Specification-Compliant Petroleum-Alternative Fuels

Presented to

5th Annual Military Energy Alternatives Conf. Washington DC

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20 January 2010

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Viable alternatives to petroleum

Viability requires:

- Specification compliance
  - No special testing needed
- Drop-in compatibility
  - No segregation or special handling required
  - Completely fungible (and pipelineable) with petroleum at any blend level
- Fit-for-purpose compliance
  - No materials compatibility or other vehicle performance hindrances

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Alternative feedstocks and pathways

- Coal
  - Direct & indirect liquefaction
- Natural gas
  - Gas-to-liquids
- Lignocellulose biomass
  - Pyrolysis, direct & indirect liquefaction
- Renewable oils
  - Hydroprocessing of crop and algal oils
- Biocatalysis
  - Creation of fuel or fuel feedstocks by microbes

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Coal: direct liquefaction

Technology

- Major research effort by Exxon in 1980s
- Economically competitive at oil price of >$40/bbl
- Smaller carbon footprint than indirect coal liquefaction, due to leveraging of inherent coal fuel chemistry

Economics (50,000 BPD)

- CAPEX: $2 Billion
- OPEX: $402.5 Million/year

Commercial start-ups

- Shenhua Group (China)
- 17,000 BPD

Coal: indirect liquefaction

Technology

- Gasification followed by Fischer-Tropsch (FT) syngas conversion
- Requires many unit operations to produce and purify syngas for FT process
- Requires oxygen plant
- Typically requires a mine

Economics (80,000 BPD)

- CAPEX: $6 Billion
- OPEX: ~$875 Million/year

Commercial operation

- SASOL

Natural gas to liquids

Technology

- Reforming followed by FT syngas conversion
- Requires only a few unit operations to produce synthetic paraffinic kerosene (SPK) jet fuel

Flight demonstration

- 50:50 SPK:Jet-A1
- Gatwick to Doha
- Airbus A340-600 with Rolls Royce engines

Economics (120,000 BPD liquids + 140,000 BPD LNG)

- CAPEX: $18-19 billion (Shell)
- OPEX: ??

Commercial operation

- Sasol: Worldwide
- Shell: Qatar & Malaysia

Lignocellulose: pyrolysis

Technology

- High-temp, short-time (<1 sec), low-oxygen treatment
- Yields “bio-oil” comprising small organics and water
- Bio-oil is typically acidic, unstable, and requires upgrading to get to finished fuel
- Currently used as boiler fuel, after chemicals extraction

Economics

- CAPEX: Bio-oil – $16/bbl

Commercial bio-oil production

- Ensyn (Canada)
- BTG (Netherlands)

Bio-oil-to-fuel (upcoming)

- UOP and Ensyn

Lignocellulose: direct liquefaction/catalytic pyrolysis

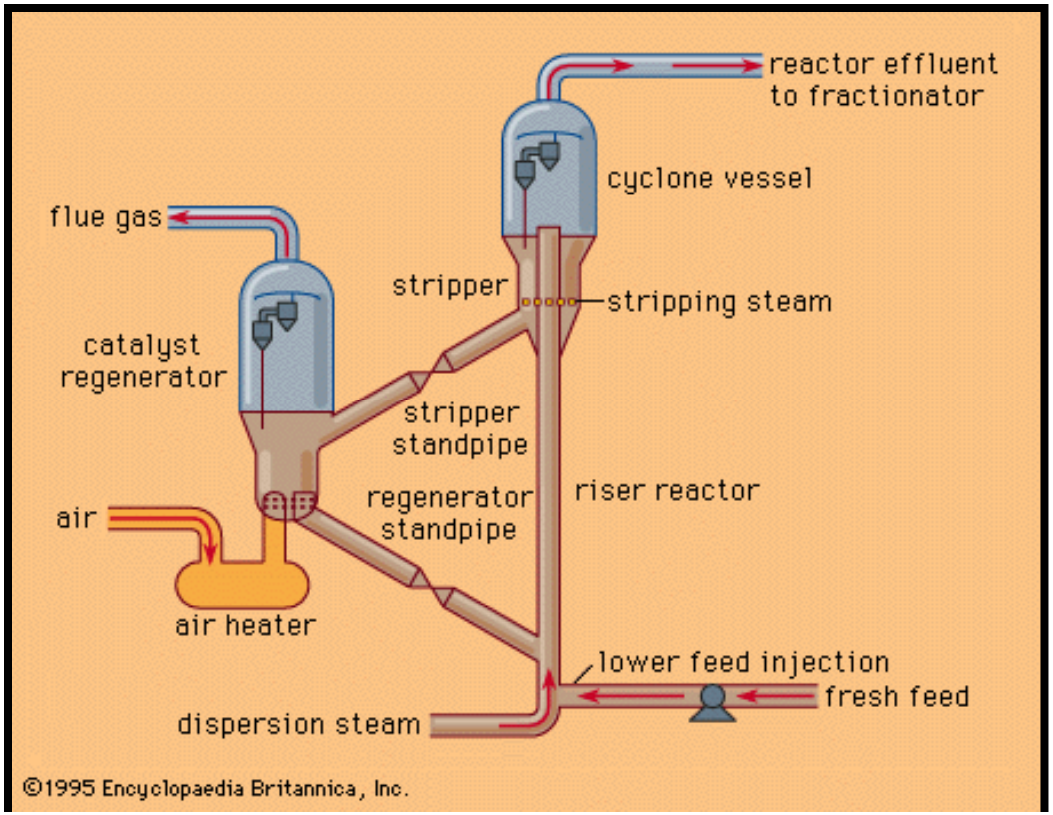
Technology

- Based on oil industry-developed fluid catalytic cracking (FCC) process
- Catalyst particles contact biomass particles at temperature and pressure
- Hydrogenated bio-oil goes directly into petroleum refinery

Economics: ??

Commercial start-ups

- BIOeCON (Netherlands)
- KiOR (USA)



Lignocellulose: indirect liquefaction

Technology

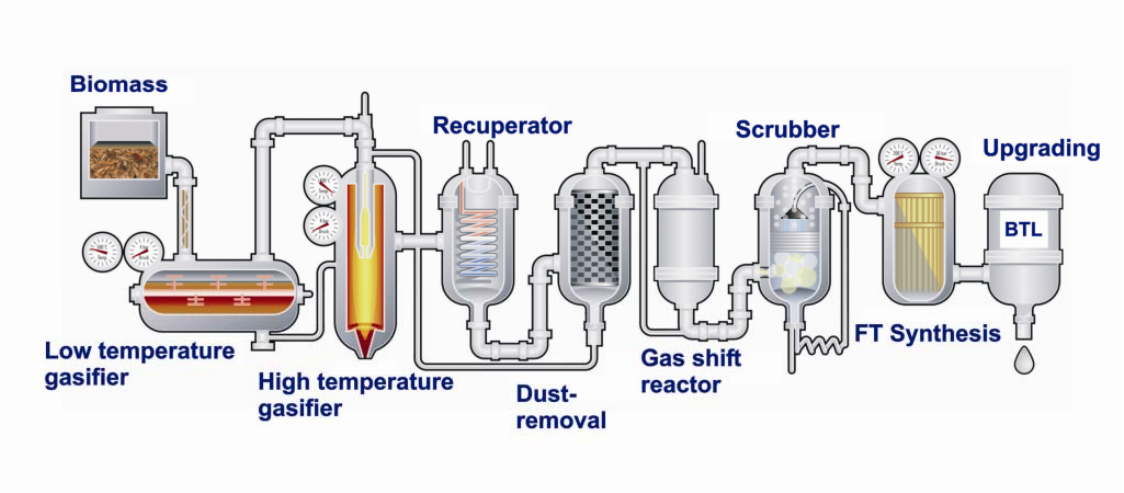
- Gasification followed by FT syngas conversion
- Requires many unit operations to produce and purify syngas for FT process
- Requires oxygen plant
- Large supply of low-cost biomass needed for economics to work

