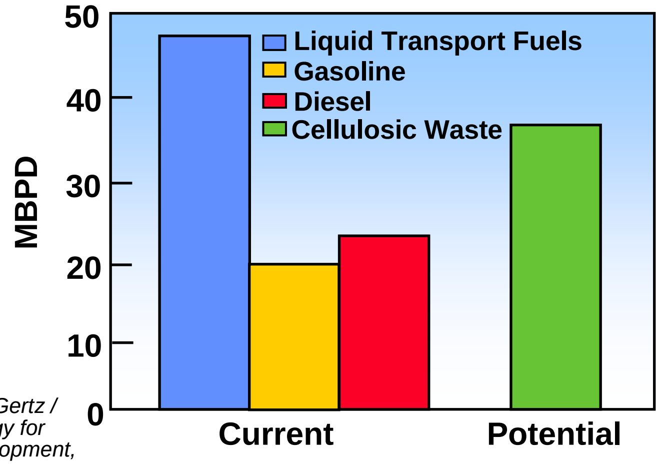
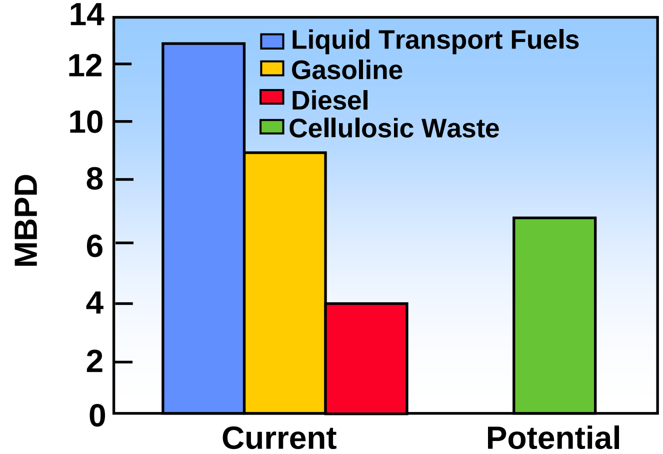
Global

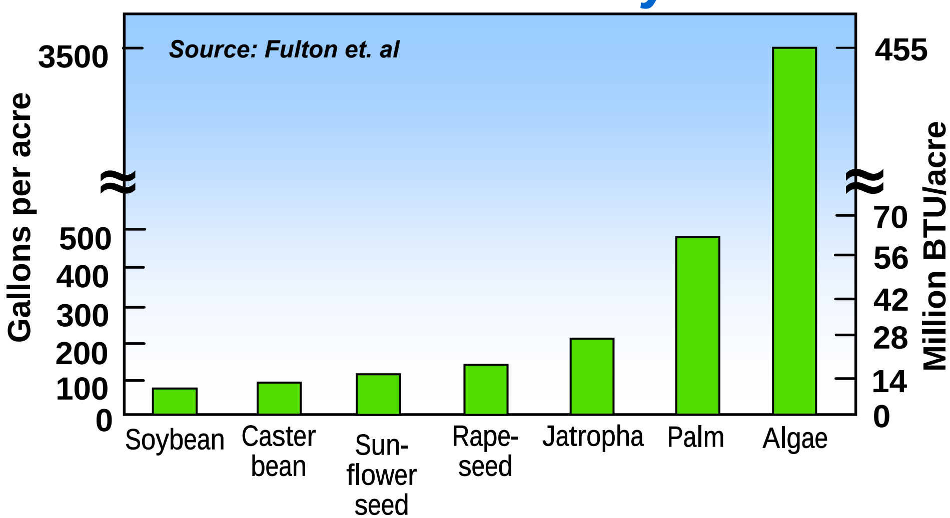


Source: Purvin & Gertz / Eric Larsen: Energy for Sustainable Development, 2000

US



Oils Productivity

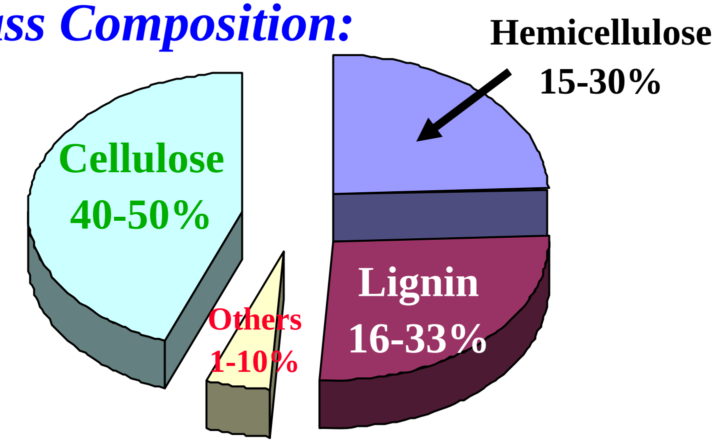


- **Cellulosic waste could make a significant contribution to liquid transportation pool.**
- **Algal Oils could enable oils route to biodiesel, Green Diesel and Green Jet.**

Increases Availability, Reduces Feedstock Cost
Technology Breakthroughs Required

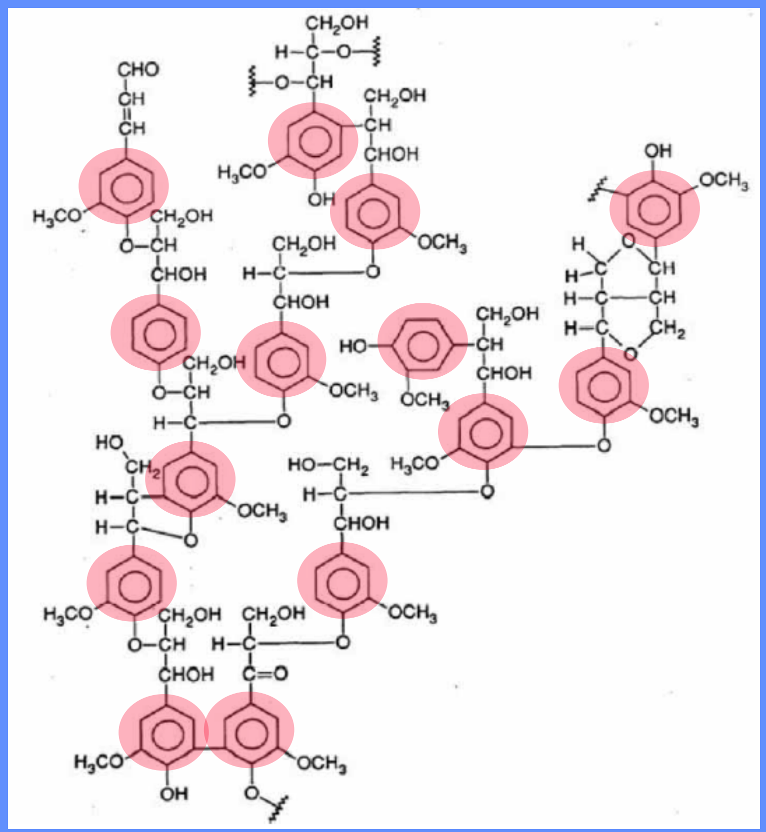
Cellulosic Background

- ***Biomass Composition:***



- ***Lignin Commercial Sources:***
  - **Major by-product from paper & pulp industry**
    - 175 million tons worldwide
    - → **31 aromatic complexes worldwide**
  - **Co-product of bioethanol production from biomass**
    - wood, forestry waste, sawdust, straw,
    - corn stover, bagasse.

