Feed-Flexible Processing of Oil-Rich Crops to Jet Fuel

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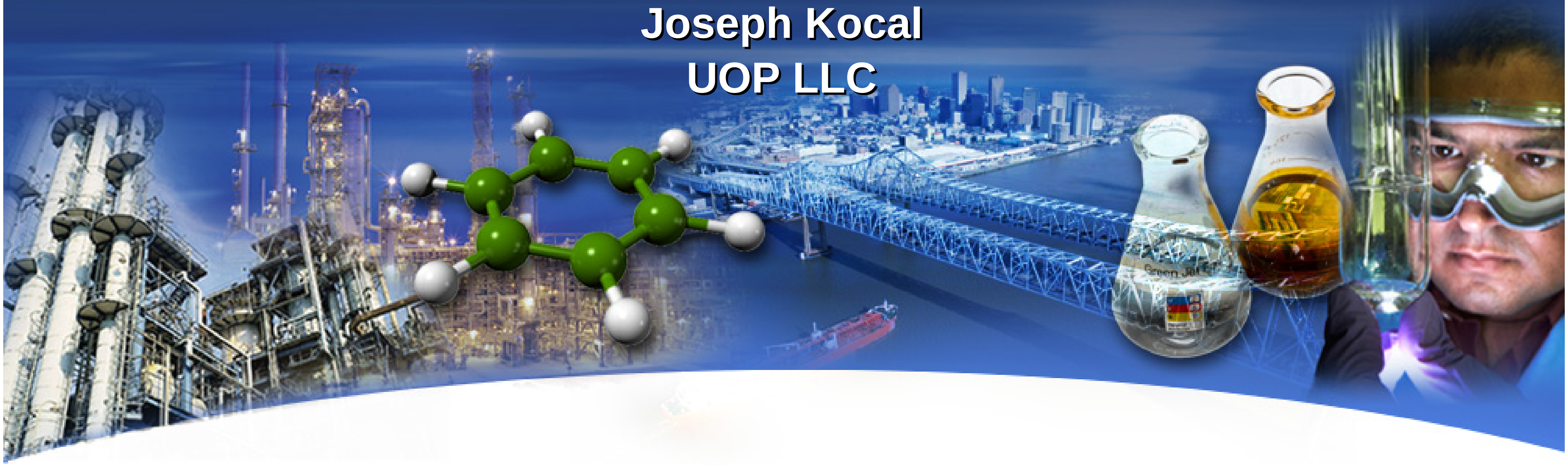

2008 AIChE Meeting
Chicago, IL
September 23, 2008

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Outline

- Background
- 1[ST] Generation Renewable Jet Fuel
  - Natural oils and fats to JP-8
- 2[nd] Generation Renewable Jet Fuel
  - Lignocellulosic biomass to jet
  - Algae to jet
- Summary

Where is Biofuels Technology Headed?

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Fuel Additives / Blends

Ethanol | Biodiesel

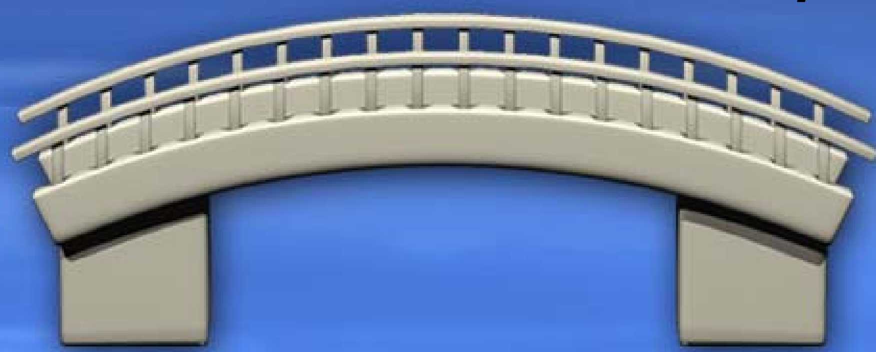
Fuels

Diesel | Jet | Gasoline

UOP's Bio-Fuels Technology Goals

Identify and utilize processing, composition, and infrastructure synergies to lower capital investment, minimize value chain disruptions, and reduce investment risk.

