NC STATE UNIVERSITY

DIVERSIFIED ENERGY

Bio Jet Fuels

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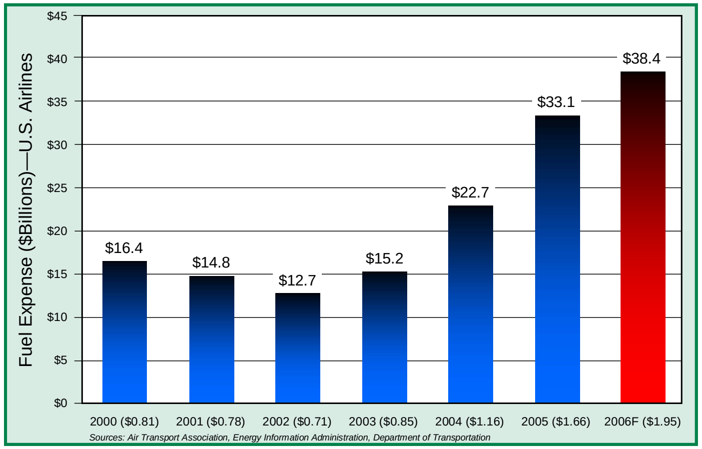
The 5th International Biofuels Conference

Centia™ is a derivation of “green power” in Latin

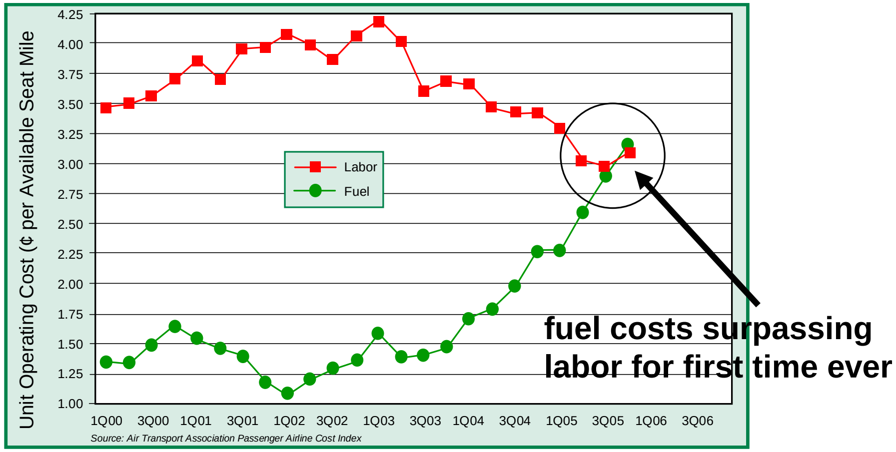
Biojet Fuel is a Big Deal with Global Implications

- **Initial technical focus is on aviation fuel**
  - A big and global market currently not being served
  - Barriers to entry due to technical challenges in making a jet compliant biofuel
  - There is a well-stated need for such a fuel - economics and environment
- **Jet fuel prices and instability are severely impacting air carriers**
  - World uses ~ 73B gallons/year of jet fuel (U.S. uses about 1/3 of this)
  - Has rippling repercussions to economies of all developed nations



Sources: Air Transport Association, Energy Information Administration, Department of Transportation

U.S. Airlines Annual Fuel Expense



fuel costs surpassing labor for first time ever

Source: Air Transport Association Passenger Airline Cost Index

U.S. Airlines Unit Operating Costs

Aviation Biofuel Challenges

- **Aviation specification compliance (chemical/physical)**
  - Cold flow properties (< -47 °C)
  - Energy density (44 MJ/kg basis)
  - Efficiency ($/kJ basis)
  - Proper ratio of *n*-alkanes, iso-alkanes, cycloparaffins, and aromatics
  - Compatibility with materials and additives
- **Aviation specification compliance (combustion/kinetic)**
  - Ignition and extinction characteristics
  - Chemical kinetics and flame speed
  - Flammability limits
- **Want aviation biofuel to have similar chemical composition as Jet-A/JP-8**
  - Lower concentrations of aromatic/naphthenes
- **Biodiesel from transesterification of crop oils will not suffice**
  - Considerably lower energy density than Jet-A/JP-8
  - Kinetic viscosity ranges from 1.9 to 6.0 cSt @ 40°C; need 1.2 cSt
  - Freezing point ~0°C
  - Material compatibility issues

JP-8 surrogate to match chemical kinetics:
43% *n*-dodecane
27% iso-cetane
15% methylcyclohexane
15%1-methylnapthalene

Market Dynamics are Encouraging New Biofuel Processing Technologies

- **Problem statement:**
  - Current biofuel conversion technologies are limited to classes of feedstock, therefore being at the mercy of commodity markets
    - Examples = corn for ethanol and virgin oils for biodiesel
    - ~ 70 - 80% of biofuel output cost is driven by the cost of the feedstock
    - Feedstock supply/demand dynamics can destroy production economics
  - Biofuels plants generally produce only one type of output – also a commodity
  - Few to date are addressing the challenges of biojet fuel
- **New biofuel processing technologies should be able to:**
  - Use a wide variety of feedstocks
    - Oils -- saturated, unsaturated, high and low free fatty acid contents, etc.
    - Non-oils -- cellulosic type approaches, gasification, etc.
  - Produce a wide variety of biofuels, including “complex” fuels like biojet fuel
  - Offer a replacement to petroleum-derived fuels
  - Deliver attractive capital and O&M costs competitive to petroleum fuels