Economics (18 Million liters/yr)

- CAPEX: €100 Million
- OPEX: Can be high
- Estimated Fuel Cost: $7.00/gallon

Commercial operation

- Choren (Germany) – Staged gasification beta plant under construction, will use Shell FT



Renewable oil hydroprocessing

Technology

- Requires one or more of crop oil, animal fat, algae oil
- 3 unit operations
  - Hydrotreating
  - Isomerization & cracking
  - Distillation
- Integrate with petro refinery for access to H_2, steam, product blending
- Jet fuel producers
  - Dynamic Fuels (Syntroleum)
  - UOP
  - EERC

Economics: Dynamic Fuels (75 million gallons/year)

- CAPEX: $138 million
- Renewable fuel tax credit

Commercial operation

- Neste Oil (Finland)
- Dynamic Fuels (USA)

Algal oil production

Cultivation

- Photosynthesis vs fermentation
- Invasive species/infection
- Open pond vs photobioreactor

Harvesting

- De-watering economics tough

Oil extraction and purification

- Proteins, cellular materials add to challenge

Economics: Difficult

- Fuel cost: ??

Commercial photosynthesis

- Petroalgae (Florida)
- A2BE (California)
- Solix (Colorado)

Commercial fermentation

- Martek (Virginia)
- Solazyme (California)

Biocatalysis: direct liquefaction

Technology

- Provide a feedstock to an anaerobe, which produces a hydrocarbon
- Additional refining may be required to obtain fuel-grade product
- Feedstocks
  - Typically, sugars
  - Cellulose?
  - Lignin??

Economics: ??

Commercial start-ups

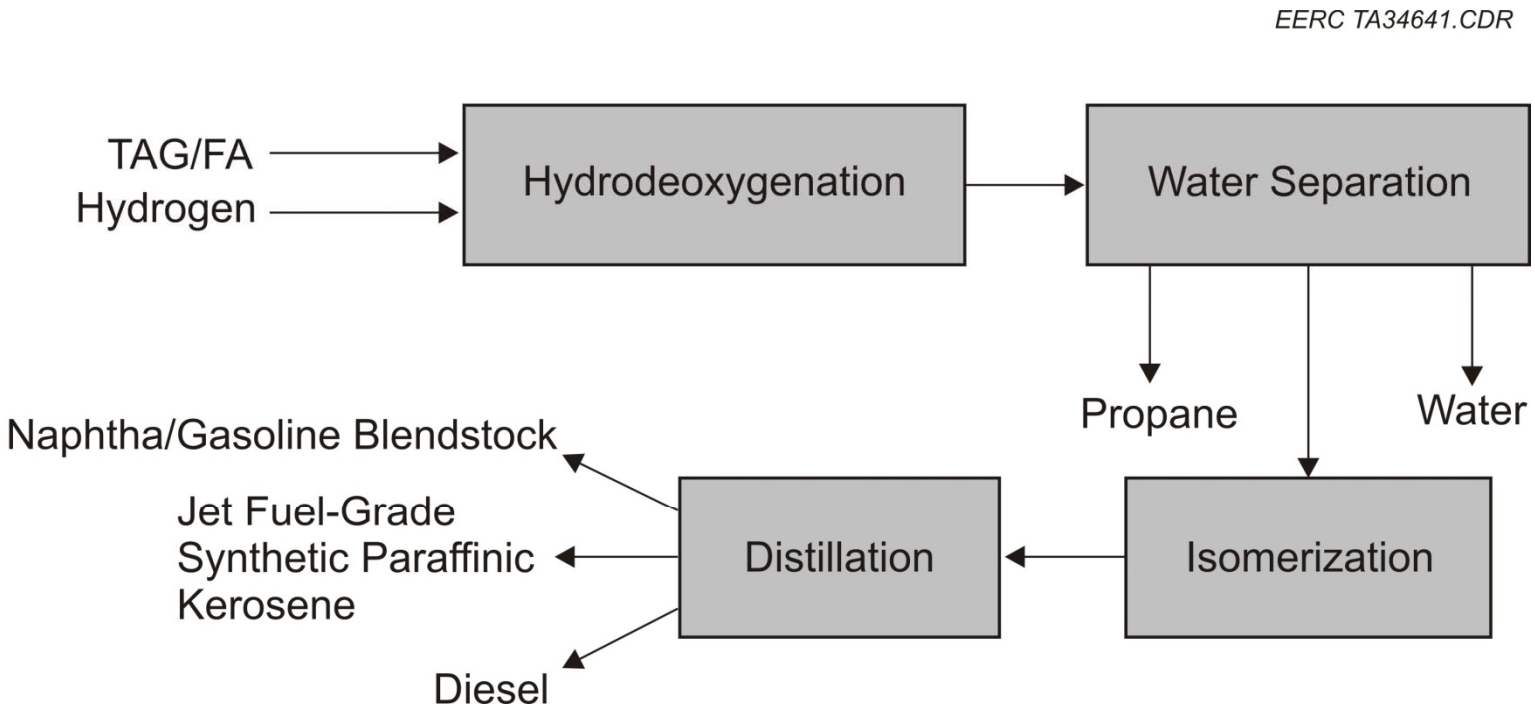
- LS9 (California)
- Gevo (Colorado)

Note: Bacteria are the small specks surrounding the large ciliated protozoan.