Schematic Structure of Lignin

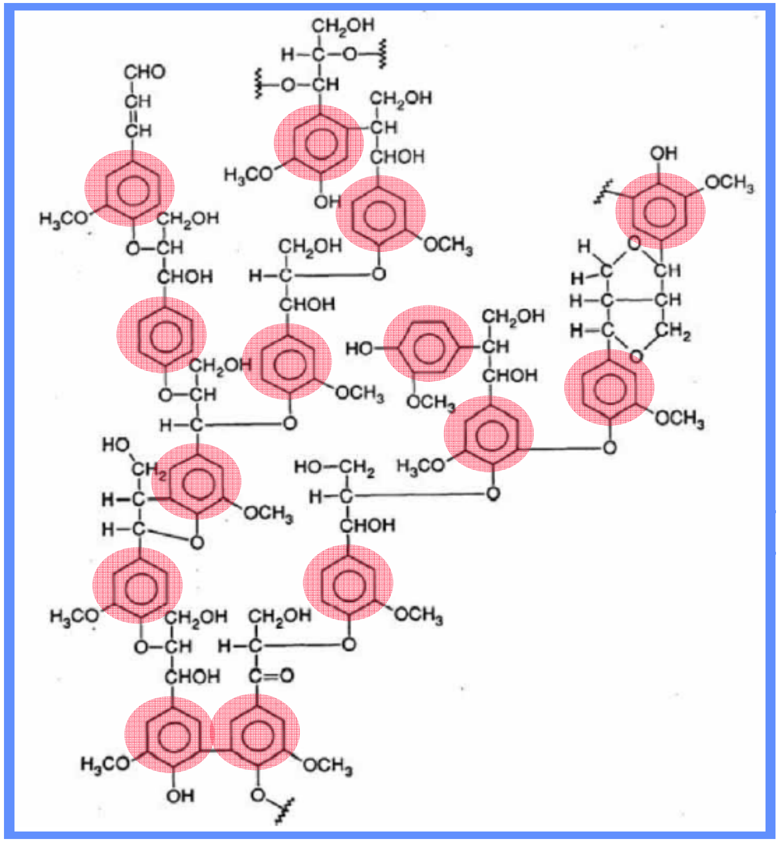


Lignin Indulin AT- 2/3 Carbon in Aromatic Ring

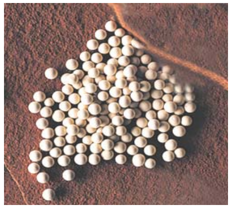
Perfect Structure for Aromatics

Lignin-to-Chemicals?

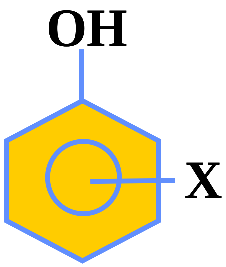
Conversion of lignin to high value oxygenates and BTX aromatics



Selectively breaking
C-O Bonds
C-C Bonds



Catalyst



Phenol Derivatives

BTX

Maintain Aromatic Ring

Lignin Conversion Studies:

- Extensively studied in the past. It's possible but very difficult!
  - Easy to form char and gases upon heating.
  - Low liquid yield via fast pyrolysis.

Comparison of Feedstock Composition and Structure

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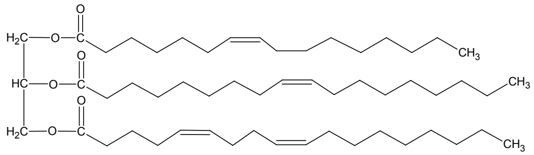
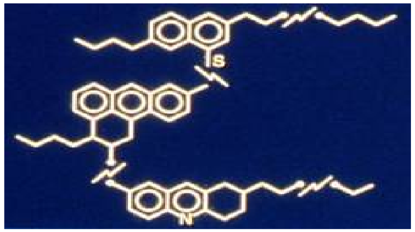
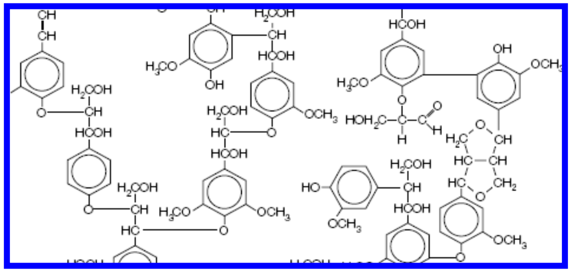
Feedstock Type	C	H	H_2O
• Vegetable oil 	1	1.77	0.23
• Asphaltene 	1	1.1	0.01
• Lignin 	1	0.32	0.33

Lignin is very poor in hydrogen

Type of Functional Groups in Lignin

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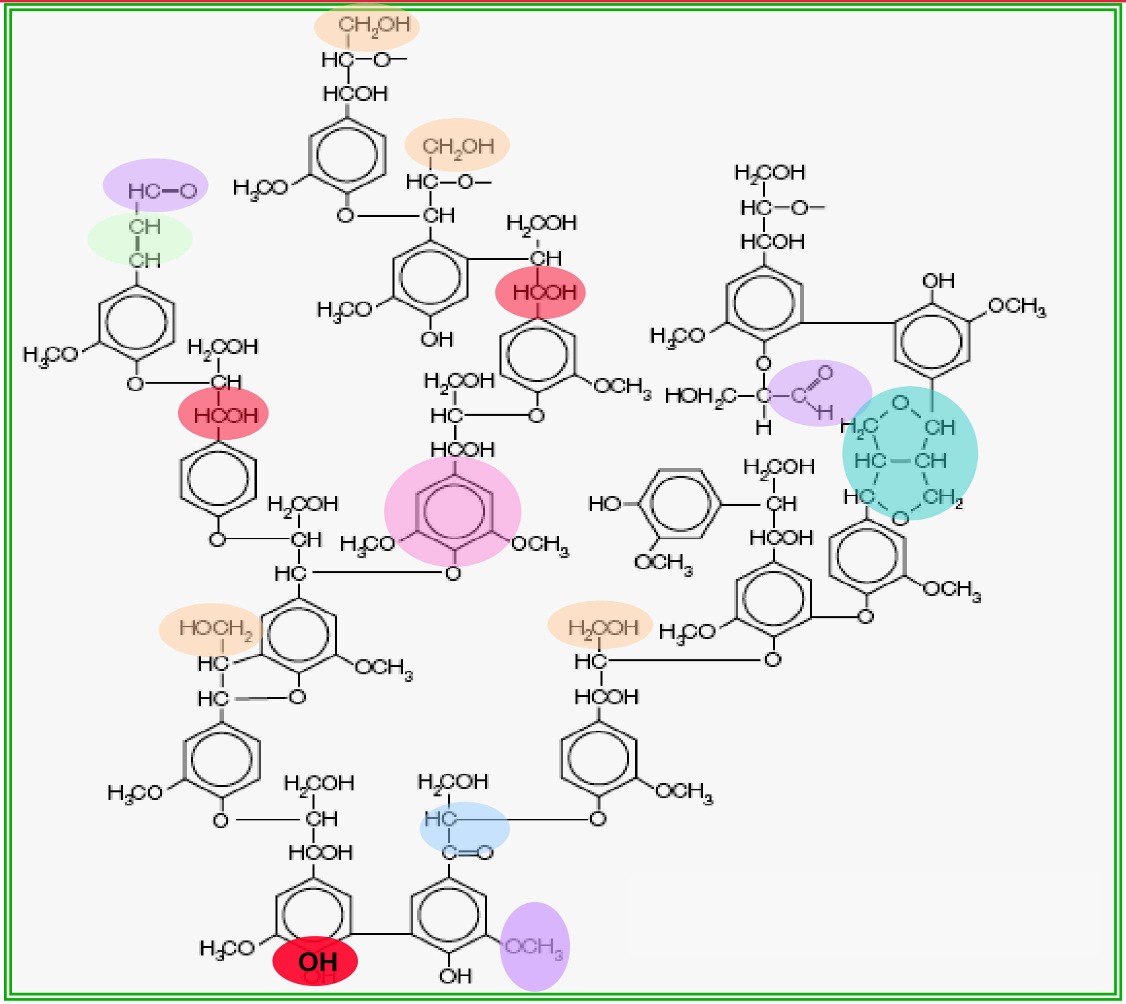