Inedible Oils: Camelina, Jatropha



Generation 1

- Vegetable oils to diesel, gasoline and jet fuel

Generation 2

- Lignocellulosic biomass to fuels
- Algal oils to fuels

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DARPA-funded Project for Renewable JP-8 Production

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Overall Program Objective

1. **Demonstrate a process for conversion of natural oils and fats to on-spec JP-8 that is technically and economically feasible**
2. **Identify viable technology to increase volume and reduce cost of renewable-oil crops**

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Honeywell
Cargill™
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Sandia National Laboratories

DARPA, Project W911NF-07-C-0049
Dr. Douglas Kirkpatrick

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

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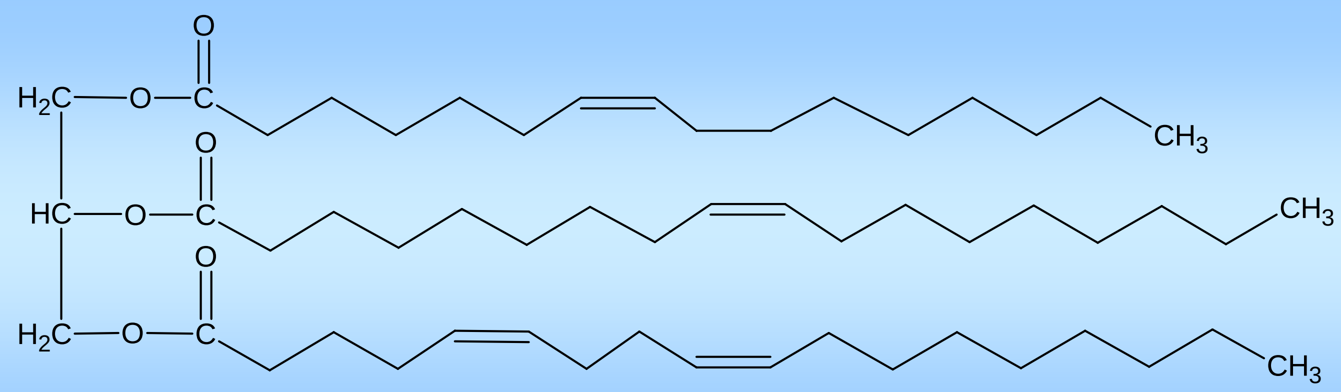
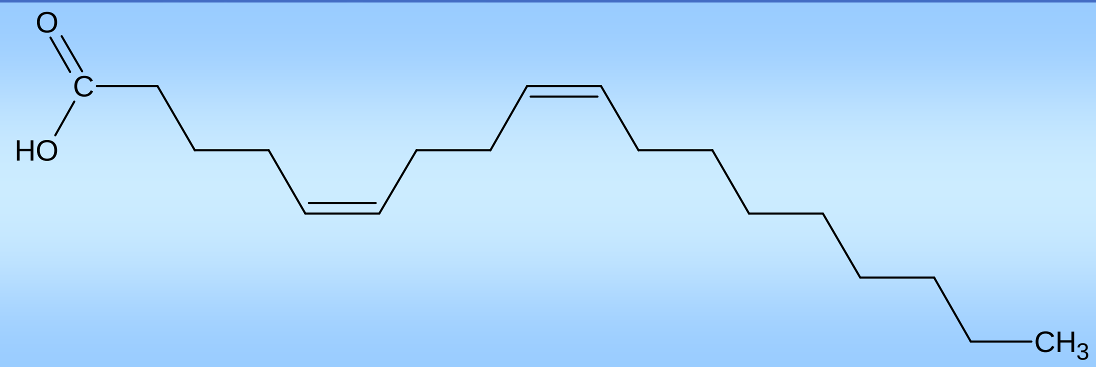
Triglycerides *MW = 700-900*



Fatty Free Acids *MW = 200-300*



Green Jet Reactions

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- **Olefin Saturation**
- **Decarboxylation/Decarbonylation**