EERC hydrotreated renewable jet (HRJ) fuels

- Convert triacylglyceride (TAG) and/or free fatty acid (FFA) feedstocks to synthetic isoparaffinic kerosene (SPK)
- As per Air Force Research Lab (AFRL) at Wright Patterson AFB, EERC SPK meets all key requirements of ASTM D7566 (Aviation Turbine Fuel Containing Synthesized Hydrocarbons)
- Use in 50/50 blend with JP-8
- EERC can also make fully spec-compliant 100% renewable JP-8 that comprises SPK plus cycloparaffins and aromatics

EERC catalytic hydrodeoxygenation–isomerization (CHI) process



DARPA Program objectives met:

- Feedstock flexible, high-efficiency fuel process
- Produces drop-in-compatible jet fuel using standard refinery process conditions
- Scalable technology enables collocation and integration

TAG/FA = triacylglyceride/free fatty acid in form of vegetable oil, animal fat, or algae oil

EERC 100% renewable JP-8 vs petroleum JP-8

Specification Test	EERC JP-8	JP-8 Avg	JP-8 Spec
Aromatics, vol%	19.8	17.9	≤25.0
Olefins, vol%	1.9	0.8	≤5.0
Specific Gravity	0.805	0.803	0.775–0.840
Flash Point, °C	49	49	≥38
Freeze Point, °C	−52	−51.5	≤−47
Heat of Combustion, MJ/kg	42.9	43.2	≥42.8

All data provided by AFRL, Wright Patterson AFB

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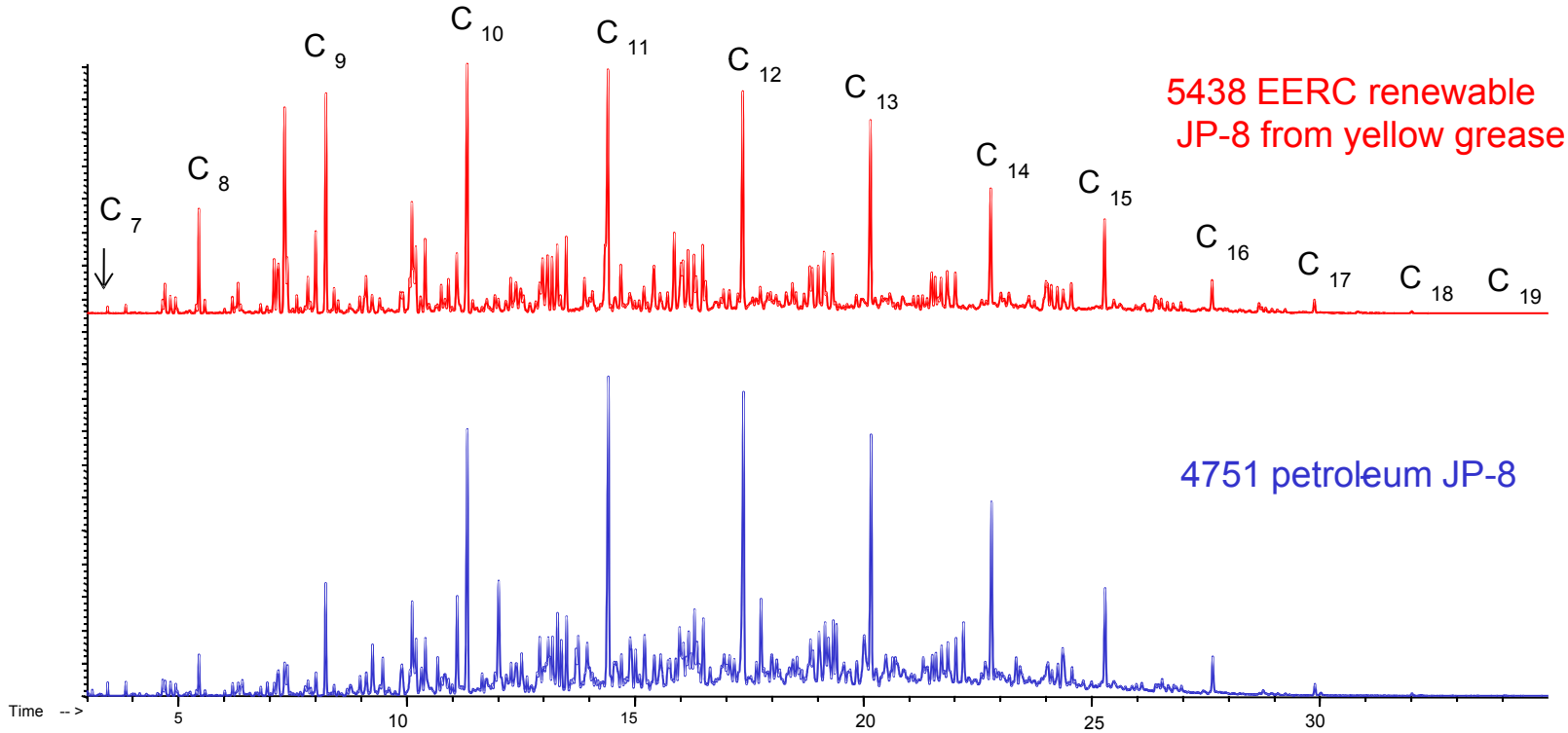
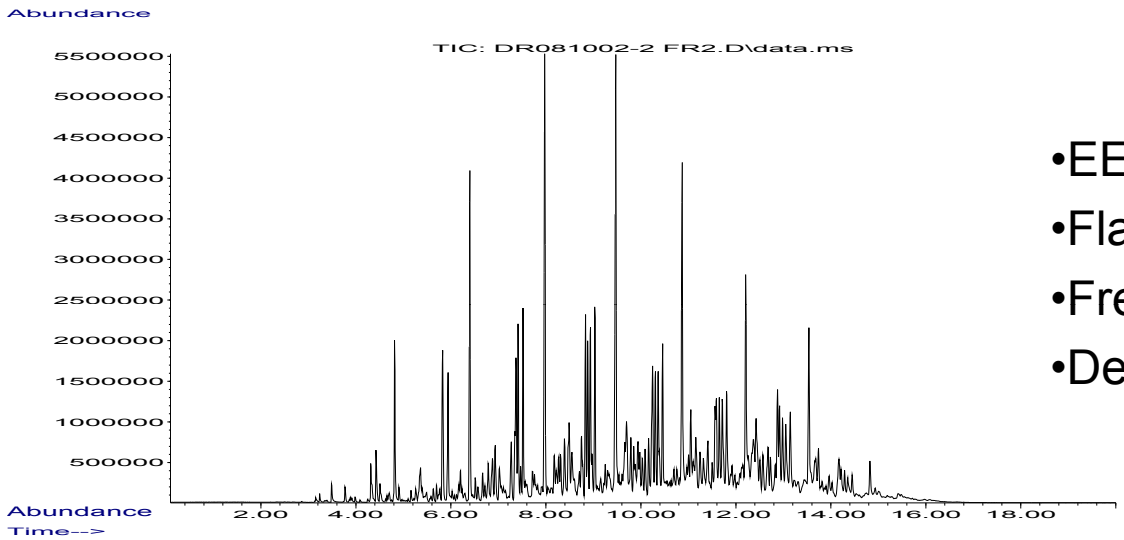
EERC 100% renewable JP-8 vs petroleum JP-8, as analyzed by AFRL