- Ketone group
- Aldehyde group
- Alicyclic group
- Primary alcohol group
- Secondary alcohol group
- Phenolic hydroxyl group
- Methoxyl group
- Alkene group
- Phenyl / Aryl group

- **<u>Rich chemistry</u>:** **Opportunities for making different chemicals**
  Challenges for processing chemistry

Lignin Base Catalyzed De-polymerization (BCD) Route

University of Utah &Sandia National Lab (US 2003/0100807 A1,US 2003/0115792 A1)

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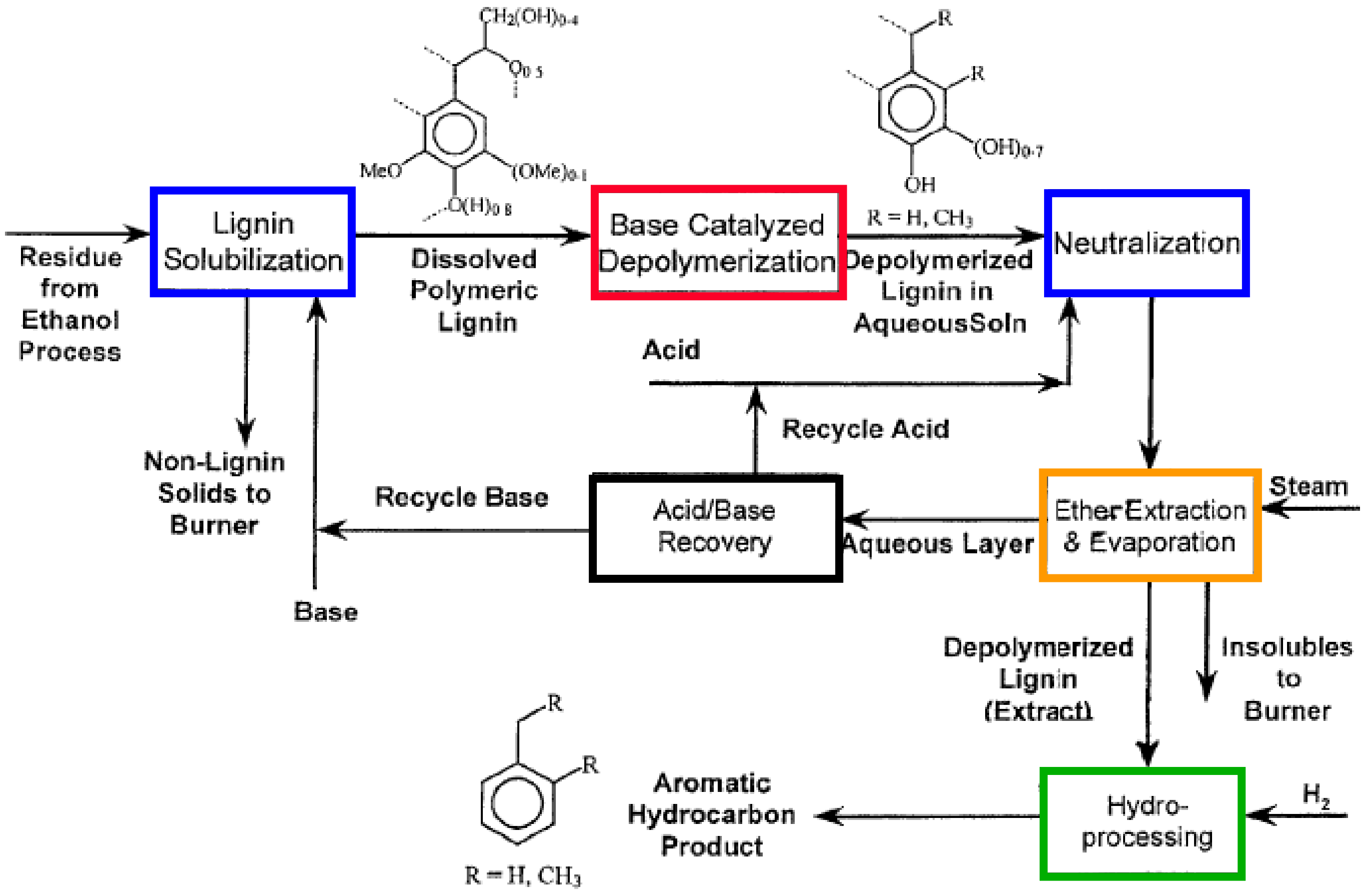

<u>Advantages</u>: - High liquid yield

- Final product has high octane (>101 octane)

- Could be used as feed for aromatics complex

Lignocellulosic Biomass to Fuels Via Pyrolysis

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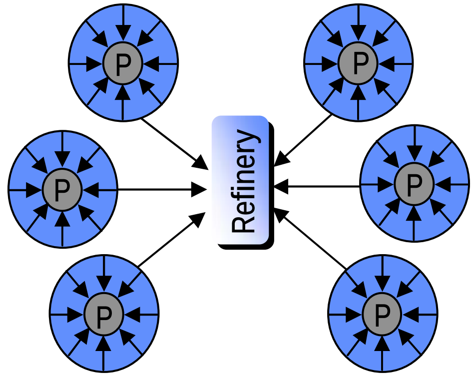