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

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

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

- **Hydrodeoxygenation**

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

- **Hydroisomerization**

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

- **Hydrocracking**

$$iC_n \xrightarrow[\text{Catalyst}]{H_2} iC_{n-y} + iC_y$$

Producing Jet-range Fuel from Deoxygenated Natural Oils and Fats

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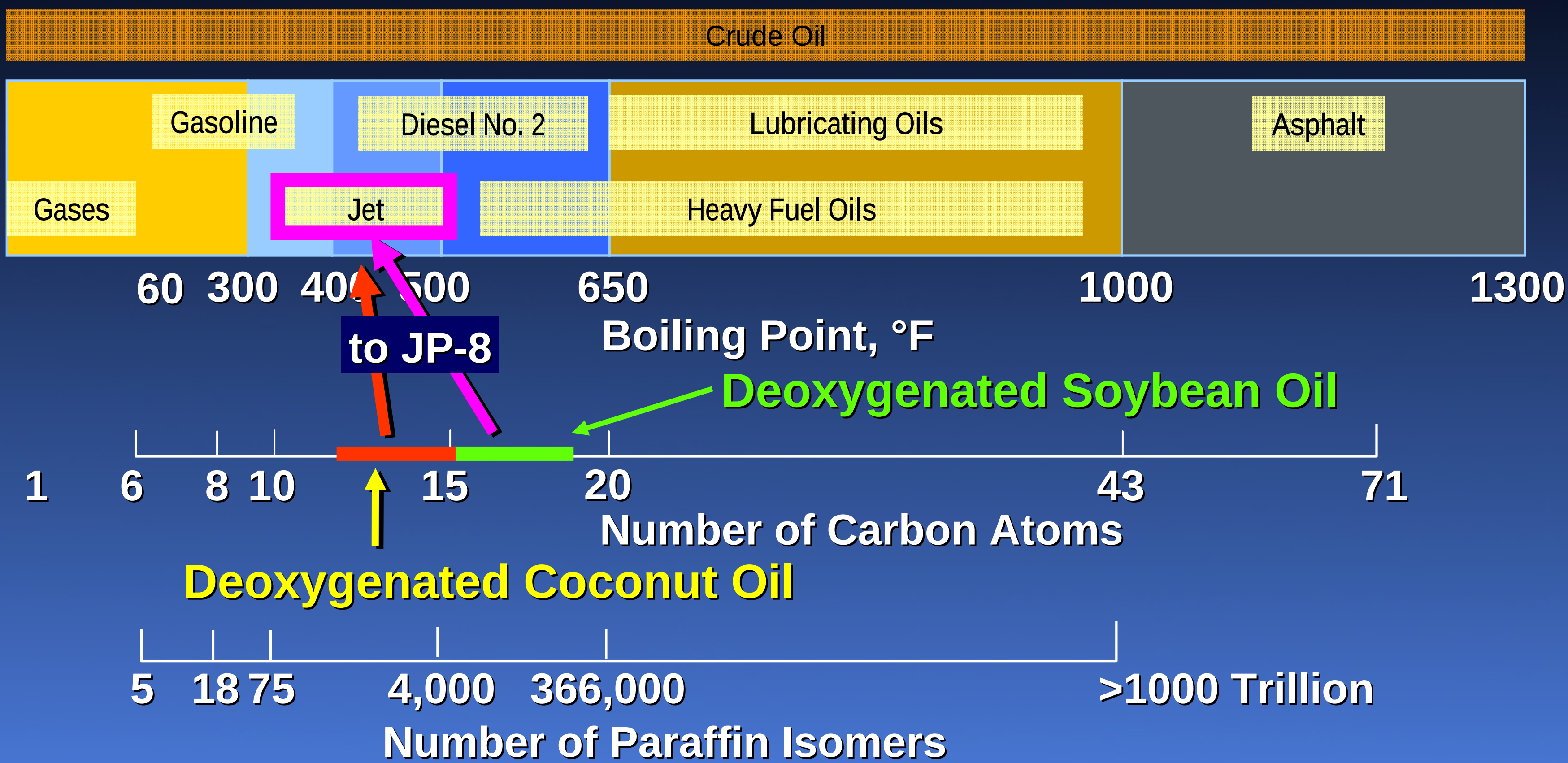

	Carbon Chain Length									
	5-10	11	12	13	14	15	16	17	18	19+
Coconut Oil	15		49		18		8		11	0
Soybean Oil	0		0		0		11		88	0
Deoxygenated Coconut Oil	15	19	29	7	11	3	5	4	6	0
Deoxygenated Soybean Oil	0	0	0	0	0	4	7	35	53	0

Production of Jet Fuel

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Ecofining™

Oil → Deoxygenation → Isomerization → Green Diesel

New Bio-Oil to JP-8 Process Based on Existing UOP Technology

Oil → Deoxygenation → Selective Cracking/ Isomerization → Green Jet

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

Maximizing Jet Fuel Production:

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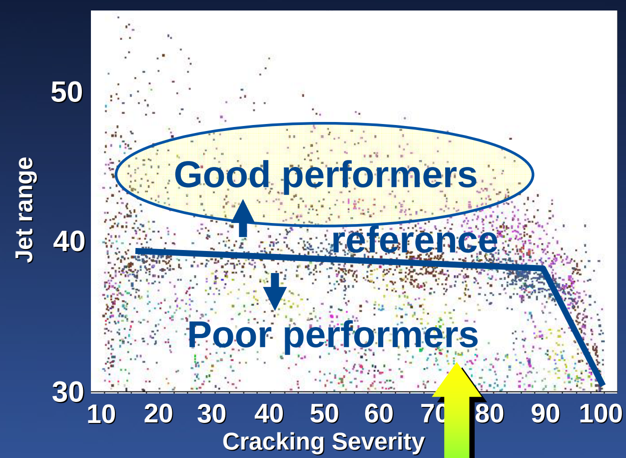
Identifying Best Catalyst Through Combinatorial Chemistry



Variables screened:

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

DeOx natural oil feed

Pilot plant screening: Yield confirmations/ short term stability

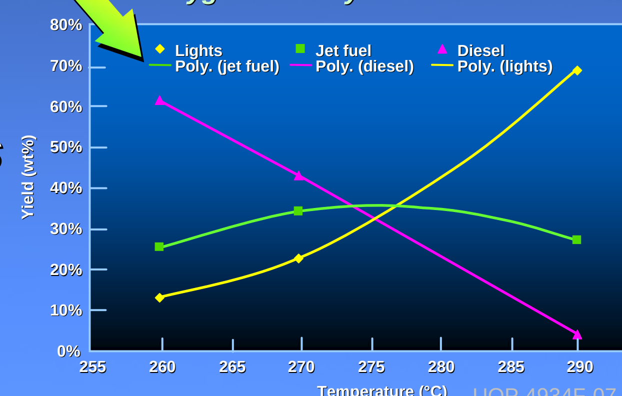
Combi Catalyst Preparation → Combi Testing → Lab Scale Preparation → Lab Plant Test Confirmation of Combi Results → Candidates for Development

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



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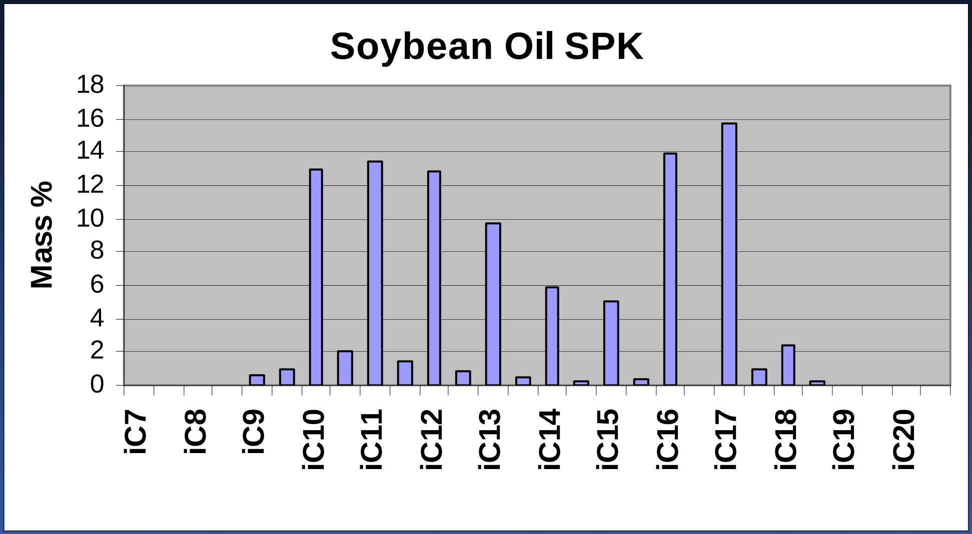
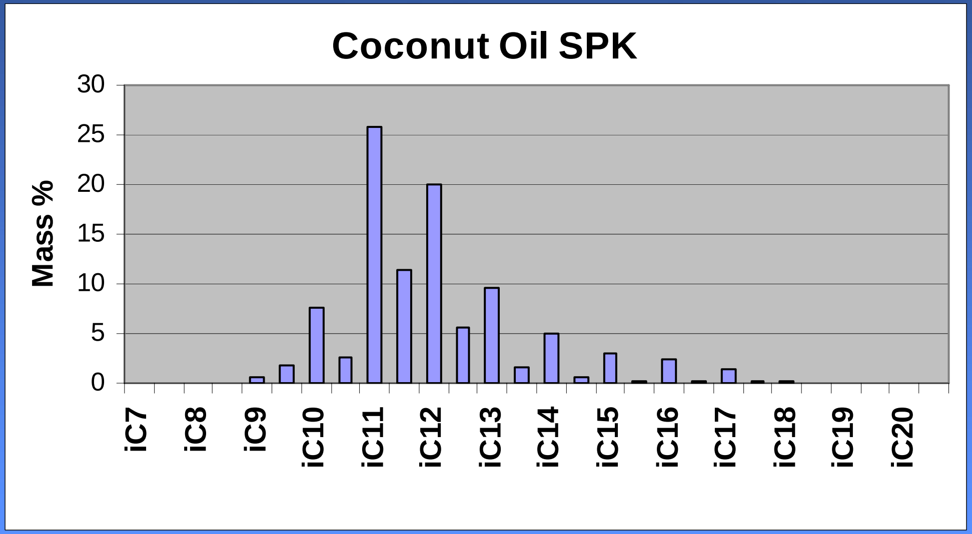
Hydrocarbon Compositions