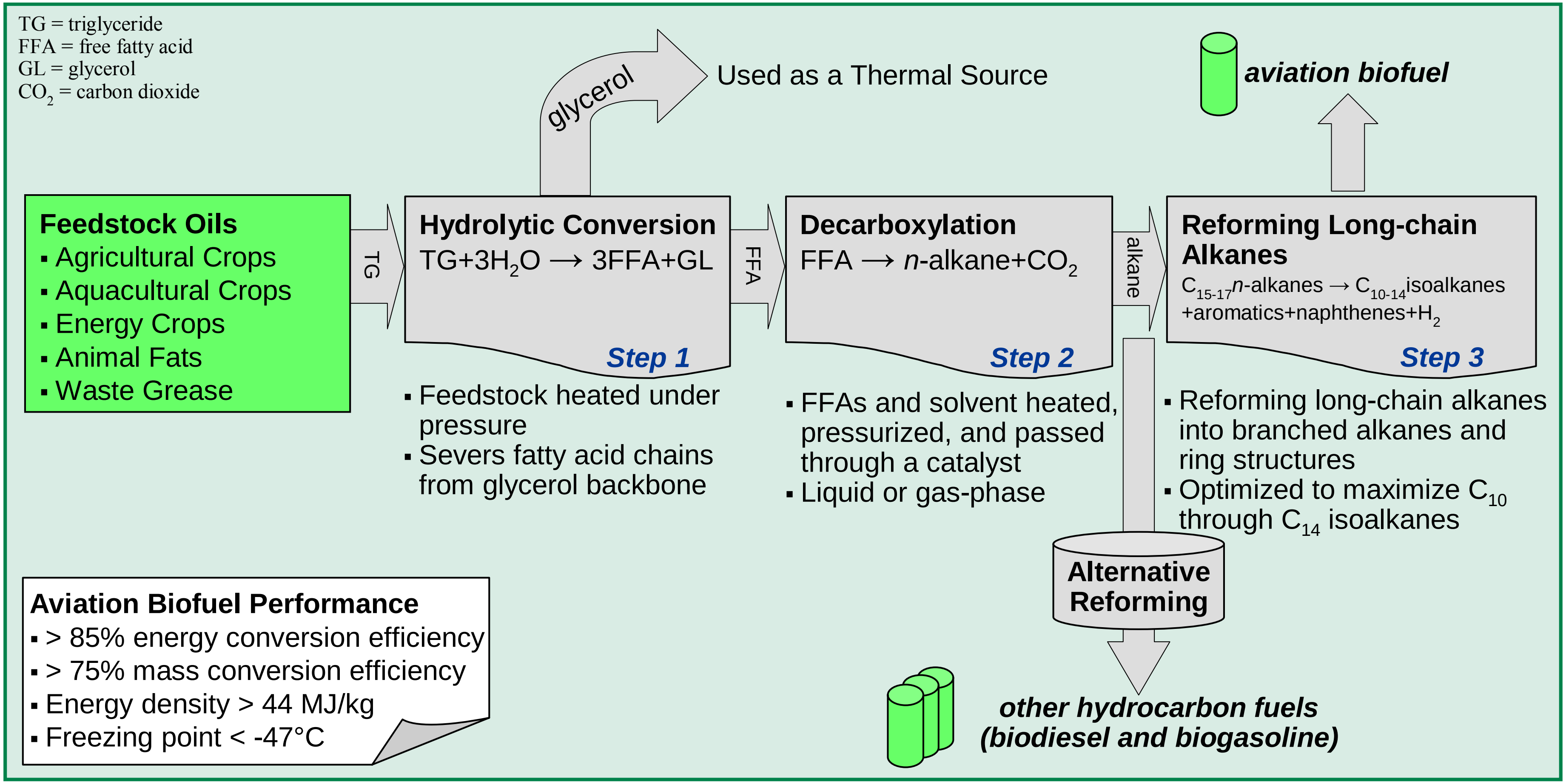
Other Aviation Biofuel Approaches

- **Biodiesel pathway as initial step in multi-step process**
  - Decarboxylate/deoxygenate methyl esters to increase energy density
  - Isomerize to decrease freezing point
  - Technically possible, but <u>prohibitively expensive</u>
- **Pyrolysis has low yields and is hard to control**
  - Need to avoid small HCs due to volatility (e.g., iso-octane flashpoint ~-40°C)
  - May also get tar
- **Enzymatic approaches are not mature**
  - Low energy input attractive (biological energy vs thermal energy)
  - ‘Magic bug’ not yet found
- **Fisher-Tropsch synthesis of large *n*-alkanes from syngas**
  - Wide selection of fuelstocks (e.g., biomass and coal) to generate syngas
  - Demonstrated, but also expensive
- **Plasma-assisted approaches**
  - Use plasmas to open chemical pathways prohibited at conventional temps
  - Promising technology, but not mature

Current Alternative Jet Fuel Producers

- **Sasol, South Africa**
  - Certified 50/50 blend of FT synthetic fuel with Jet-A
  - FT feedstock is coal and natural gas
- **Syntroleum, US**
  - FT synthetic fuel with natural gas as feedstock
  - USAF flew B-52 in Sept 07 on 50/50 blend with JP-8
  - Also working Tyson Foods on animal fats to jet fuel technology (unknown)
- **Universal Oil Products, US**
  - Hydro-deoxygenation of FFA's
    - Cost/source of hydrogen a concern
  - Have delivered some biojet fuel to DARPA for testing and certification
- **EERC, US**
  - Using new feedstock (cuphia) and transesterifing directly to biojet fuel
- **GE, US**
  - Biomass gasification to bio-oil, hydroprocessing of bio-oil

Centia™ Process Overview



TG = triglyceride
FFA = free fatty acid
GL = glycerol
CO_2 = carbon dioxide

glycerol

Used as a Thermal Source

aviation biofuel

Feedstock Oils
- Agricultural Crops
- Aquacultural Crops
- Energy Crops
- Animal Fats
- Waste Grease

TG

Hydrolytic Conversion

$TG+3H_2O \longrightarrow 3FFA+GL$

Step 1

- Feedstock heated under pressure
- Severs fatty acid chains from glycerol backbone

FFA

Decarboxylation

$FFA \longrightarrow n\text{-alkane}+CO_2$

Step 2

- FFAs and solvent heated, pressurized, and passed through a catalyst
- Liquid or gas-phase

alkane

Reforming Long-chain Alkanes

$C_{15\text{-}17}\,n\text{-alkanes} \rightarrow C_{10\text{-}14}\,\text{isoalkanes} + \text{aromatics}+\text{naphthenes}+H_2$

Step 3

- Reforming long-chain alkanes into branched alkanes and ring structures
- Optimized to maximize C_{10} through C_{14} isoalkanes

Alternative Reforming

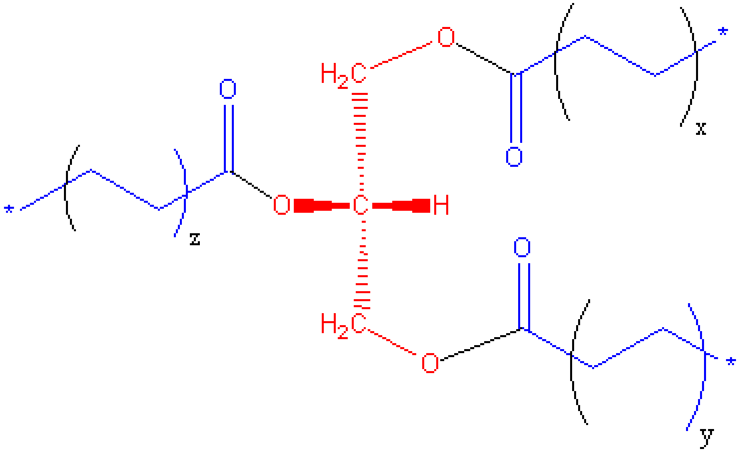
other hydrocarbon fuels (biodiesel and biogasoline)