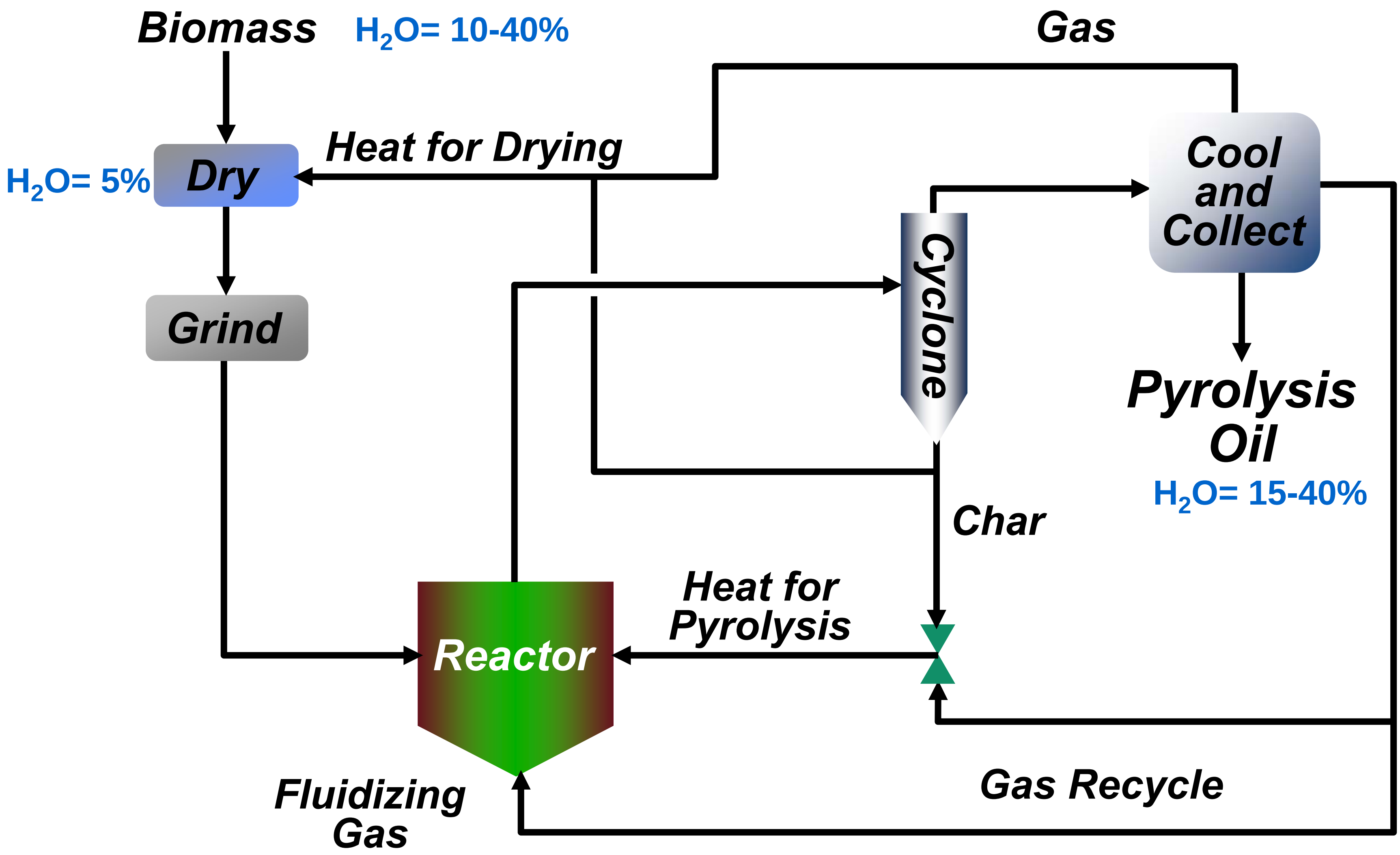
Renewable Fuel Oil

Biomass → Pyrolysis → Stabilization → Biocrude → Deoxygenate / Other Refinery Processes →

- Gasoline
- Diesel
- Jet
- Chemicals

Collaboration with DOE, NREL, PNNL

Typical Fast Pyrolysis Process



From "Fast Pyrolysis of Biomass: A Handbook." A.V. Bridgwater et al.

Biorenewable Feeds: Composition

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	Crude Typical	Resid	Soyoil	Yellow Grease	Pyrolysis Oil
% C	83-86	84.9	77.6	76.4	56.2
%H	11-14	10.6	11.7	11.6	6.6
%S	0-4 (1.8avg)	4.2	.0006	.04	-
%N	0-1 (.1avg)	.3	.0011	.03	.3
%O	-	-	10.4	12.1	36.9
H/C	1.8-1.9	1.5	1.8	1.8	1.4
Density	.86(avg)	1.05	.92	.89	1.23
TAN	<1	<1	2	30	78
ppm alkali metals	60	6	100	100	100
Heating value kJ/kg	41,800	40,700	37,200	37,200	15,200

Deoxygenated Product Properties

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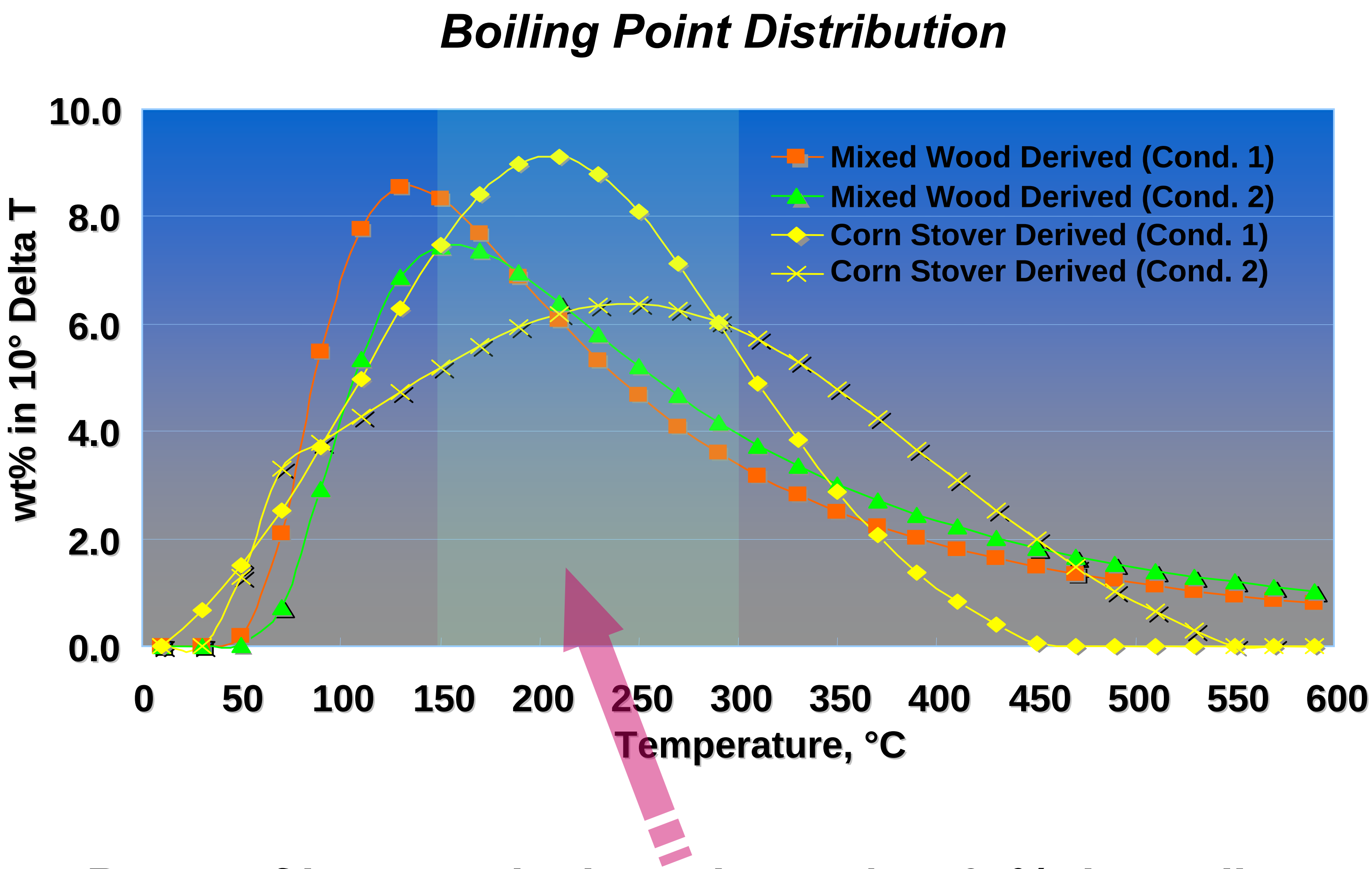
	Biofuel (from mixed wood)		Conventional (from petroleum)	
	Min	*Max*	*Gasoline Typical*	*ULS Diesel Typical*
Paraffin, wt%	5	10	44	10-60 Limited by cold flow
Iso-Paraffin, wt%	17	25		
Olefin, wt%	0.6	0.9	4	Nil
Naphthene, wt%	40	55	7	10-80
Aromatic, wt%	10	35	38	35 max Limited by emissions
Oxygenate, wt%	0.1	0.8	Nil	Nil