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





Properties of UOP's Bio-Based SPK

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Property		*SPK*	*ASTM Test Method*	*Composition*			
				Jatropha	*Coconut*	*Soybean/ Canola*	*Soybean*
Paraffin, vol %	min	99.8	D2425				
Cycloparaffin, vol %	max	5	D2425				
Paraffin, vol % [1]			difference from D 1319	99.3	99.5	99.5	100
1. Aromatics, vol %	max	0.05	D 1319	0	0	0	0
2. Aromatics, vol %	max	0.053	D 6379	0	0	0	0
Sulfur, total mass %	max	0.015	D 1266, D 2622, D 4294, or D 5453				0.0008
1. Physical Distillation			D 86				
Distillation temp, °C:							
10% recovered, temp (T10)	max	205		172	188	189	186
50% recovered, temp (T50)		report		192	200	214	226
90% recovered, temp (T90)		report		223	231	248	280
Final boiling point, temp	max	300		243	263	261	286
T90-T10, °C	min	25		51	43	59	94
Distillation residue, %	max	1.5		1.2	1.3	1.2	1.4
Distillation loss, %	max	1.5		0.4	0.5	0.8	1.0
2. Simulated Distillation			D 2887				
Distillation temp, °C							
10% recovered, temp	max	185		151.6		168	166.8
50% recovered, temp		Report		195		218.6	226.6
90% recovered, temp		Report		237.6		267.2	297
Final boiling point, temp	max	340		273.8		284.4	310.6
Flash Point, °C	min	38	D 56 or D 3828	50	64	62	60
Density at 15 °C, kg/m^3		751 to 840	D 1298 or D 4052	751	755	763	766
Fluidity							
Freezing Point, °C	max	-47 Jet A-1	D 5972, D 7153, D 7154, or D 2386	-63	-56	-52	-36
Viscosity -20°C, mm 2/s *H*	max	8.0	D 445				
Combustion							
Net heat of combustion, MJ/kg	min	42.8	D 4529, D 3338, or D 4809	44.4	44.2	43.5	43.8
Metal Content			D7111				
Copper, ppb	max	100		<0.01 ppm	<0.01 ppm	<0.01 ppm	<0.03 ppm
Iron, ppb	max	100		<0.01 ppm	<0.01 ppm	0.04 ppm	<0.03 ppm
Zinc, ppb	max	100		<0.01 ppm	<0.01 ppm	<0.01 ppm	<0.03 ppm
Vanadium, ppb	max	100		<0.01 ppm	<0.01 ppm	<0.01 ppm	<0.03 ppm
Thermal Stability							
JFTOT (2.5 h at control temp of 260°C min)							
Filter pressure drop, mm Hg	max	25	D 3241	<0.1	25	0	
Tube deposits less than		3		<1	<1	1	

[1] Balance of composition is olefins.

Meeting JP-8 Specifications: Aromatics to Meet Density Specs

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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
- Renewable sources
  - Deoxygenated pyrolysis oil

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

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Ethanol | Biodiesel

Fuels

Diesel | Jet | Gasoline

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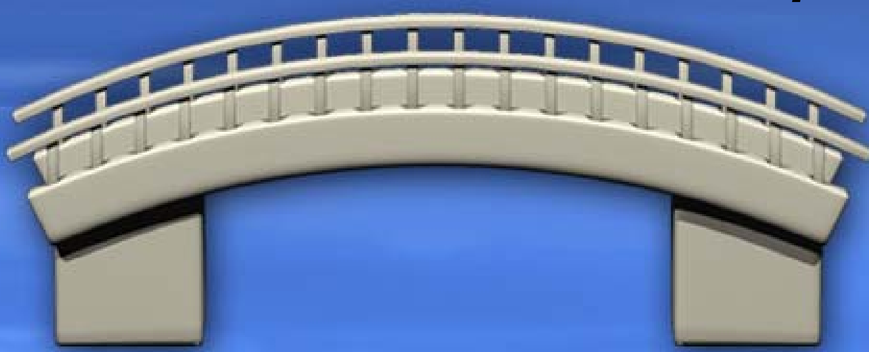