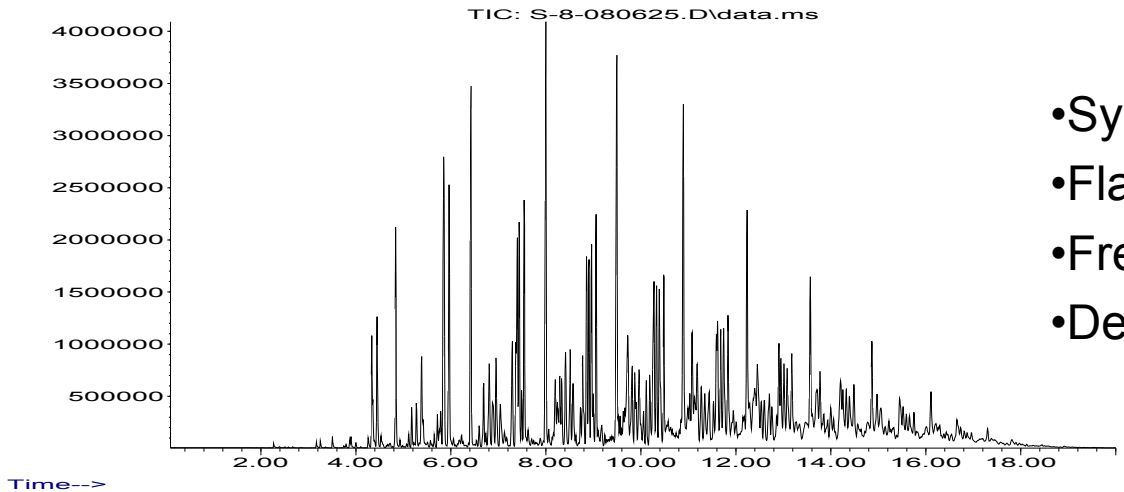
Weight % n-Paraffins				
	C_7-C_9	C_{10}-C_{13}	C_{14}-C_{16}	C_{17}-C_{19}
5438	5.8	14.3	2.7	0.16
4751	1.6	13.2	3.0	0.12



EERC canola-derived SPK vs S8



- EERC Canola SPK – 81% Isomer
- Flash = 44°C
- Freeze = -56°C
- Density = 0.757g/mL



- Syntroleum S-8 – 85% Isomer
- Flash = 45°C
- Freeze = -57°C
- Density = 0.753 g/mL

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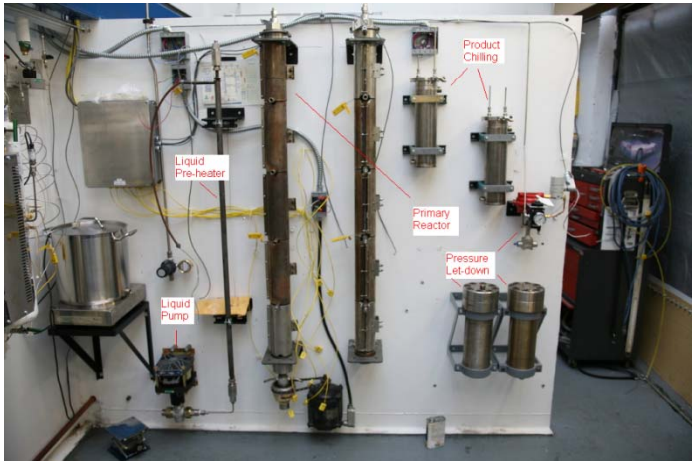
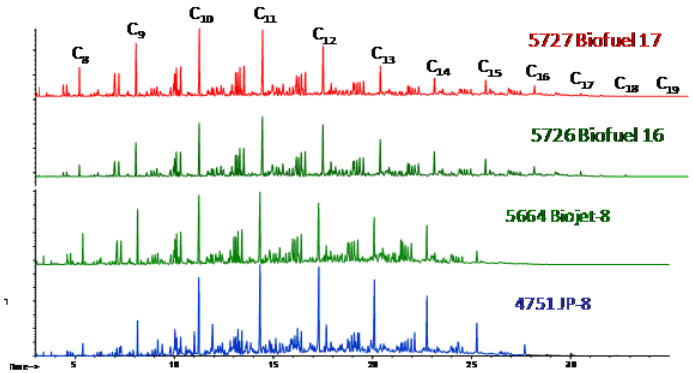
EERC algal oil hydroprocessing

- Currently producing SPK and JP-8 fuels from algae oil feedstocks
- Essentially identical to crop oil processing
- Investigating methods for integrating de-watering, purification, and conversion processes





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EERC renewable oil refining – status update

- Completed Defense Advanced Research Projects Agency (DARPA) project with delivery of 50 gallons renewable jet fuel
- Feedstocks converted to jet fuel include waste grease, animal fats, and oil from crambe, camelina, canola, soy, coconut, cuphea, and algae
- Currently working as DARPA subcontractor, using CHI process to convert algae oils to jet fuel
- Will soon complete bid-ready design for 1.7-million-gallon/year pilot-plant to be integrated with operations at Tesoro Corporation petroleum refinery in Mandan, North Dakota