Hydrocarbon product rich in cyclic hydrocarbons: product can produce gasoline, jet fuel, diesel, and chemicals

Deoxygenated Pyrolysis Oil to Jet Fuel



Range of jet range hydrocarbons: 45 – 65% depending on feed source and process conditions

Meeting JP-8 Specifications: Aromatics to Meet Density Specs

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Aromatics (<25%) → Renewable JP-8

Sources of Aromatics

- Renewable sources
  - Deoxygenated pyrolysis oil

2nd Generation Renewable Jet Fuel from Oils and Biomass

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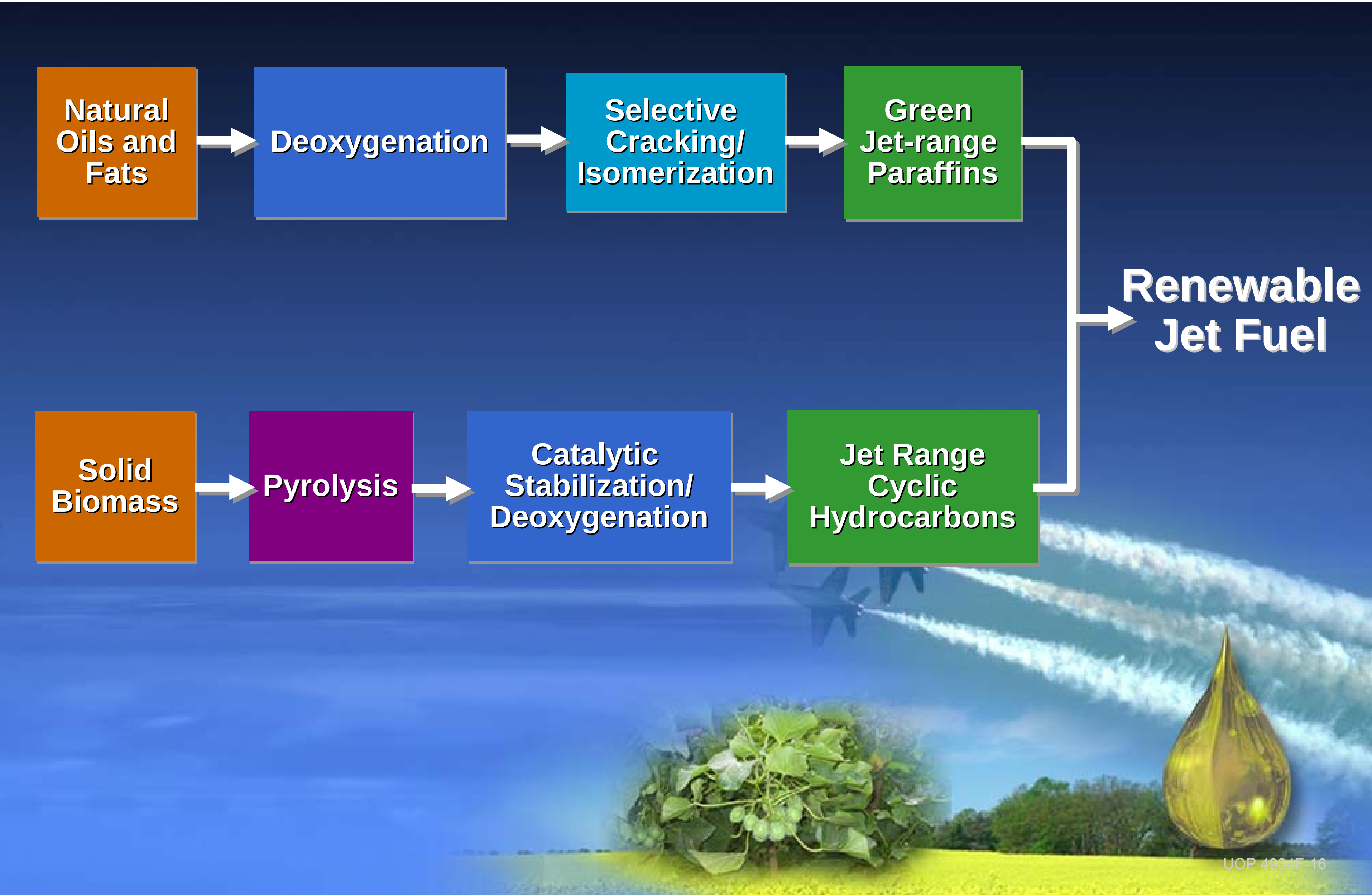
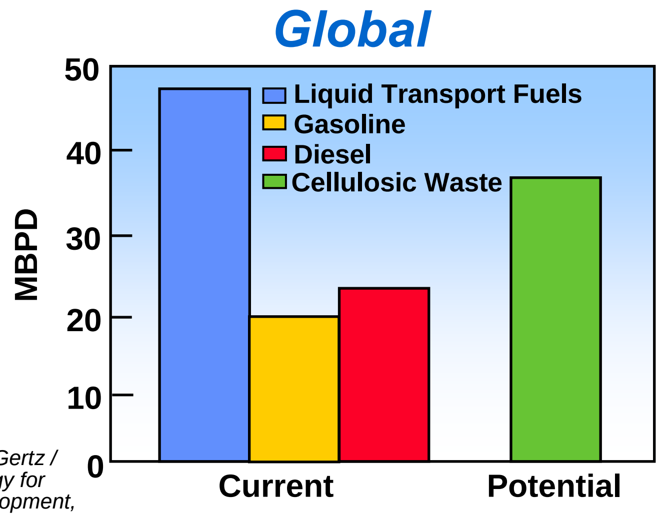
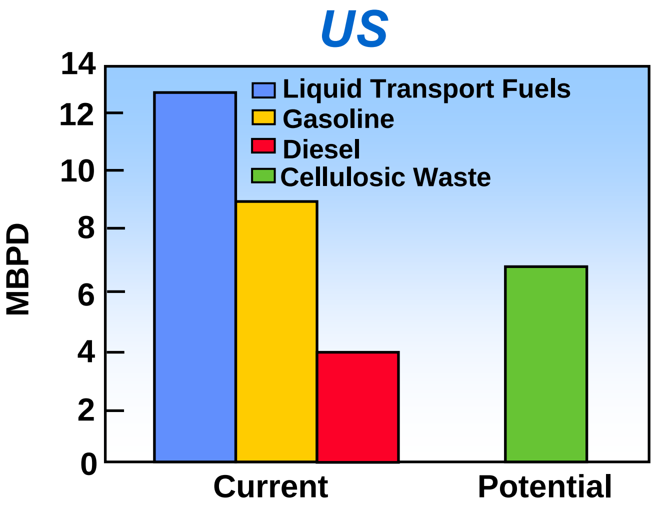
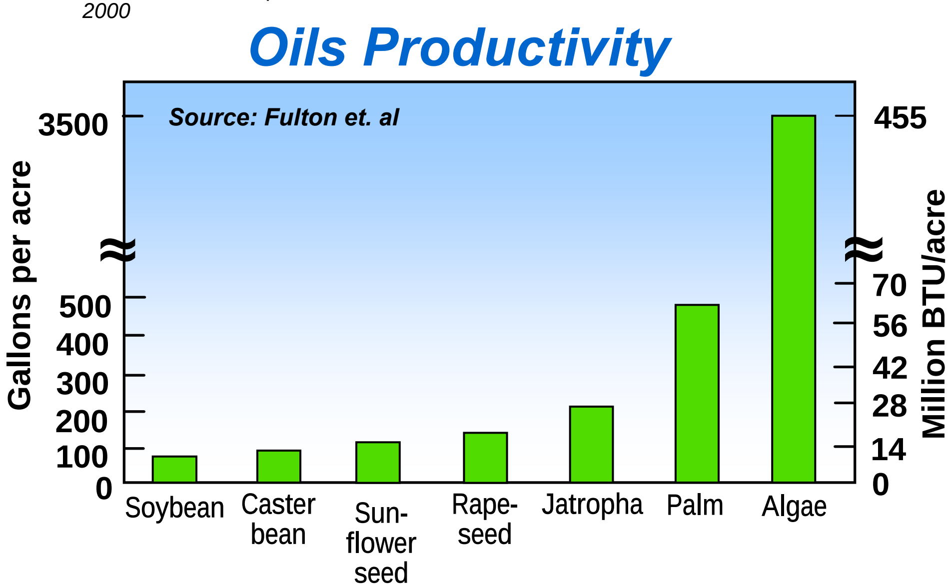