Generation 1

- Vegetable oils to diesel, gasoline and jet fuel

Generation 2

- Lignocellulosic biomass to fuels
- Algal oils to fuels

Lignocellulosic Biomass to Fuels Via Pyrolysis

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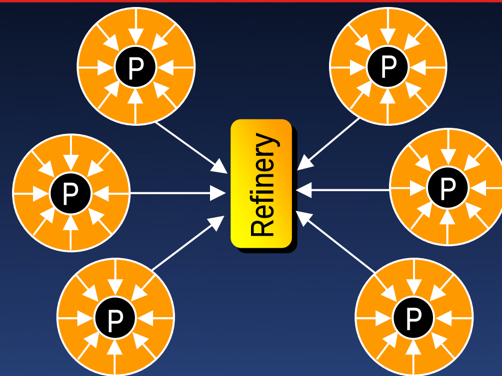
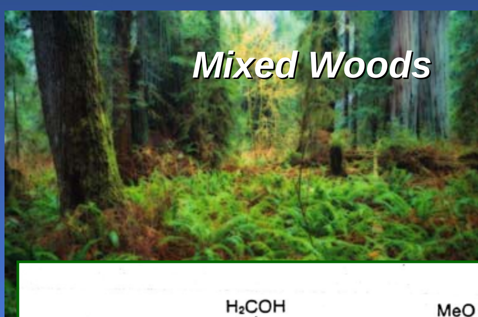
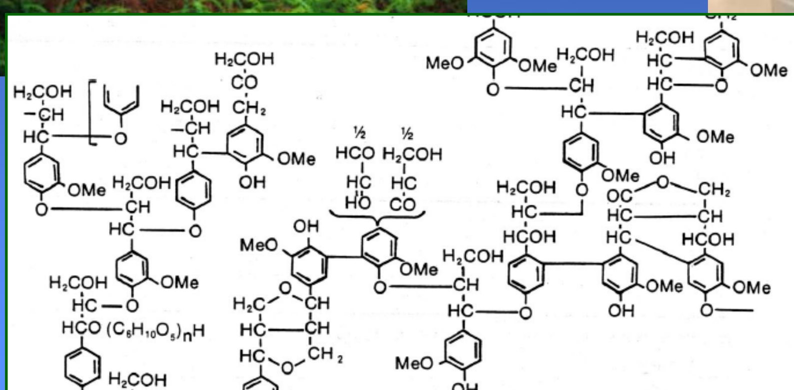
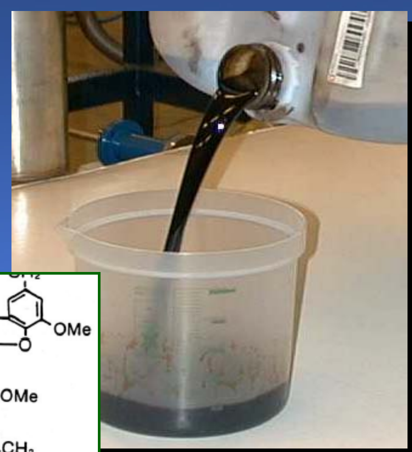


Biomass → Pyrolysis → Stabilization → Biocrude → Deoxygenate / Other Refinery Processes →

- Gasoline
- Diesel
- Jet
- Chemicals







Collaboration with DOE, NREL, PNNL

Typical Fast Pyrolysis Process

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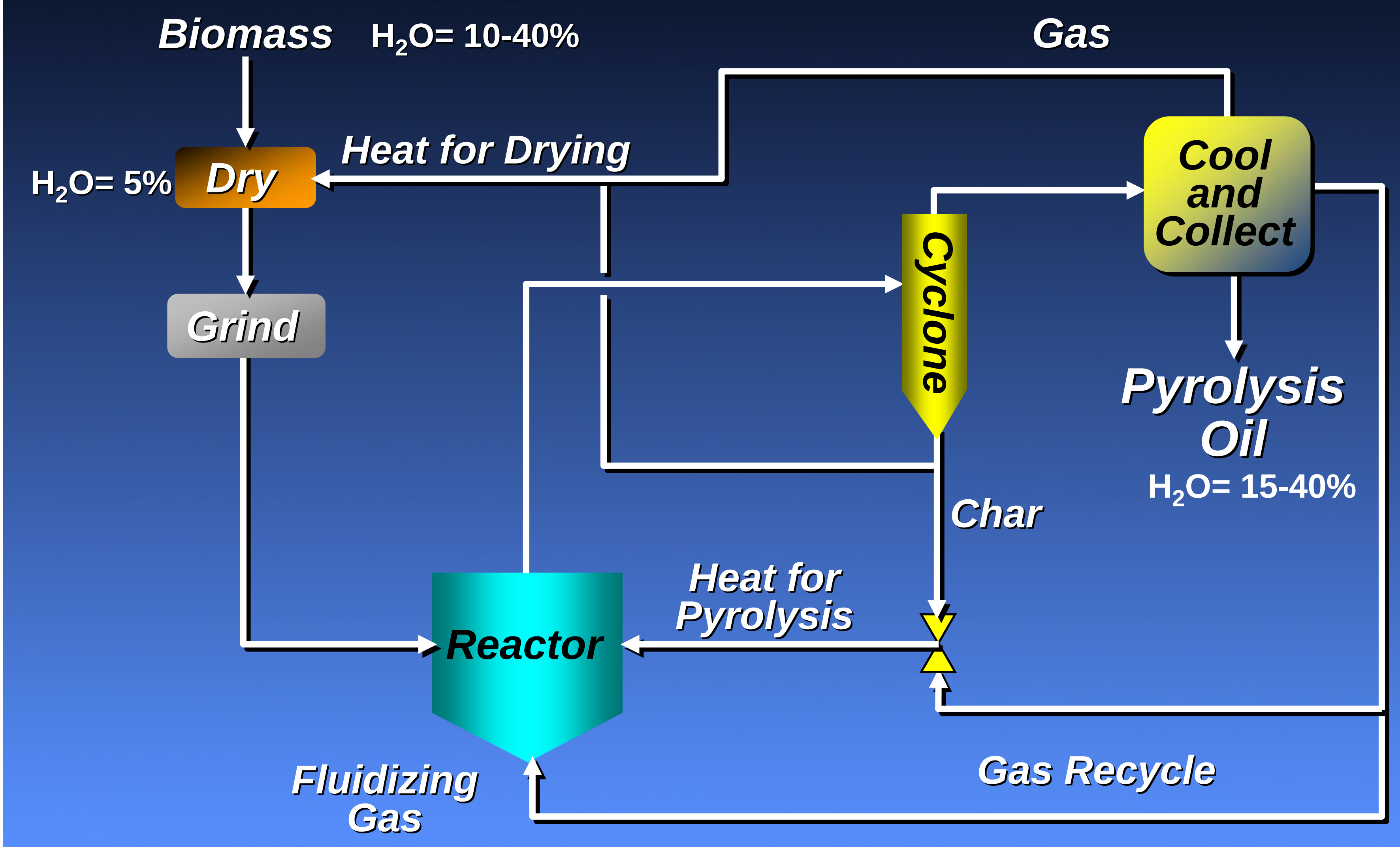