Aviation Biofuel Performance
- > 85% energy conversion efficiency
- > 75% mass conversion efficiency
- Energy density > 44 MJ/kg
- Freezing point < -47°C

Attributes of the Process

- **Feedstock (input) flexibility**
  - Process can use almost any renewable oil source
    - Agriculture crops, aquaculture crops, energy crops, animal fats, waste greases, etc
  - Allows for the use of the cheapest and most readily available feedstock at any given time or location
- **Biofuel (output) flexibility**
  - Can produce biojet fuel, 2nd generation biodiesel/additive, and biogasoline
  - Allows for output options to maximize the economics; also provides for interim markets during fuel qualification testing
- **Performance and aviation compliance**
  - > 85% energy conversion efficiency expected
  - Compliant to biojet fuel requirements – cold flow, energy density, etc
  - Translates into higher yields, lower costs, and easier qualification
- **Maturity, scalability and affordability**
  - Demonstrated results drive down risk; scalability well-understood
  - Initial economics shows attractive operating costs per gallon of output

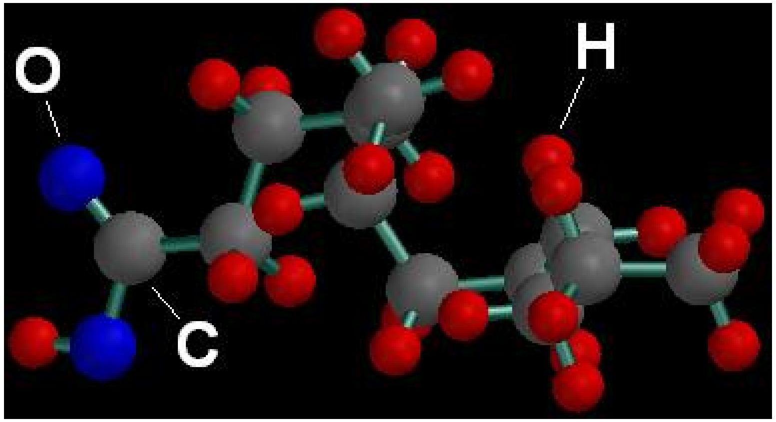
Step 1 - Hydrolysis: TG to FFA

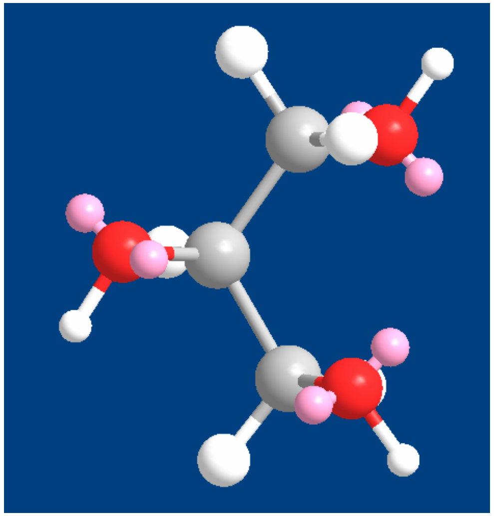


+ 3 H_2O

yields

$3\ CH_3(CH_2)_xCOOH + C_3H_5OH_3$

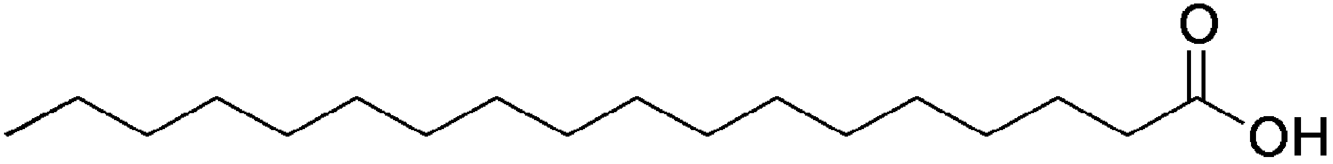




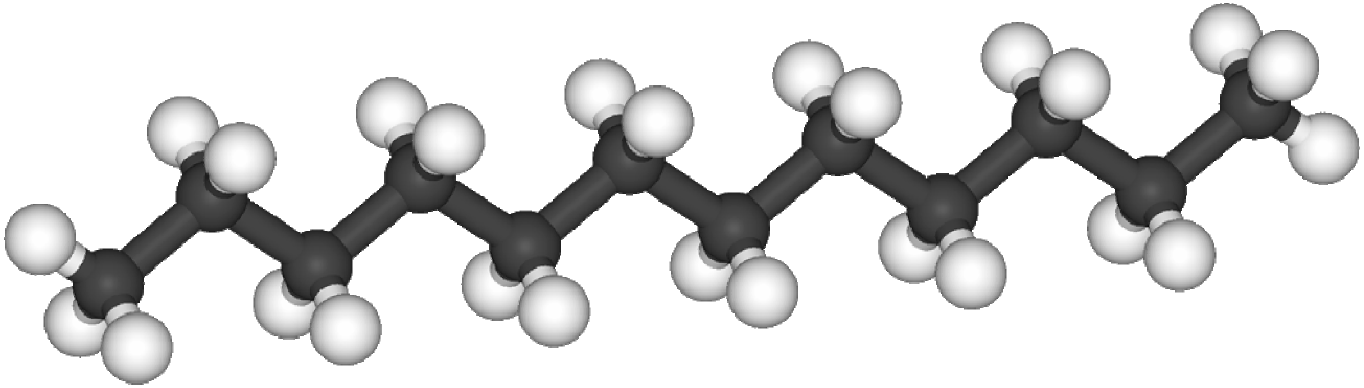
Step 1 - Hydrolysis

- **Fuelstock consists of mixture of triglycerides and FFA**
  - Composition a function of source
    - Beef tallow primarily stearic acid (saturated)
    - Pork lard primarily oleic acid (mono-unsaturated)
  - Price a function of free fatty acid content
    - Edible lard ~0.4% FFA, ~$0.20/lb
    - Inedible lard ~4% FFA, $0.15/lb
- **Hydrolyze at high temperature and pressure**
  - Convert triglycerides into FFA and glycerol
  - 250 °C, 5 MPa, 2 hours, 40% water and 60% oil
  - Counterflow geometry
  - 99%+ efficient conversion
- **Mature technology, demonstrated at industrial scale**
  - Colgate-Emery Process most common
  - Energy intensive, but not necessarily bad for Centia™
  - No problems anticipated
- **Working on faster process (higher temperature)**