Enablers for a Sustainable Biomass Infrastructure



Source: Purvin & Gertz / Eric Larsen: Energy for Sustainable Development, 2000





- Cellulosic waste could make a significant contribution to liquid transportation pool.
- **Algal Oils could enable oils route to biodiesel, Green Diesel and Green Jet.**

Increases Availability, Reduces Feedstock Cost
Technology Breakthroughs Required

2nd Generation Renewable Fuels from Algae

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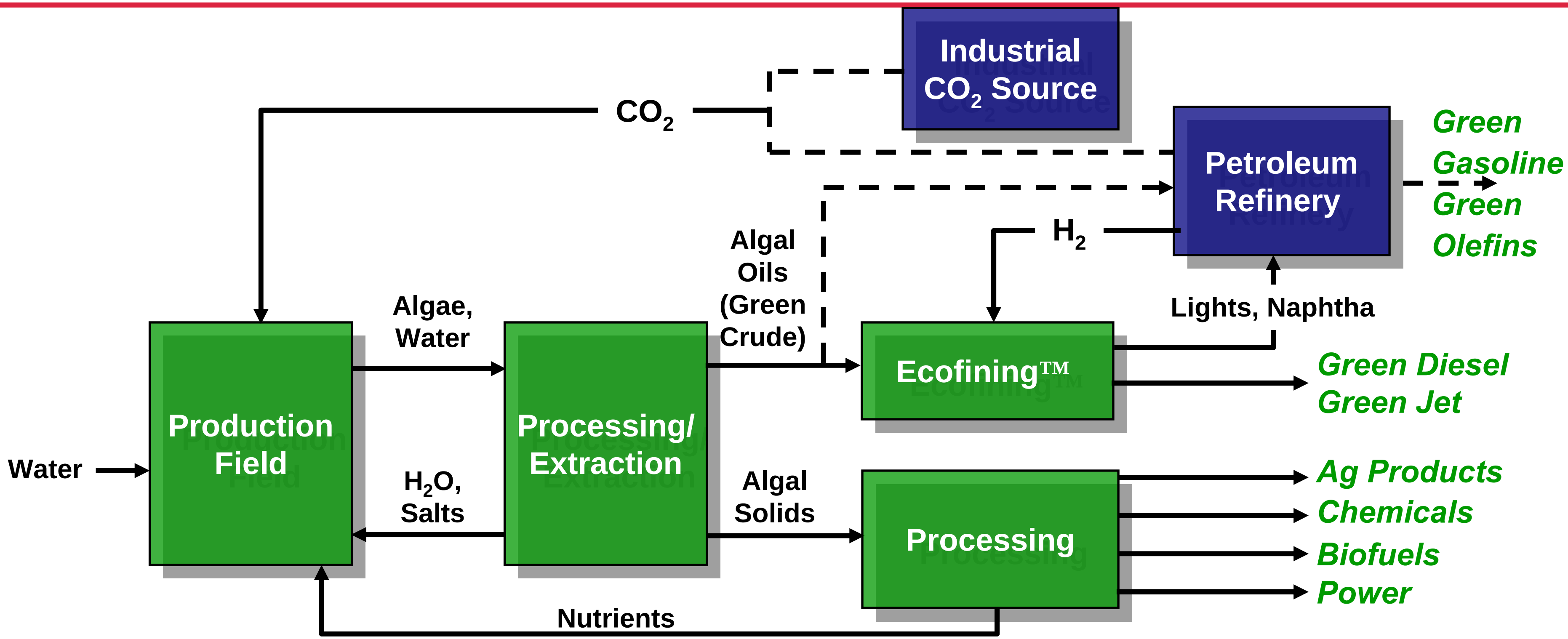
- High cellular oil content (~50% of dry weight)
- High photosynthetic efficiency (10~20%)
- Excellent CO_2 capture and sequestration capability
- Water requirement: less than 1/40 of land plants and thrive in saline/brackish/waste water
- Land requirement: desert and arid lands

Source: Q. Hu, ASU

An Integrated Algal Biorefinery



INPUTS

- CO_2 input approx. 150,000 MT/yr
- Brackish water input approx. 20000 acre-ft/yr
- 1000 acres non-arable land
- 735,000 SCFD Hydrogen

OUTPUTS

- 350bpd – Green Crude
- 110 MT/day – Solids
- Minimum 330 bpd – Green Diesel or other biofuels
- Remaining products defined by refinery configuration
- Power output defined by system economics

Advantages of Algal Feedstocks

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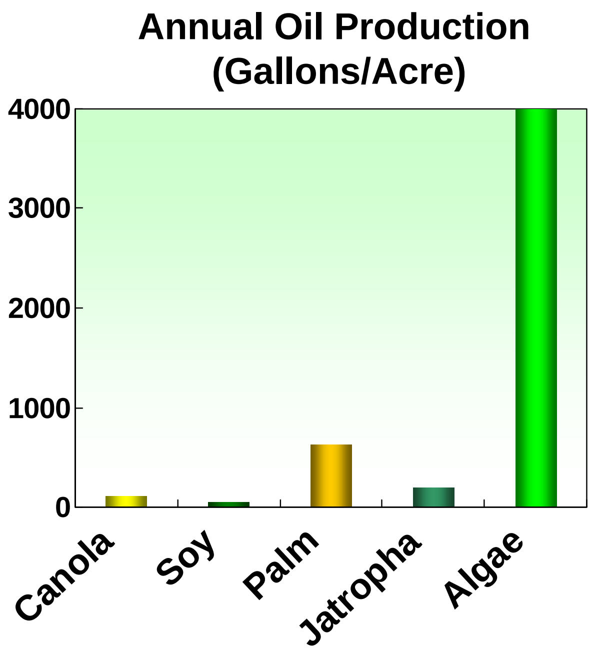
- No competition with food or agriculture
- Highest productivity per acre
- Environmentally friendly
  - Grow on low quality land
  - Grow in brackish/saline water
  - Capture CO_2
  - Recycle nutrients
- High-quality products (fuel and feed)