From "Fast Pyrolysis of Biomass: A Handbook." A.V. Bridgwater et al.

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

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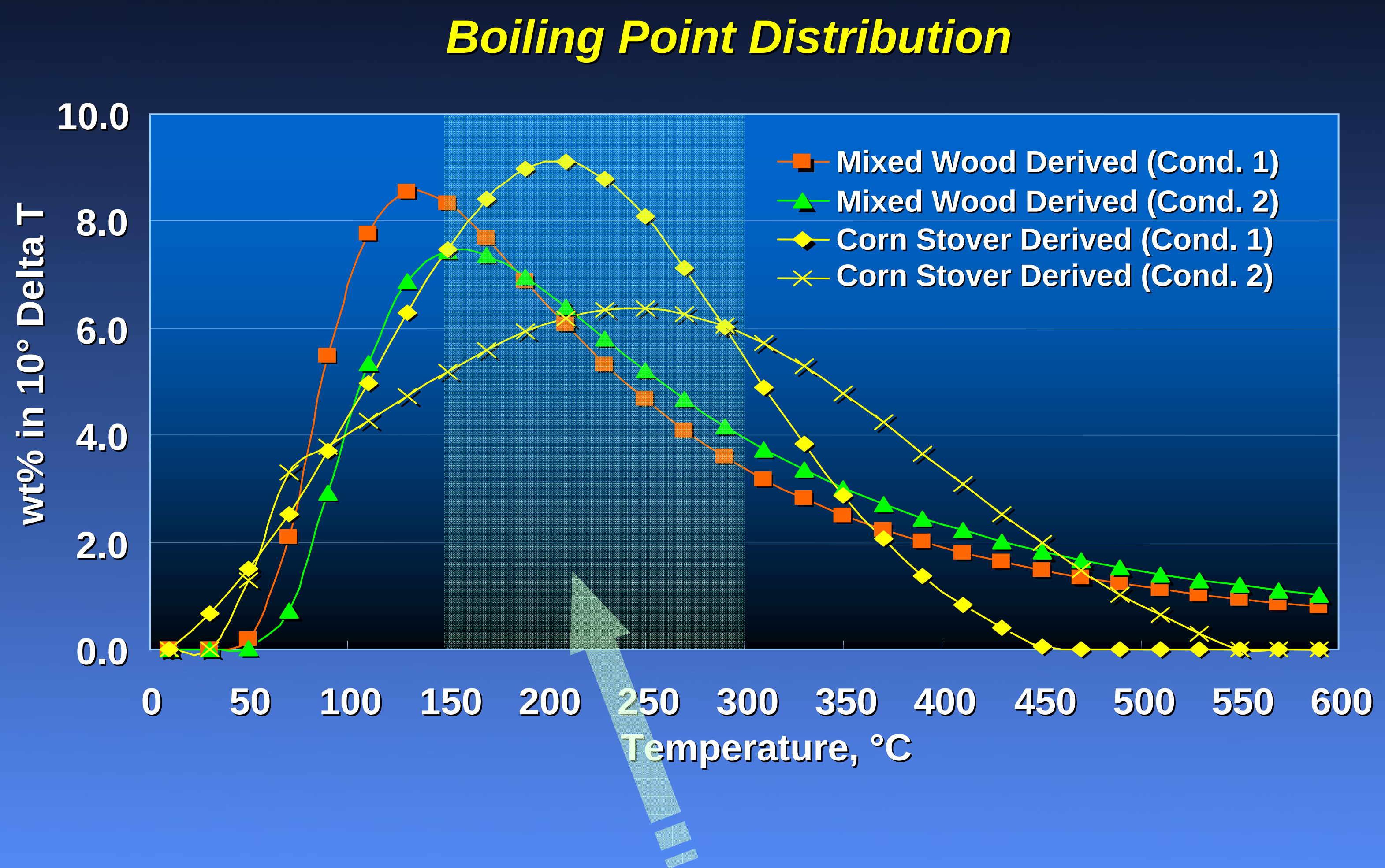