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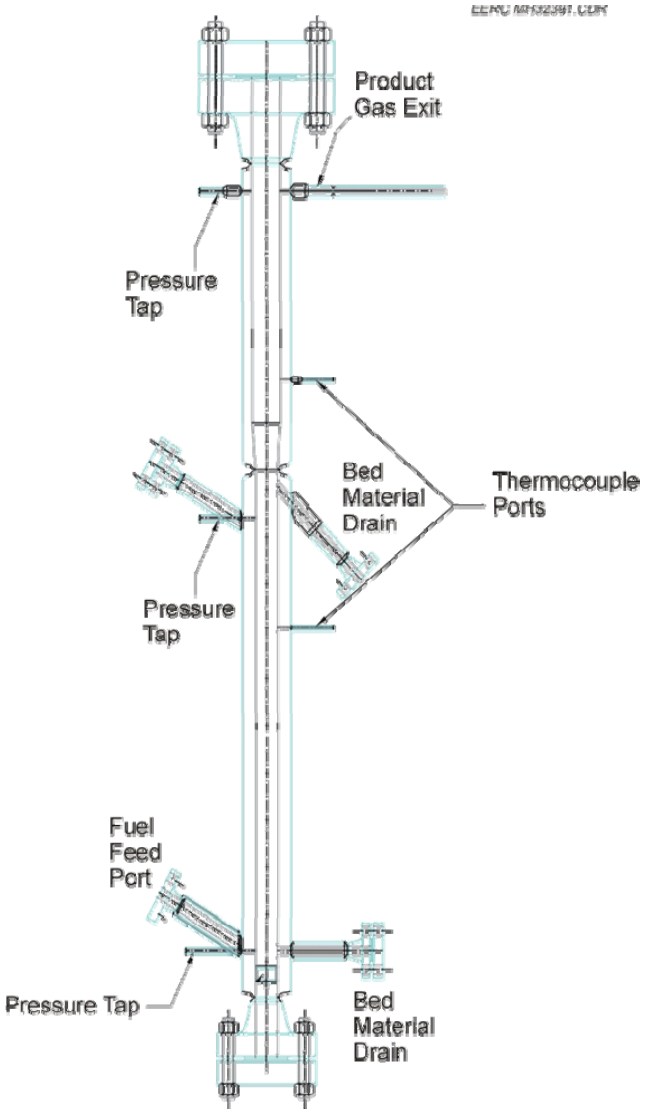
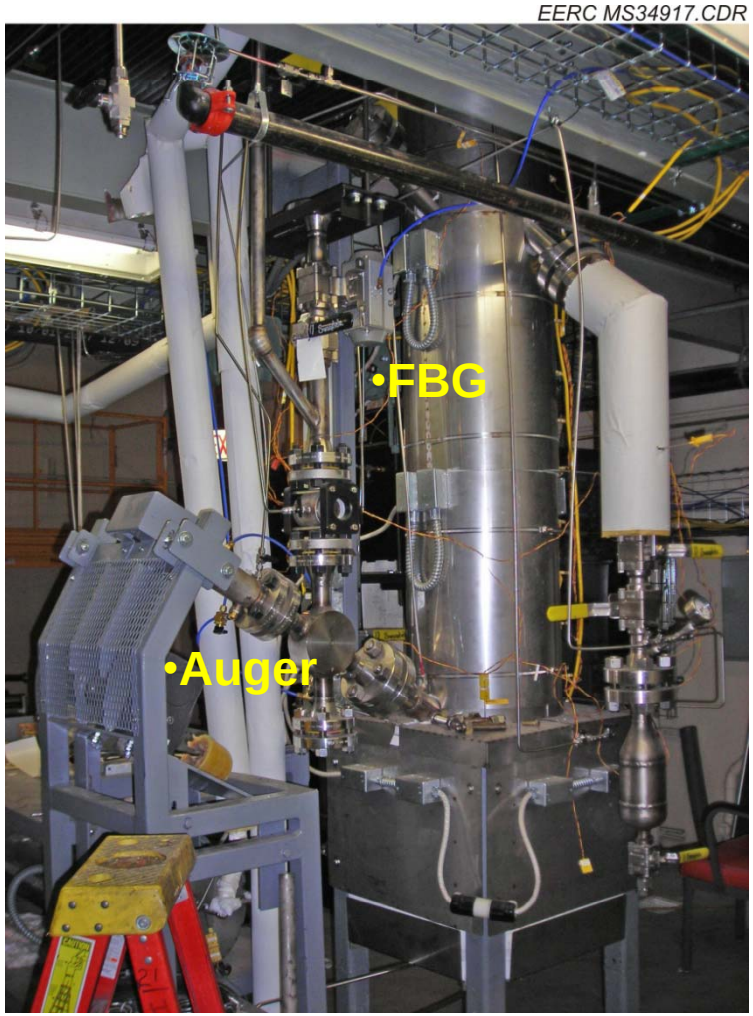
EERC fluid bed gasifier (FBG)

- 4–20-lb/hr feed rate
  - K-Tron feeder provides real-time feed rate
- Syngas recycle
- O_2-blown
- Up to 1000 psig
- 1550°F at max pressure
- Full-stream warm syngas cleanup
- Multiple thermocouple ports up bed to watch for hot spots, agglomeration



FBG reactor operation



- Bed initially charged with sand or other inert solids
- Electrically heated to operating temperature
- Pressurized coal feed from K-tron augered rapidly into bottom of gasifier
- Large solids exiting gasifier removed by cyclone
- Cyclone drain positioned such that solids can be recirculated back to FBG

Transport desulfurizer

- First step after syngas exits FBG cyclone
- Recirculated fluid bed of sulfur sorbent removes >99% of H_2S in syngas
- Demonstrated successfully on wide variety of coals

EERC MS34916.CDR

Hot-gas filter vessel

EERC MS34913.CDR

- After transport desulfurizer, syngas passes through candle filter
- Removes fine particulate to below ambient air concentration
- Filter cleaned using nitrogen or syngas backpulse
- Used successfully over many 1000s of hours of operation

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Fixed-bed sorbent vessels

- Four fixed beds can be loaded with sorbent or catalyst
- Have tested:
  - Sulfur polishing
  - High- and low-temperature water-gas shift
  - Mercury and chlorine guard beds

EERC MS34914.CDR

Quench pots

- After exiting fixed beds, clean, shifted syngas passes through 3-6 water-cooled quench pots to remove moisture and tars.
- Clean, dry syngas is then routed three ways:
  - Most is compressed, recycled to FBG.
  - Some diverted to FT reactor.
  - Remainder vented to maintain system pressure.

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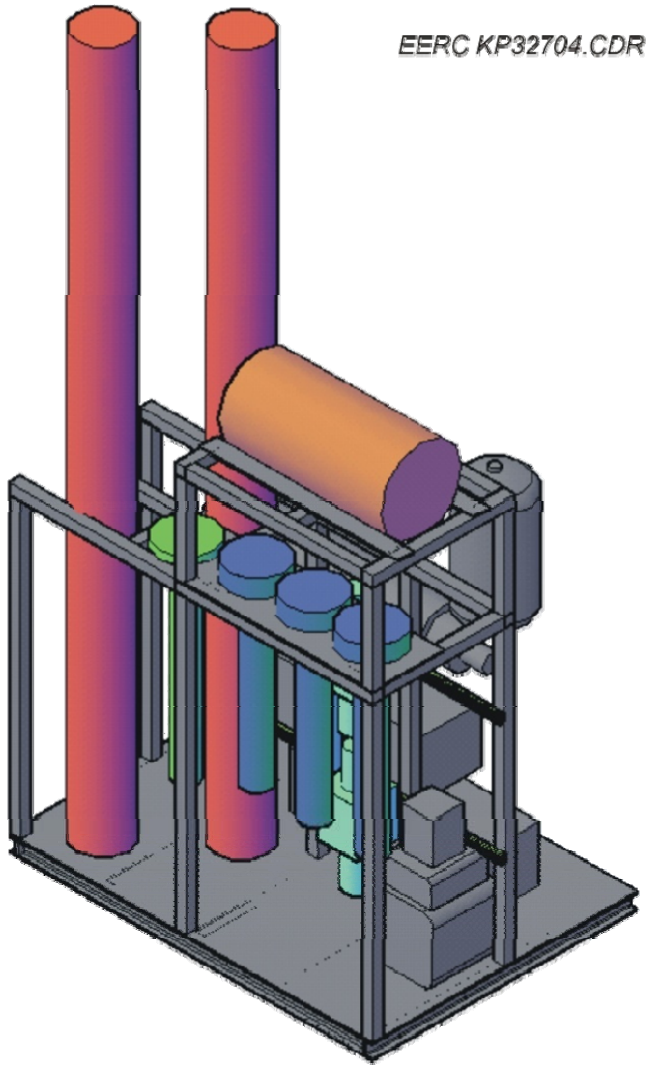
FT reactor design

- Design from Brigham-Young University
- Two Dowtherm-cooled packed-bed FT reactors
  - Space and modules for expansion to four beds
- Syngas preheat
- Both gas and FT liquid recycle



EERC FT reactor

- 1 Lph nominal production rate with all beds running
- 1” i.d.-, 10’-tall reactor (2x, room for 4x)
- 2 kg catalyst required
- Multiple thermocouples throughout each bed length, plus independent inlet and outlet temperatures for each stream and unit operation