Step 2 - Decarboxylation: FFA to *n*-alkane



Catalyst, heat and pressure

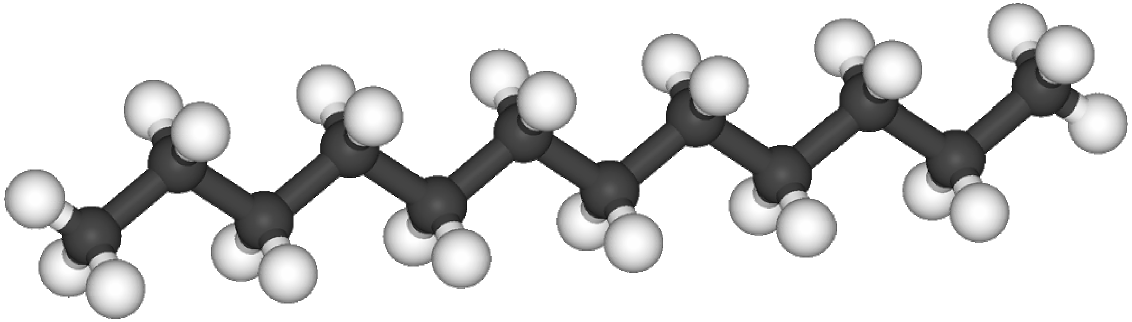


+ CO_2

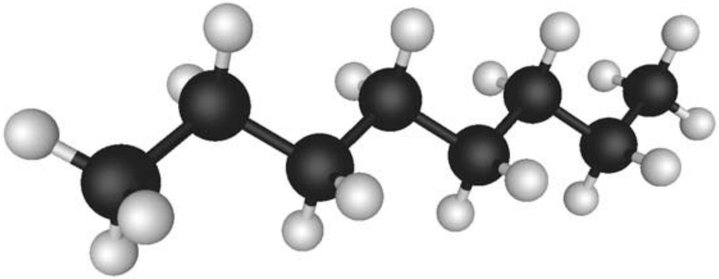
Decarboxylation

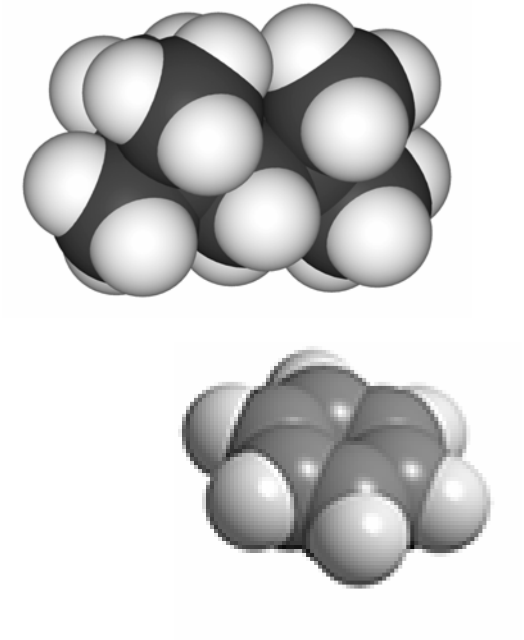
- **Liquid phase demonstrated with both saturated and unsaturated fats**
- **Gas phase demonstrated, unsaturated fats yielding interesting results**
  - May be a possible approach to simultaneous decarboxylation and hydro-reforming
  - May also be a path way to aromatics directly for the ~8% desired
  - Most likely more difficult to control the product composition
    - Tar and coke
    - Light hydrocarbons
- **Will move forward aggressively with <u>liquid phase</u> and continue to investigate gas phase**
  - Liquid phase is EM baseline
  - Gas phase an area to be explored in project

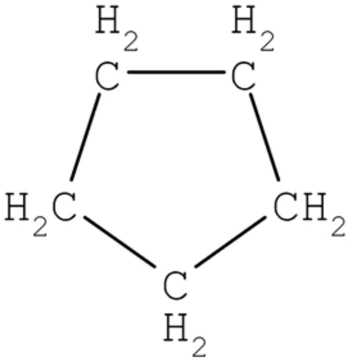
Step - 3: Hydroisomerization/Hydrocracking



Catalyst, heat and pressure



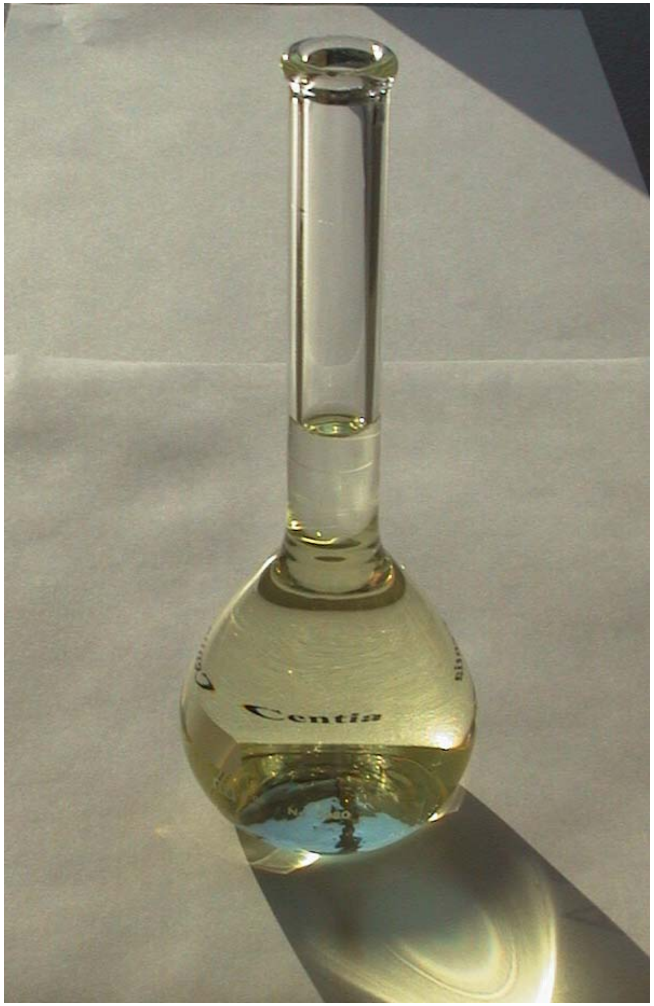




Hydroaromatization
Hydrocyclization

HC/HI of *n*-Heptadecane

- **Good catalyst identified**
- **Run times varied from 30 minutes to 360 minutes**
- **Typical temperatures between 250 and 300 °C**
- **Typical pressures between 20 and 35 atm**
- **Selectivity and yield optimization continuing**