Range of jet range hydrocarbons: 45 – 65% depending on feed source and process conditions

Renewable Aromatics

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	JP-8 Spec	Starting Paraffin	Deoxygenated Pyrolysis Oil (Corn Stover derived)	Deoxygenated Pyrolysis Oil (Mixed wood derived)
Freeze Point (°C)	-47	-53	-56	-54
Flash Point (°C)	39	53	49	54
Density (g/mL)	0.775	0.759	0.790	0.782

100% Bio-derived JP-8 product is possible

2^{nd} Generation Renewable Jet Fuel from Oils and Biomass

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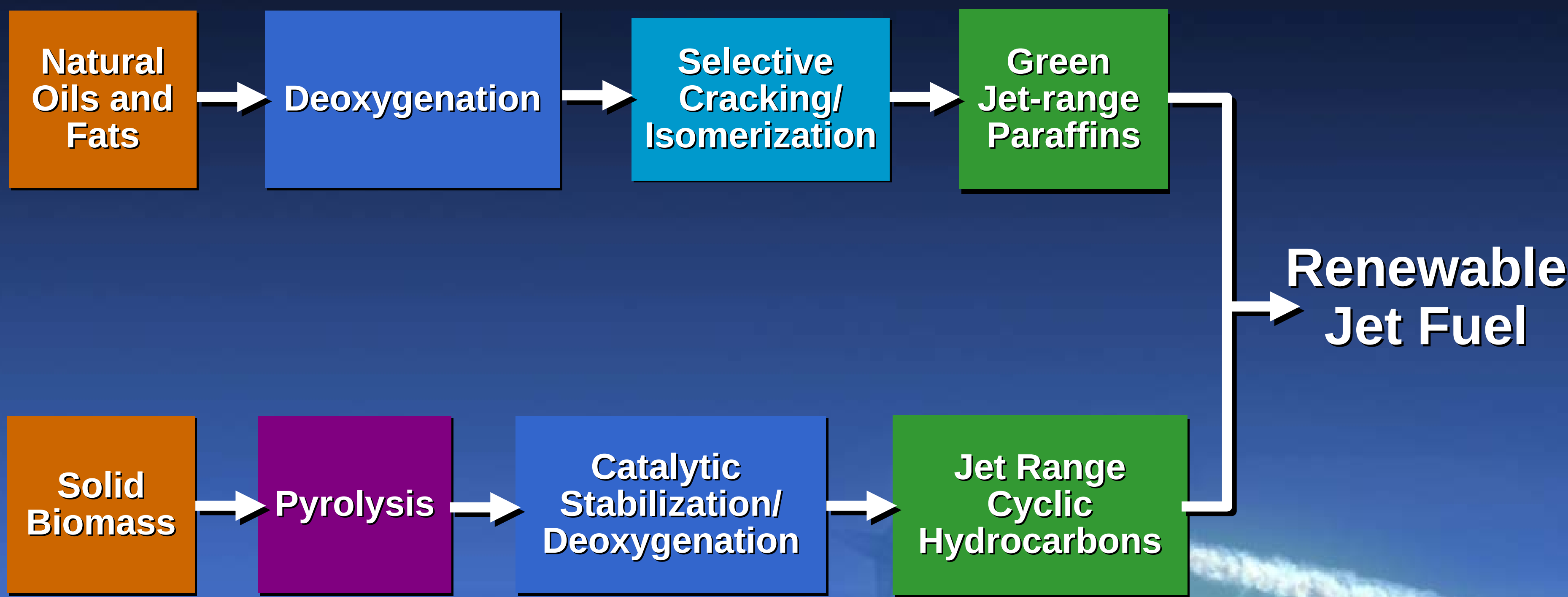

Biomass contribution can be >50%

2nd Generation Renewable Jet Fuel from Algae

- 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

Integrated Algal Processing for Jet Fuel Production

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CO_2

Oil

Green Jet (paraffin-rich)
Other Products: Green diesel and chemicals

2nd Generation On-spec Renewable Jet Fuel

Biomass

Green Jet (rich in cyclic hydrocarbons)
Other products: Green gasoline; diesel; chemicals

Summary

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- 1^{st} generation renewable jet fuel process in development: Natural oils and fats to jet fuel
  - Samples produced from multiple feedstocks meet JP-8 specifications
  - Process and catalyst development in progress
- 2^{nd} generation renewable jet fuel: Biomass and algae to jet fuel
  - Proof of principle work completed in NREL-PNNL-UOP CRADA: Biomass to jet fuel via pyrolysis oil hydrodeoxygenation
  - Algae offers great potential to produce large quantities of oils and biomass for sustainable jet fuel production
- Technologies discussed also produce many other valuable fuels and chemicals

Acknowledgements

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  - Rich Marinangeli
  - Terry Marker
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Dr. Douglas Kirkpatrick

Q&A