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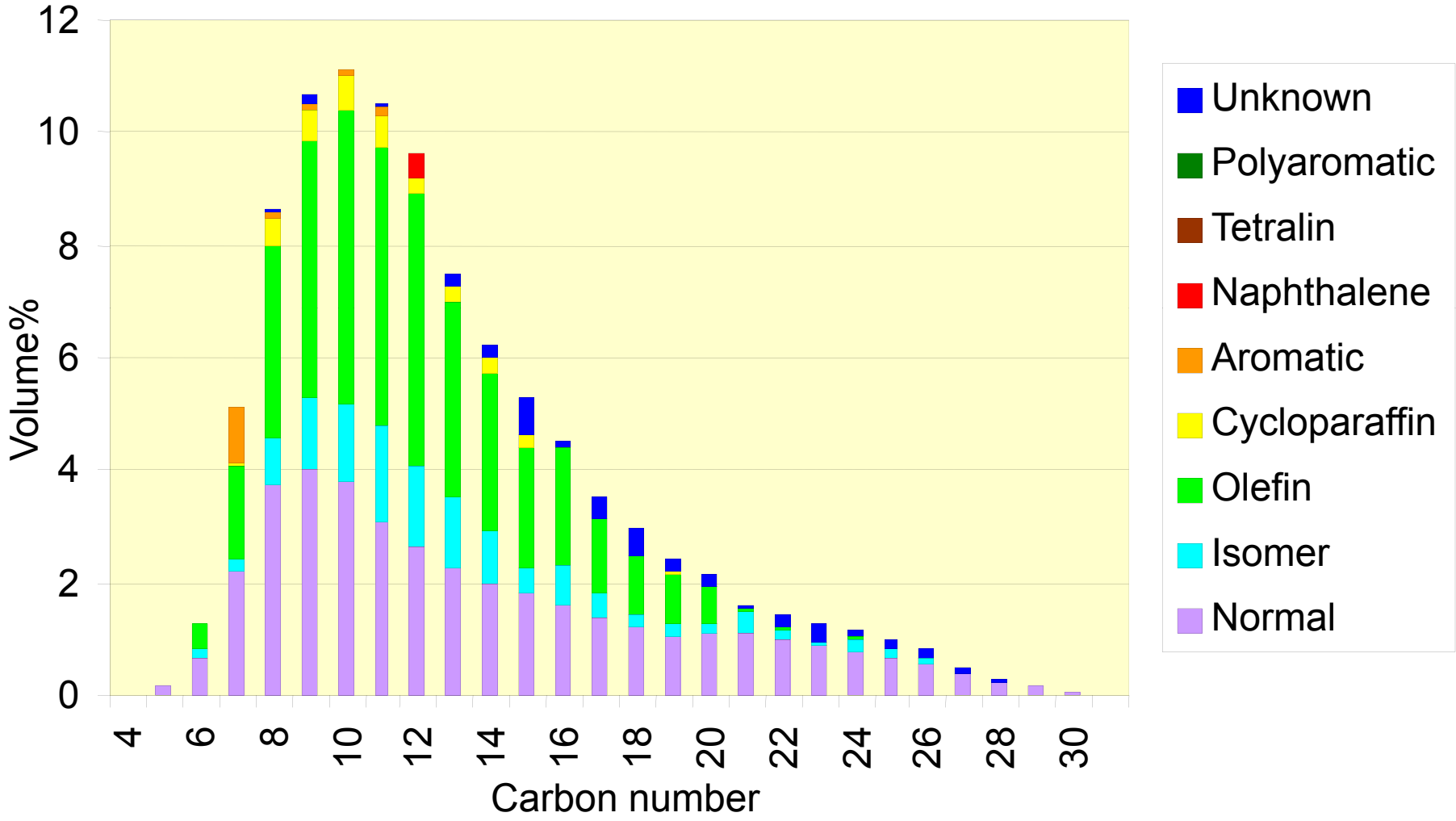
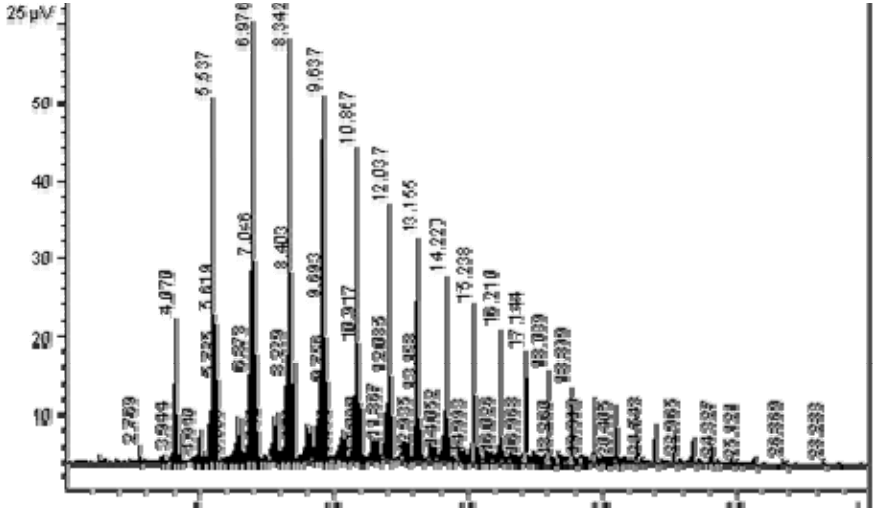
Raw FT product breakdown

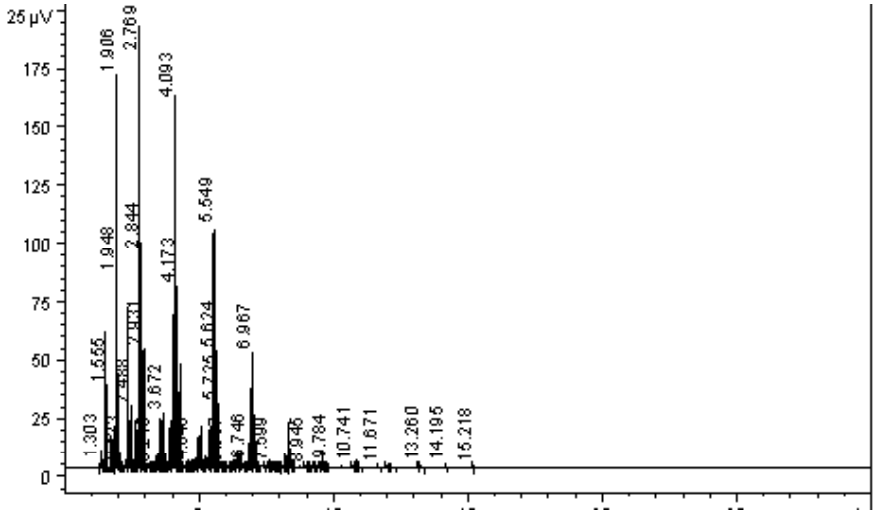


Aromatics (including tetralin and naphthalene) present because of gasfier blow-through