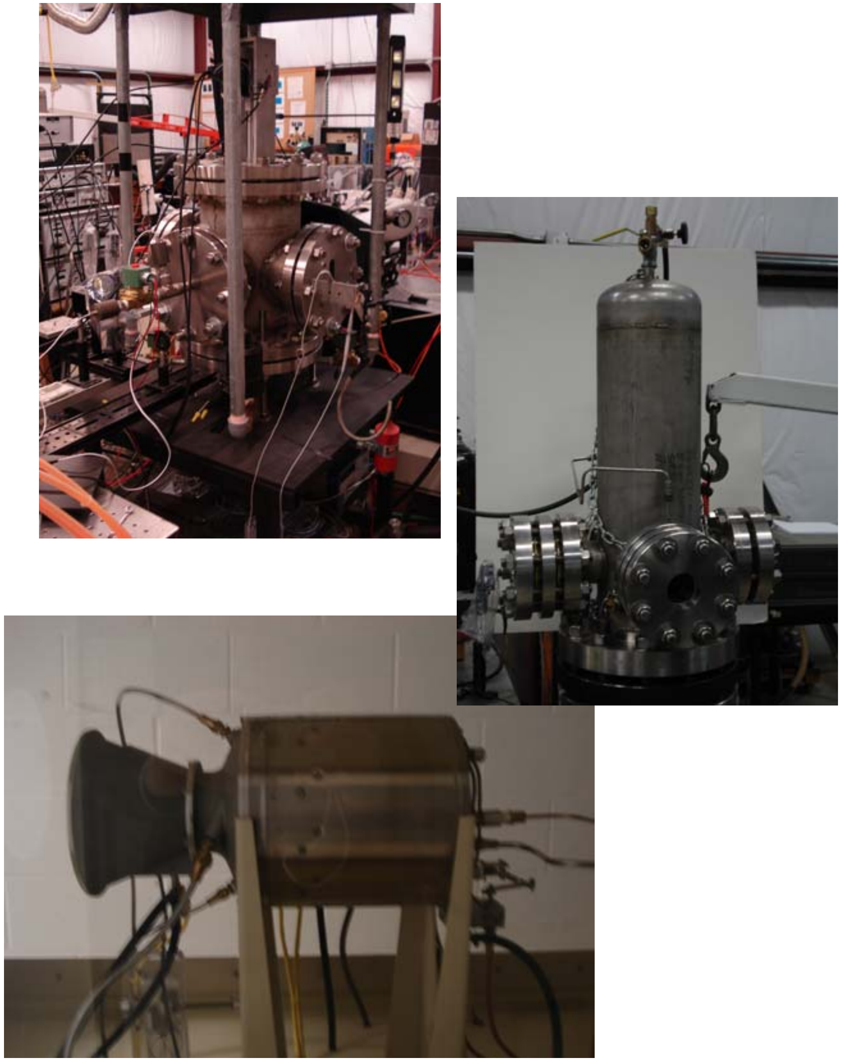
Path Forward

- **Build upon successes already accomplished**
  - Lab Scale results
  - Engineering Model design and performance/economic modeling completed
  - Commercial vendors established for reactor vessels
- **Engineering Model objectives include:**
  - End-to-end, integrated demonstration of the technology in Raleigh, NC
  - Scaled up to approximately 20k gallons/year in volume (~ 10 liters/hour)
  - Demonstrate the production of a biojet fuel
  - Demonstrate multiple feedstocks – e.g., oils from soy bean, canola/palm, algae, inedible and edible animal fats, and blends thereof
  - Test and qualify all fuels produced
  - Explore production of alternative fuels – e.g., 2nd gen biodiesel & biogasoline
  - Validate performance and refine economics
  - Start commercialization planning

Thank you for your kind attention!

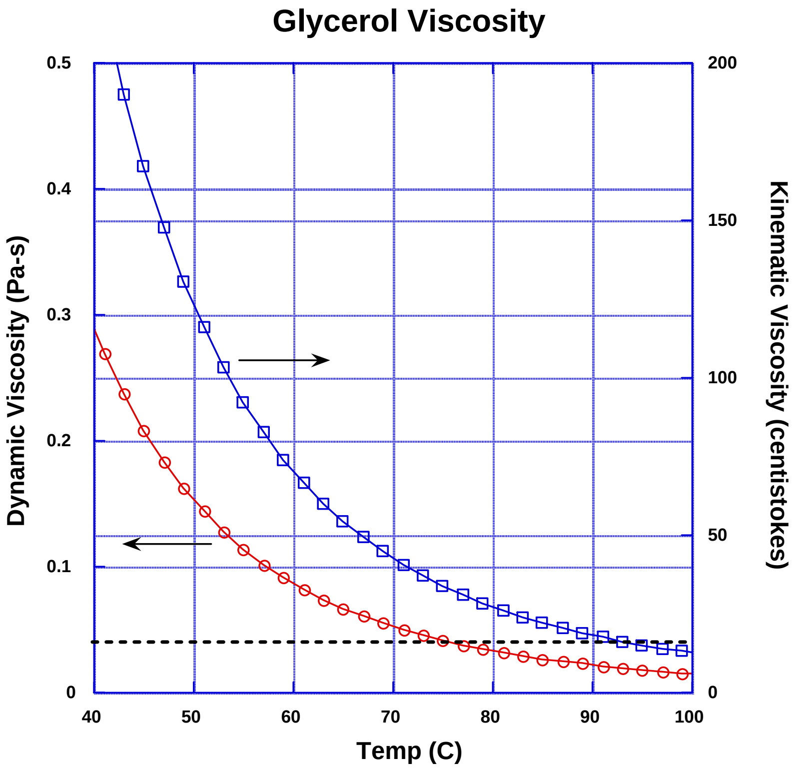
Fuel Characterization

- **Need to meet physical properties**
  - Viscosity
  - Flash Point
  - Energy Density
  - Freeze Point
- **Need to meet chemical kinetic properties**
  - Ignition characteristics
  - Laminar burning velocity
  - Extinction strain rate
  - Smoke point
- **Need to demonstrate in a jet engine**
  - Thrust
  - Emissions