- Meet key requirements for economic and environmental sustainability
  - Compliant with existing infrastructure
  - Compatible with existing ground and air fleets
  - Sufficient domestic growth potential to meet demand
  - Fully renewable and compliant with GHG reduction targets

Algae-based fuels are the only biofuels meeting all criteria

Algal Oil

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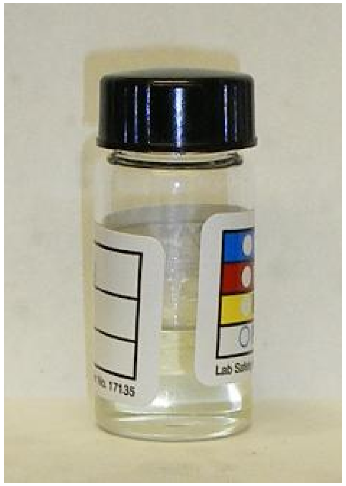
Raw Aglal Samples

Property	Palm Oil	Soybean Oil	Algae Oil #1	Algae Oil #2
Density	.915	.92	0.9169	pending
TAN	1.2	.04	0.31	1.8
% oxygen	11.2	11.3	11.0	11.0
Water,ppm	500	150	482	499
Metals (Na+Ca+K+Mg +Al),ppm	2	<1	<1	1.7
Sulfur,ppm	3	<1	3	47
Nitrogen	2	11	16 ppm	<0.1%
Chloride,ppm	2	<.1	2	pending

- 3 samples of varying quality analyzed
- Processing:
  - Deoxygenation *followed by*
  - Isomerization *and/or*
  - Cracking

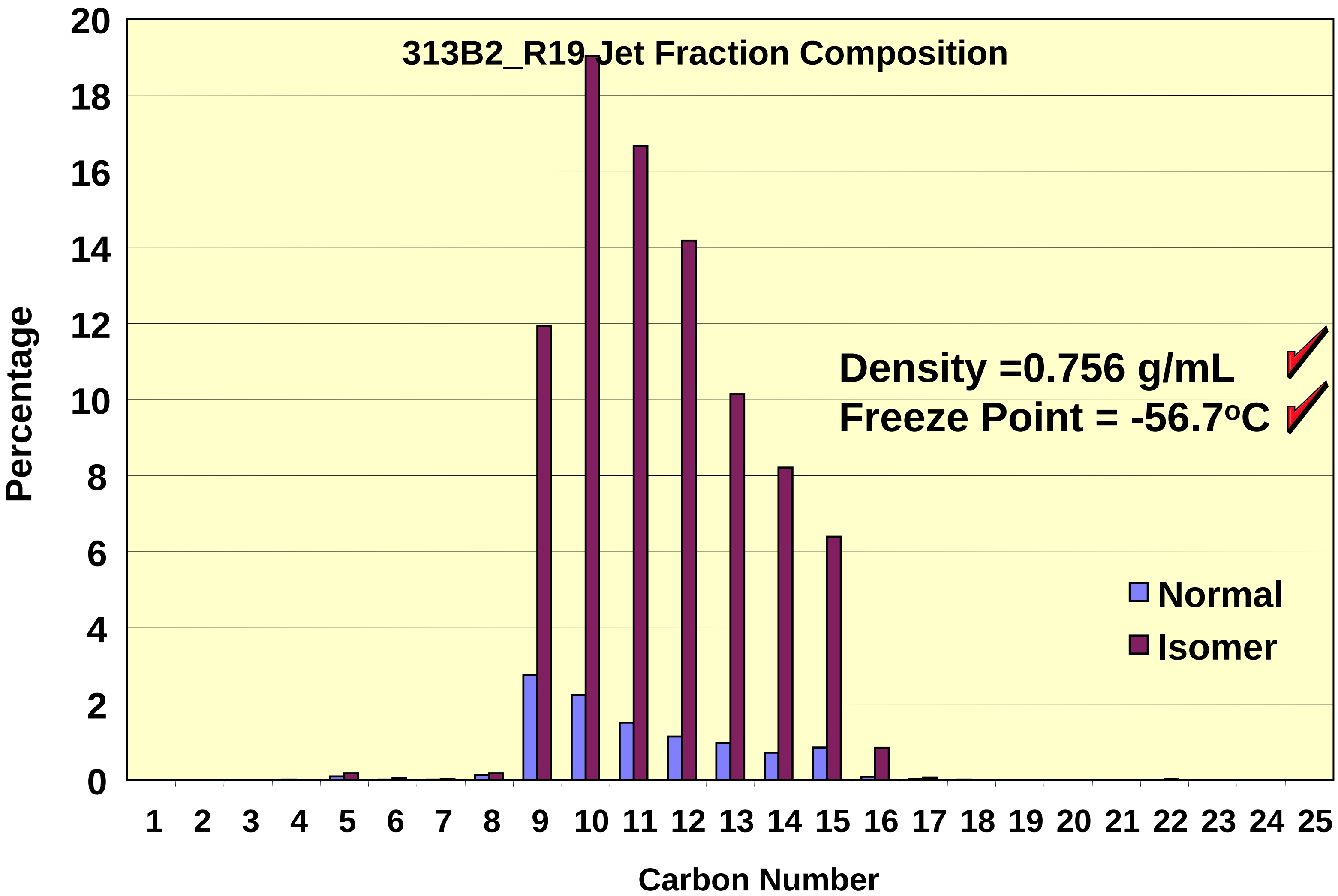


- 100% DeOxygenation achieved
- Substantially similar composition to deoxygenated natural oils
- Comparable DeOxy yields to palm
- Readily isomerizable to Green Diesel

Deoxygenated Samples

Component	Typical Product (mass %)	Algal Oil #1 Product (Mass %)	Algal Oil #2 Product (Mass %)
$<C_{15}$	0.9	1.3	2.1
C_{15} *iso*	<0.1	<0.1	1.1
C_{15} *n*	3.2	3.3	12.3
C16 *iso*	0.1	<0.1	1.7
C_{16} *n*	6.6	4.4	12.8
C_{17} *iso*	1.0	0.3	2.1
C_{17} *n*	29.2	39.8	30.0
C_{18} *iso*	2.2	0.5	2.3
C_{18} *n*	54.7	48.4	29.8
$>C_{18}$	2.1	1.9	5.7