Hydrotreated and distilled FT product

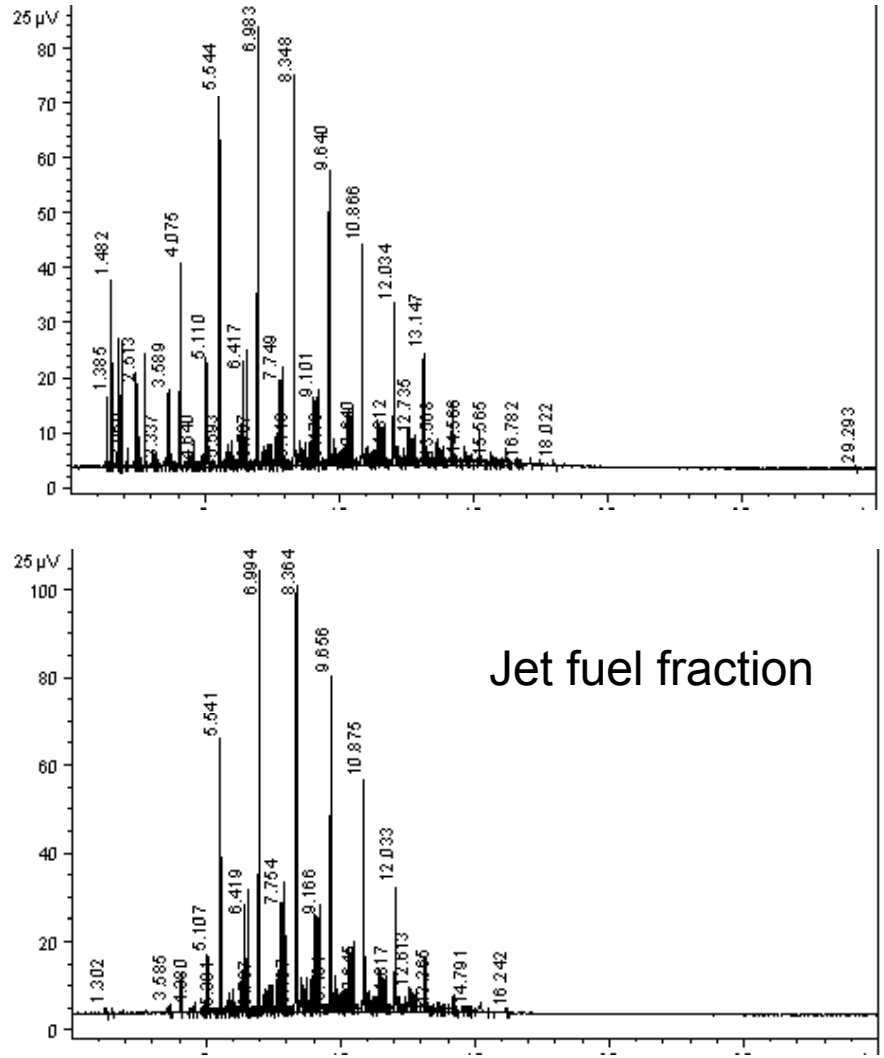
- Heavier fraction suitable for upgrading to jet and diesel; major peak at C10, extends to C30+
- Lighter naphtha fraction potential gasoline feedstock; major peak at C7, only traces above C11





Hydrotreated FT product isomerization, cracking, and distillation to yield jet fuel

- Heavy product isomerized over commercial catalyst
- Achieved 67% isomerization, wax cracking, complete olefin saturation
- Product distilled to naphtha, jet fuel, diesel fractions



EERC–Accelergy Corporation partnership

- Accelergy is an emerging leader in advanced coal- and biomass-to-liquids (CBTL) processing using micro-catalytic liquefaction (MCL) technology licensed from ExxonMobil
- Objective: Integrate EERC CHI and Accelergy CBTL technologies to commercialize low-cost, low-carbon-footprint diesel and jet fuels from biomass and coal
- Recently produced sample of Illinois #6-derived specification-compliant JP-8 for submittal to AFRL at Wright Patterson AFB

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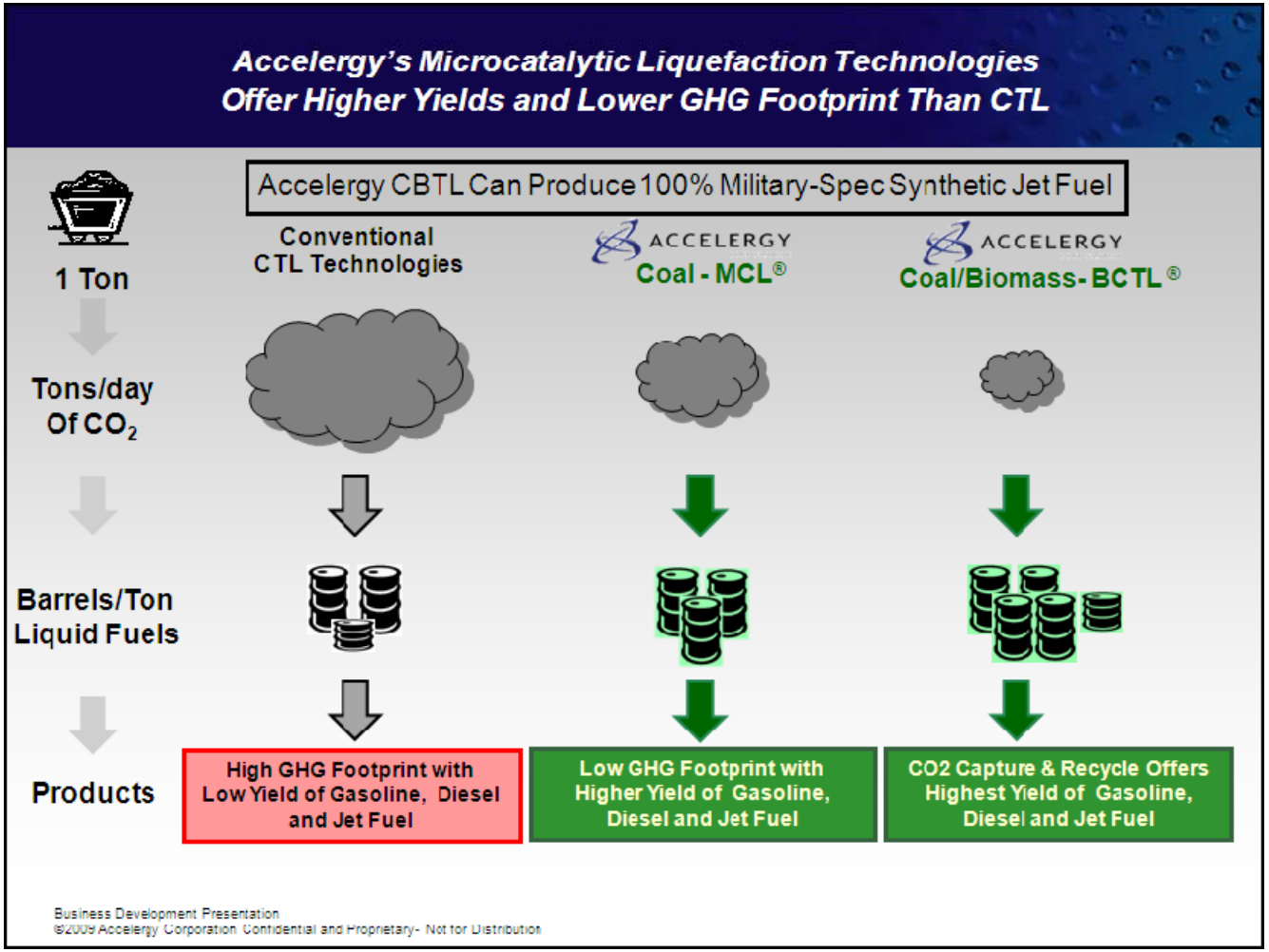
MCL vs indirect liquefaction-based coal-to-liquids (CTL)