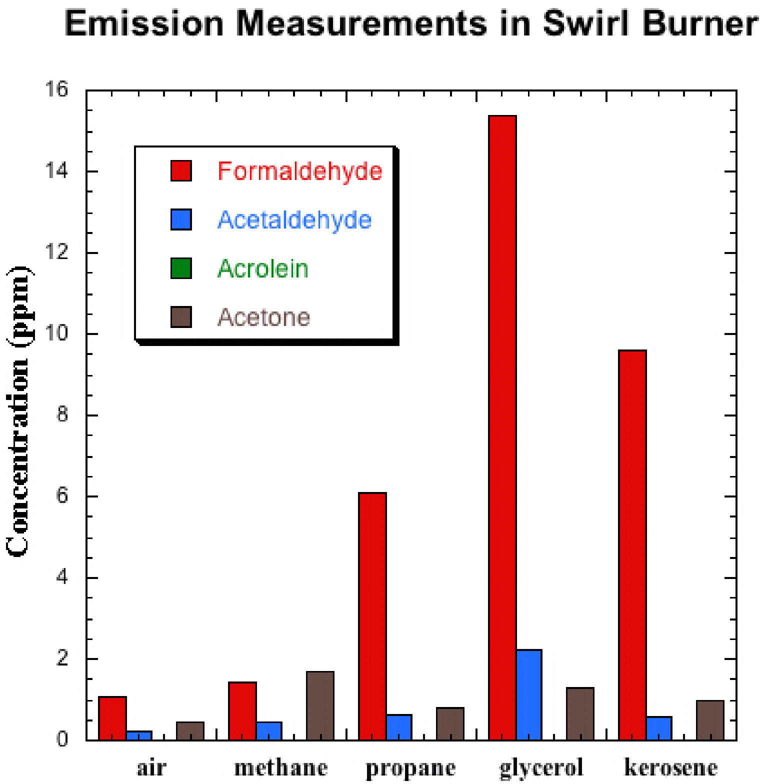


Glycerol Combustion

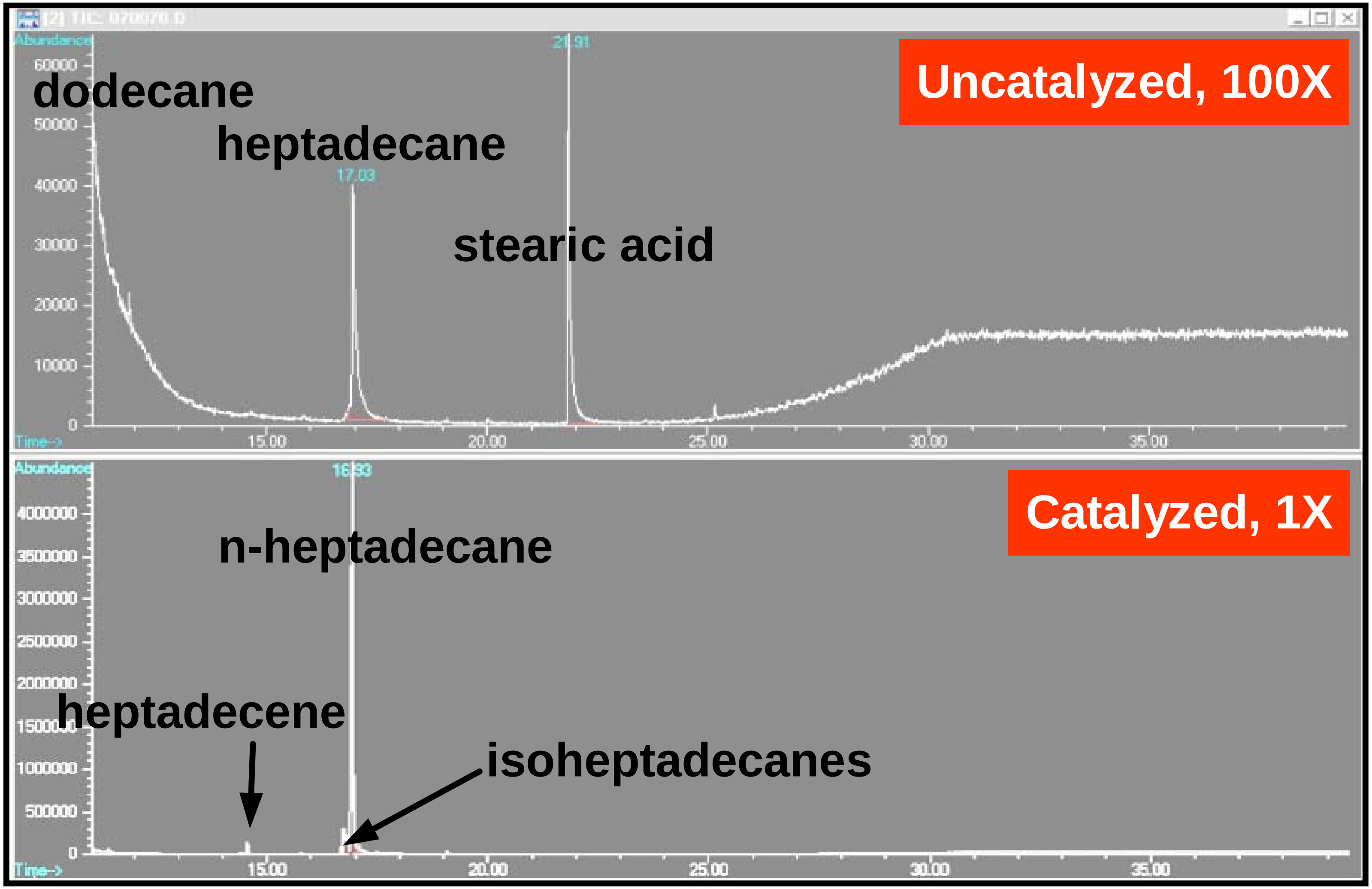
- **One mole of glycerol produced for each mole of triglyceride**
  - 10% by weight
  - Low value and often considered waste
- **Oxygenated hydrocarbon**
  - 'free' energy source for thermal inputs into process
    - ~16 MJ/kg
  - Potentially a clean burning fuel
  - Problems
    - Auto-ignition temp 170 °C higher than n-alkanes of interest
    - Viscosity
    - Acrolein emission?
- **Investigating oxidation characteristics using swirl burner**
  - Can adjust residence time and burning characteristics
  - Measuring emission to detect aldehydes