Algal Oil #2: Deoxygenated & Isomerized - Properties



Density =0.756 g/mL ✓

Freeze Point = -56.7°C ✓

JP-8 SPK quality specs met

2nd Generation bio-feedstocks

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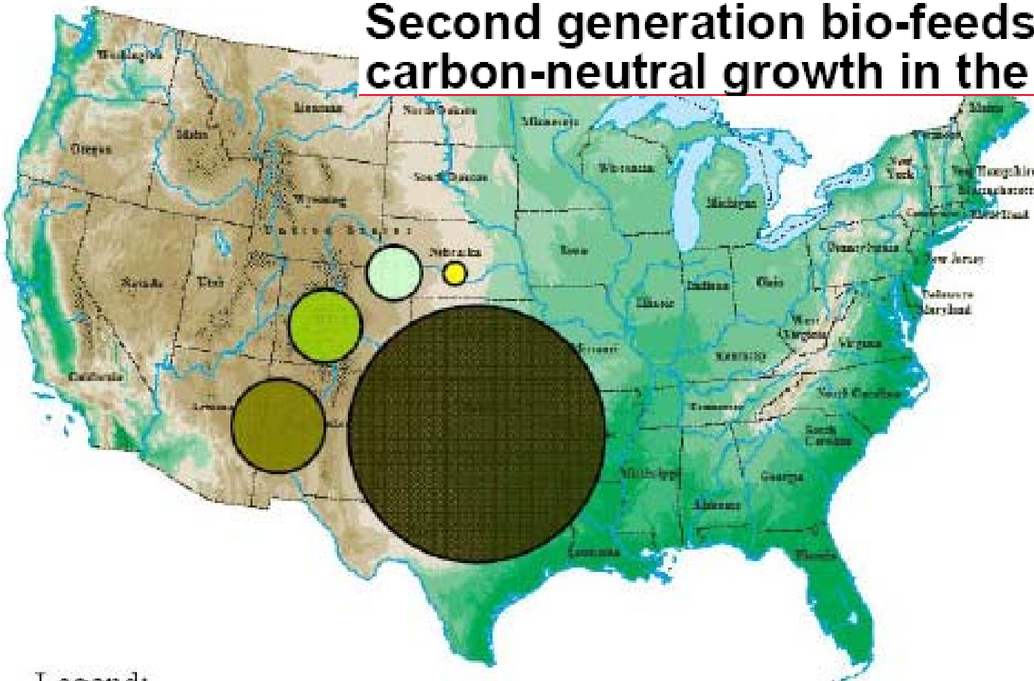
Second generation bio-feedstocks can make carbon-neutral growth in the aviation industry possible*



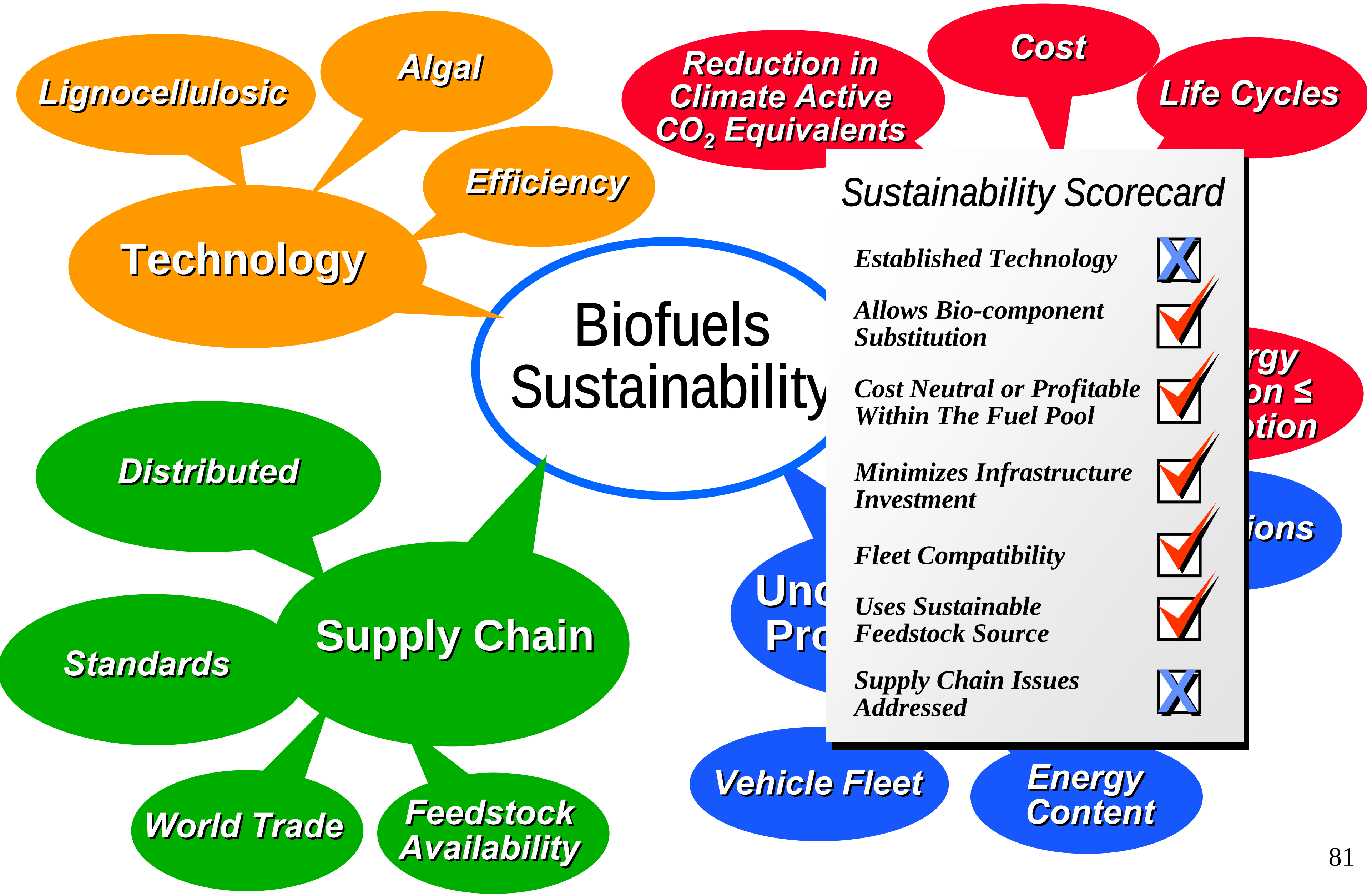
Legend:
- Soy oil (oil yield~550L/ha)
- Herbaceous biomass (using F-T process with ~11,000 kg biomass/ha)
- Palm oil (oil yield ~5600 L/ha)
- Feedstock B (oil yield~10,000L/ha)
- Feedstock C (oil yield~50,000L/ha)

} 2nd Generation Feedstock such as algal oil

Figure 6: Land Requirement to Maintain Carbon-neutral Aviation Growth in 2025 Using Varied Feedstocks (Map taken from http://www.united-states-map.com/us402112.htm)

* **Life-cycle Assessment of Greenhouse Gas Emissions from Alternative Jet Fuels by Hsin Min Wong** submitted to the Engineering Systems Division on August 8, 2008 in Partial Fulfillment of the Requirements for the Degree of Master of Science in Technology and Policy

Renewable Fuels: Unlocking the Potential



Achieving Sustainability

- Renewables are going to make up an increasing share of the future fuels pool
  - Multitude of bioprocessing approaches possible
  - Fungible biofuels are here
- First generation biofuels, though raw material limited, are an important first step to creating a biofuels infrastructure.
- Second generation feedstocks, cellulosic waste and algal oils, have the potential to make significant contributions.
- Important to promote 1) R&D&E investment, and 2) technology neutral and performance based standards and directives to avoid standardization on old technology.

Catalyst Development

- There are many, many opportunities for catalyst discovery and development.
- In most cases catalysts have not been optimized.
- Reaction mechanisms not known – e.g. how to control lignin depolymerization.
- Deoxygenation vs. debarboxylation – how to selectively control these?
- How to increase yield of pyrolysis oil?

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