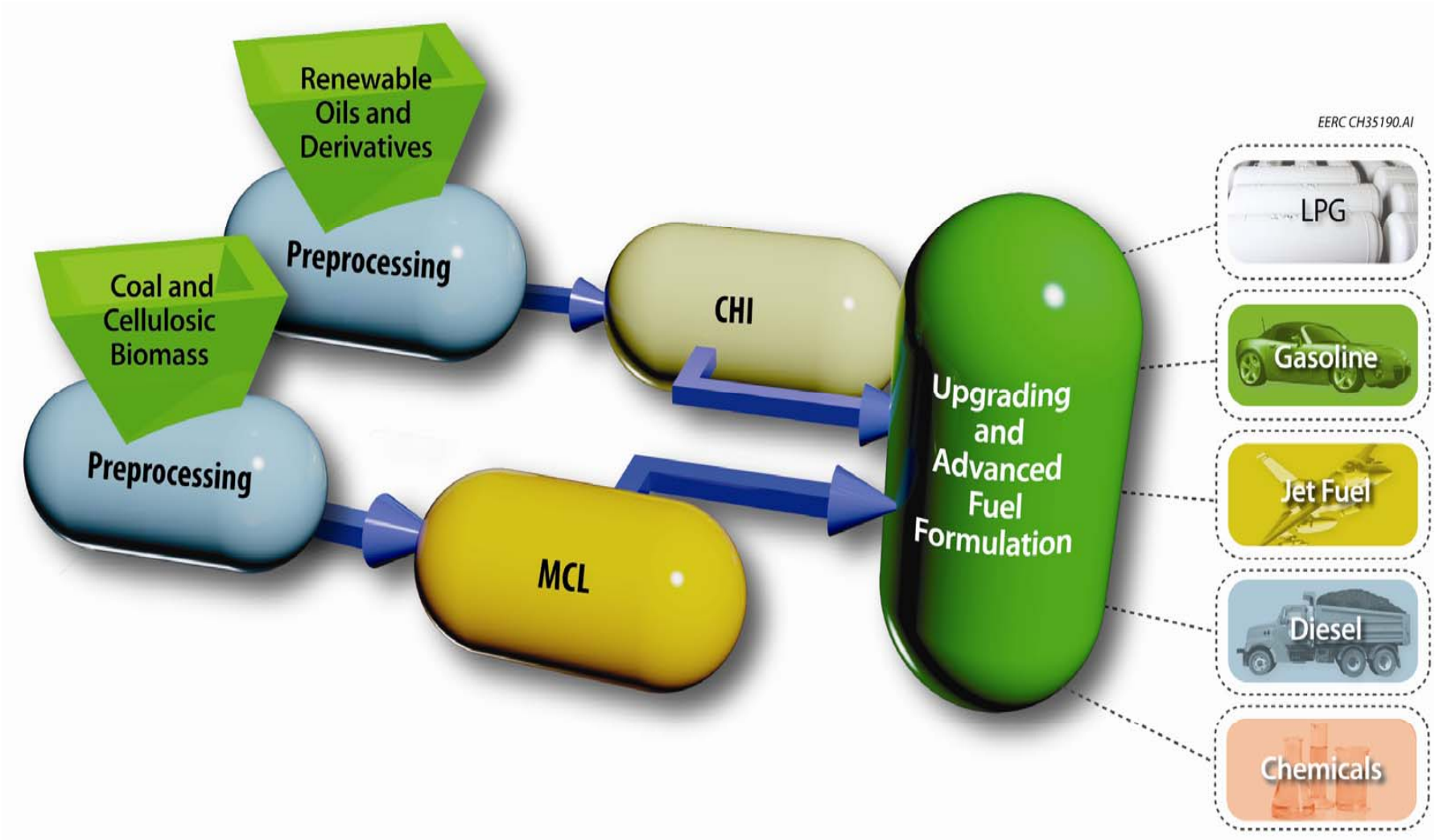


Key reason for higher yield and lower GHG footprint versus indirect liquefaction: Less energy needed to partially break down coal to hydrocarbons and upgrade to fuel, than to completely break down coal to hydrogen and carbon monoxide and upgrade to fuel.

CHI and coal-derived MCL fuels meet critical JP-8 specification requirements

Fuel property	MIL-DTL-83133F requirement	EERC CHI Jet	EERC MCL Jet
Thermal stability tube deposit rating	<3 visual	1.1	1.7
Aromatics, vol%	25 max.	19.8	<1
Olefins, vol%	5 max	1.9	1.8
Sulfur, wppm	3000 max.	Nil	<1
Density, g/cc@15°C	0.775–0.840	0.805	0.840
Flash Point, °C	38 min.	49	45
Freeze Point, °C	-47 max.	-52	-64
Naphthalene, vol%	3.0 max.	0.00	0.00
HV, BTU/lb	18,400 min	18,500	18,550

MCL–CHI integration



Rationale for MCL–CHI integration

Fuel property/ performance feature	Coal to liquids – MCL	Biomass to liquids – CHI	Coal + biomass to liquids (CBTL) MCL + CHI
Chemistry	Cycloparaffinic	Isoparaffinic	Adjustable
JP-8/JP-8+100 quality	Fuel/blendstock	Fuel/blendstock	Premium fuel
Diesel quality	Low cetane	High cetane	Adjustable
Gasoline quality	High octane	Low/mid octane	Adjustable
Meet EPA GHG target	No	Possible	Possible
Land requirement	Low	High	Balanced
Net power production	Importer	Potential exporter	Balanced
Production cost/barrel	Low*	High	Affordable

*Cost competitive at $80/barrel oil

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First new refinery in 35 years?

- By May 2010, the EERC will complete bid-ready design for 1.7-million gallon/year renewable oil refinery to be fully integrated with operations at Tesoro petroleum refinery in Mandan, North Dakota
- Of approximate $6.5 million construction cost, $4.5 million is secured
- Refinery slated for August 2011 commissioning
- Feedstocks to include high free fatty acid-content waste grease, regionally produced crambe and camelina, and—optimistically—algae

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