Swirl Burner on Pure Glycerol



Liquid Phase Decarboxylation of Stearic Acid



Uncatalyzed, 100X

dodecane

heptadecane

stearic acid

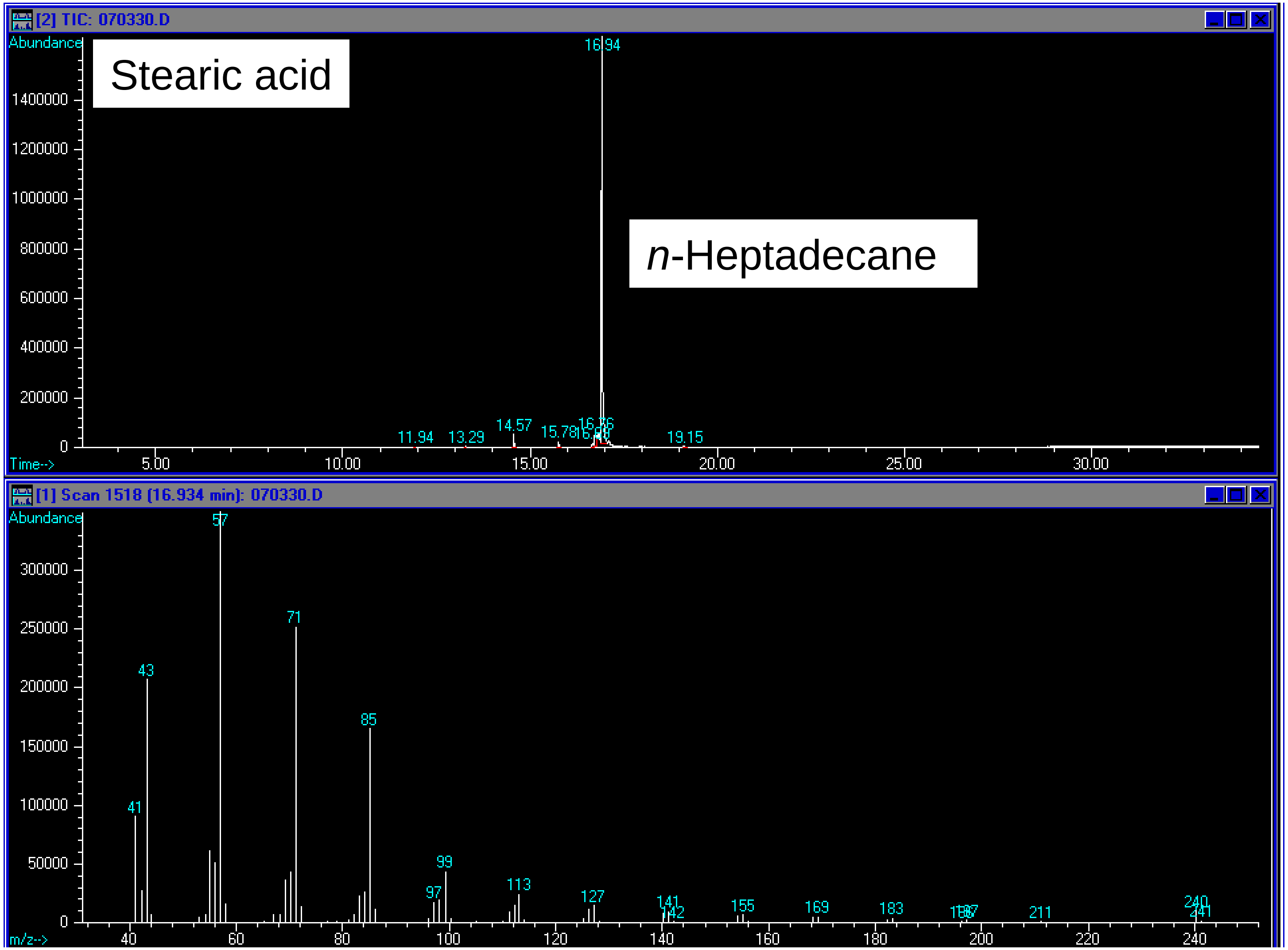
Catalyzed, 1X

n-heptadecane

heptadecene

isoheptadecanes

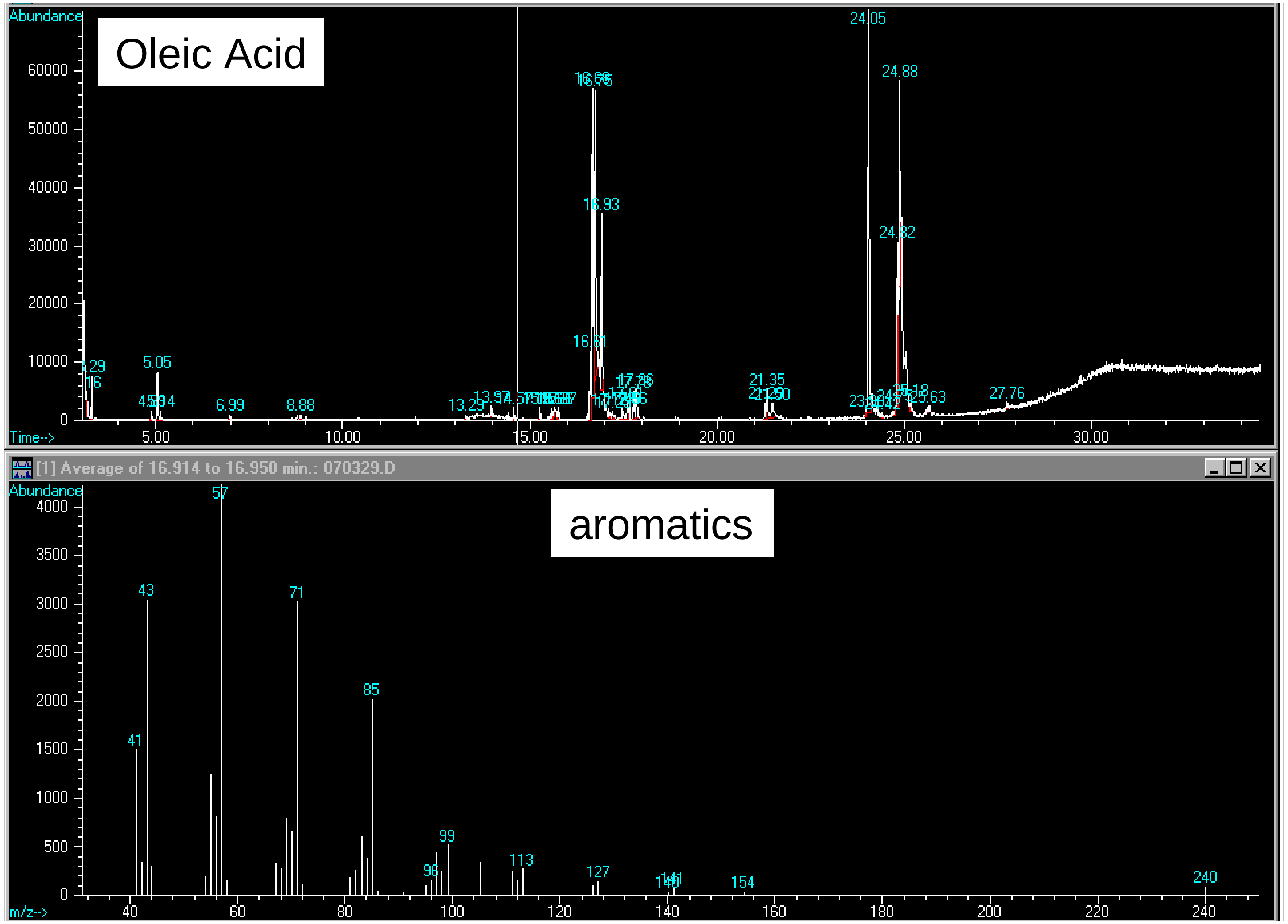
Gas Phase Decarboxylation



Stearic acid

n-Heptadecane

Gas Phase Decarboxylation


Oleic Acid

aromatics

[1] Average of 16.914 to 16.950 min.: 070329.D

Who’s pushing Biojet fuels forward?

- **DARPA**
  - Primarily interested in ‘alternative jet fuels’ of which biojet fuel is a subset
  - 4 18m grants at ~$5M each
- **Virgin Fuels**
  - Part of The Virgin Group
  - Set aside up to ~$3B over next decade for biofuels
  - Committed approx $300M this year, primarily to ethanol production
  - Committed to fly 747 on biojet fuel in 2008
- **Air New Zealand + Boeing + Rolls Royce**
  - Major push to be first commercial airline to fly biojet fueled aircraft
- **Tecbio (Brazil)**
  - Pushing their crop, the Babassu palm, for biokerosene (18 Mha wild)
  - Working with NASA in US
- **EU in general**
  - Carbon counting will be a primary driver for aviation biofuels

Step 2 - Decarboxylation

- **Remove carboxyl group from FFA to form *n*-alkane**
  - FFA → *n*-alkane + CO_2
- **Catalytic process**
  - Catalyst with high efficiency and selectivity identified
- **Demonstrated at lab scale**
  - Liquid-phase stirred catalytic slurry in HC solvent
  - Gas-phase in continuous flow heated vessel
  - Both currently under investigation at NC State
    - Promising results from both
- **Engineering challenges to be addressed**
  - Gas phase vs. liquid phase
  - Optimal characteristics of catalyst (physical and chemical)
  - Catalyst deactivation and regeneration
  - Role of hydrogen carrier gas
    - Separation of CO_2 from H_2
  - Role of solvent in liquid reaction

Integrated Engineering Model (EM) is the Next Step

- **12-month program and $7M budget**
- **Build upon successes already demonstrated at Lab Scale**
- **EM objectives include:**
  - End-to-end, integrated demonstration of the technology in MAE West facility
  - Scaled up to approximately 20k gallons/year in volume (~ 10 liters/hour)
  - Demonstrate the production of a biojet fuel
  - Demonstrate multiple feedstocks – e.g., oils from soy bean, canola/palm, algae, inedible and edible animal fats, and blends thereof
  - Test and qualify (internally and with SWRI) fuels produced
  - Validate performance and refine economics
  - Explore production of alternative fuels – e.g., 2^{nd} gen biodiesel & bio-gasoline
- **Begin commercialization planning**
  - Pilot-plant (~ 1 – 5 M gal/yr) requirements definition and conceptual design
  - Conduct key trades and other technology risk activities
  - Administration – IP filings, funds for long-term operations, etc
  - Continues for at least 24 month period under this funding profile

Decarboxylation of FFAs

- Continuously stirred autoclave reactor for liquid-phase process
- Stearic acid in dodecane solvent with Pd/C catalyst
- 300°C temp and 15 atm pressure
- Reaction time of 300 minutes
- Monitor CO_2 evolution to determine reaction progress
- Decarboxlyation successful
- Have also used heptadecane as solvent successfully

EM Scale Hydrolysis Reactor

- **Have demonstrated hydrolysis at small scale in batch mode**
- **Currently constructing continuous flow Engineering Model scale reactor**
- **Pressures up to 50 atm and temps up to 250 °C**
- **EM will use inductive heating rather than glycerol combustion**
- **10 liter/hr capacity**
- **Flash vaporization to remove water for reuse and water-free glycerol for combustion**
- **Heat exchanger for glycerol - animal fats / vegetable oils**

Example of Commodity Risks

Commodity Market

Corn Price (cents/bushel), weekly

trouble spot

Commodity Market

Ethanol Price (dollars/gallon), weekly

Re-Cap -- Key Advantages of Centia™ Process

- **Feedstock (input) flexibility**
  - Process can use almost any renewable oil source
    - Agriculture crops, aquaculture crops, energy crops, animal fats, waste greases, etc
  - Allows for the use of the cheapest and most readily available feedstock at any given time or location
- **Biofuel (output) flexibility**
  - Can produce biojet fuel, 2nd generation biodiesel/additive, and bio-gasoline
  - Allows for output options to maximize the economics; also provides for interim markets during fuel qualification testing
- **Performance and aviation compliance**
  - > 85% energy conversion efficiency
  - Compliant to biojet fuel requirements – cold flow, energy density, etc
  - Translates into higher yields, lower costs, and easier qualification
- **Maturity, scalability and affordability**
  - Demonstrated results drive down risk; scalability well-understood
  - Initial economics shows attractive operating costs per gallon of output

Centia™ Background

- **Technology developed by North Carolina State University (NCSU)**
  - A recognized leader in bioenergy
  - Leveraging development and know-how from decades of biofuels work
- **3 U.S. Patent and Trademark Office provisional patents filed**
  - More likely coming . . .
  - Conversion to non-provisional and Patent Cooperation Treaty filings this Fall
- **Licensed on an exclusive worldwide basis to DEC**
  - DEC bringing systems engineering and commercialization expertise
- **Broader team of 5 strategic partner companies established**
- **Lab Scale demonstration successfully completed to validate the fundamental science and engineering**
- **Next steps**
  - 12 month Integrated Engineering Model demonstration
  - Commercial planning: system design, pilot-plant location and feasibility

Step 3 - Hydroisomerization

- **Straight chain C_{15}-C_{17} alkanes do not have required chemical or physical properties**
- **Catalytically isomerize/crack *n*-alkanes**
  - Shorter chain length (C_{10}-C_{14})
  - Introduce chain branching
    - Changes cold flow properties significantly
    - Dramatic change in ignition characteristics
  - Introduce cyclic compounds
- **Demonstrated at industrial scale**
  - HI/HC a commercially viable process in petrochemical industry
  - Heptadecane HI/HC demonstrated at NCSU
    - Stirred autoclave reactor, similar to reactor used for decarboxlyation
- **Determining catalyst and “recipe” to produce jet fuel**