Hydrotreating of Triglycerides to make Aviation Biofuels

Research I Technology I Catalysts

Biomass 2011, National Harbor, Maryland. 27th July, 2011

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HALDOR TOPSØE

Topsøe Group

Headquarters, Lyngby, DK

Catalyst plant, Frederikssund, DK

- Turnover: DKK 4.2 bn (USD 820 MM)
- Result: DKK 470 MM (USD 91 MM)
- Approx. 2100 employees

Catalyst plant, Houston, Texas

Haldor Topsøe Refinery Technologies

- Hydrotreating
  - Ultra low sulphur diesel
  - Coker distillates
  - Naphtha hydrotreating
  - Kerosene hydrotreating
  - Aromatics saturation
  - FCC pretreatment
  - Processing of biofuels
- Hydrocracking
- Staged partial conversion
- Aroshift
- Polyshift
- Color control
- Sulphur management
- Hydrogen

HALDOR TOPSØE

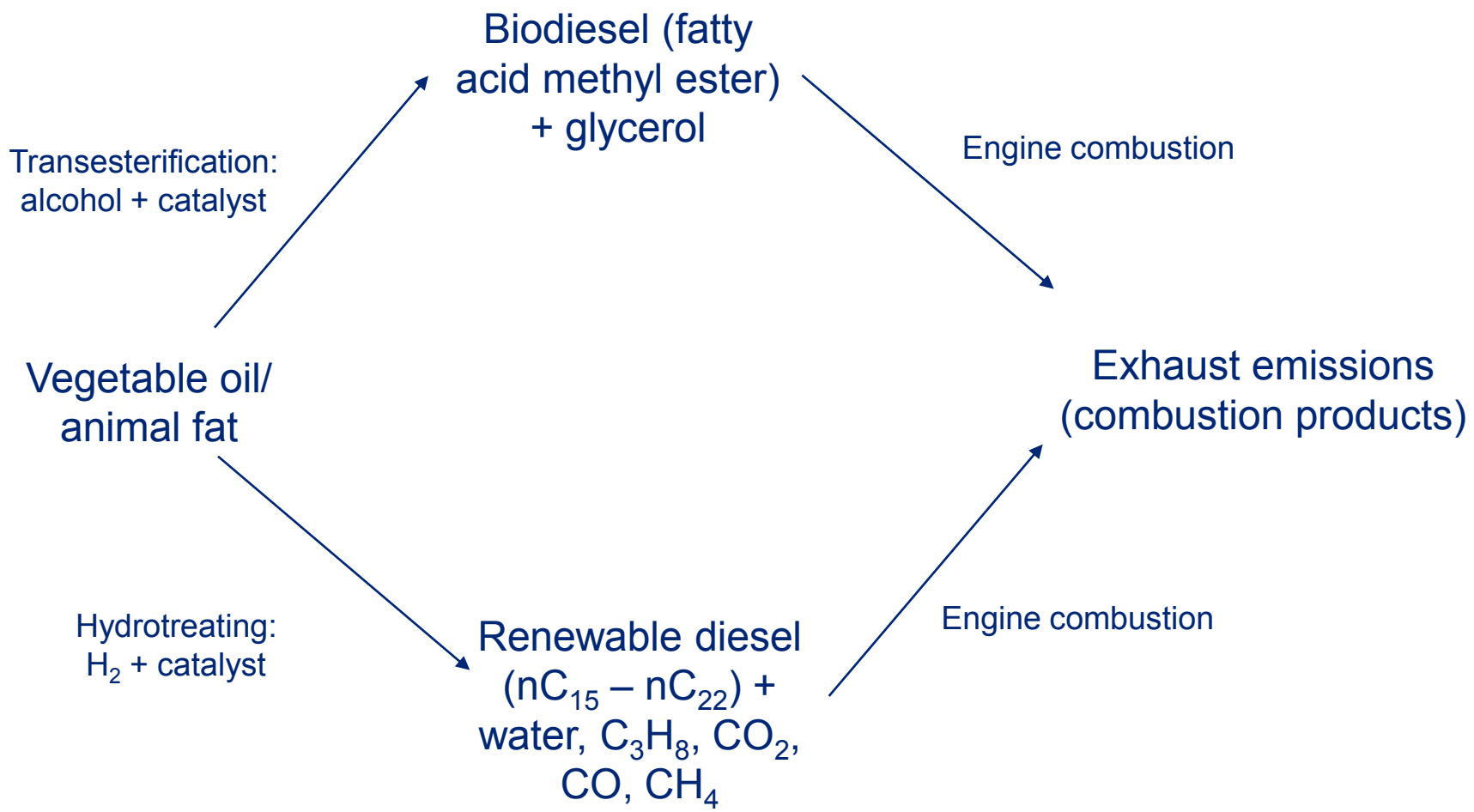
Presentation Outline

- Utilization of triglycerides for fuel purposes
- Background
  - Process and Chemistry
- Pilot Test
  - Corn Oil to Jet Fuel
- Industrial Case
- Challenges
- Catalysts

Known Biofuel Challenges

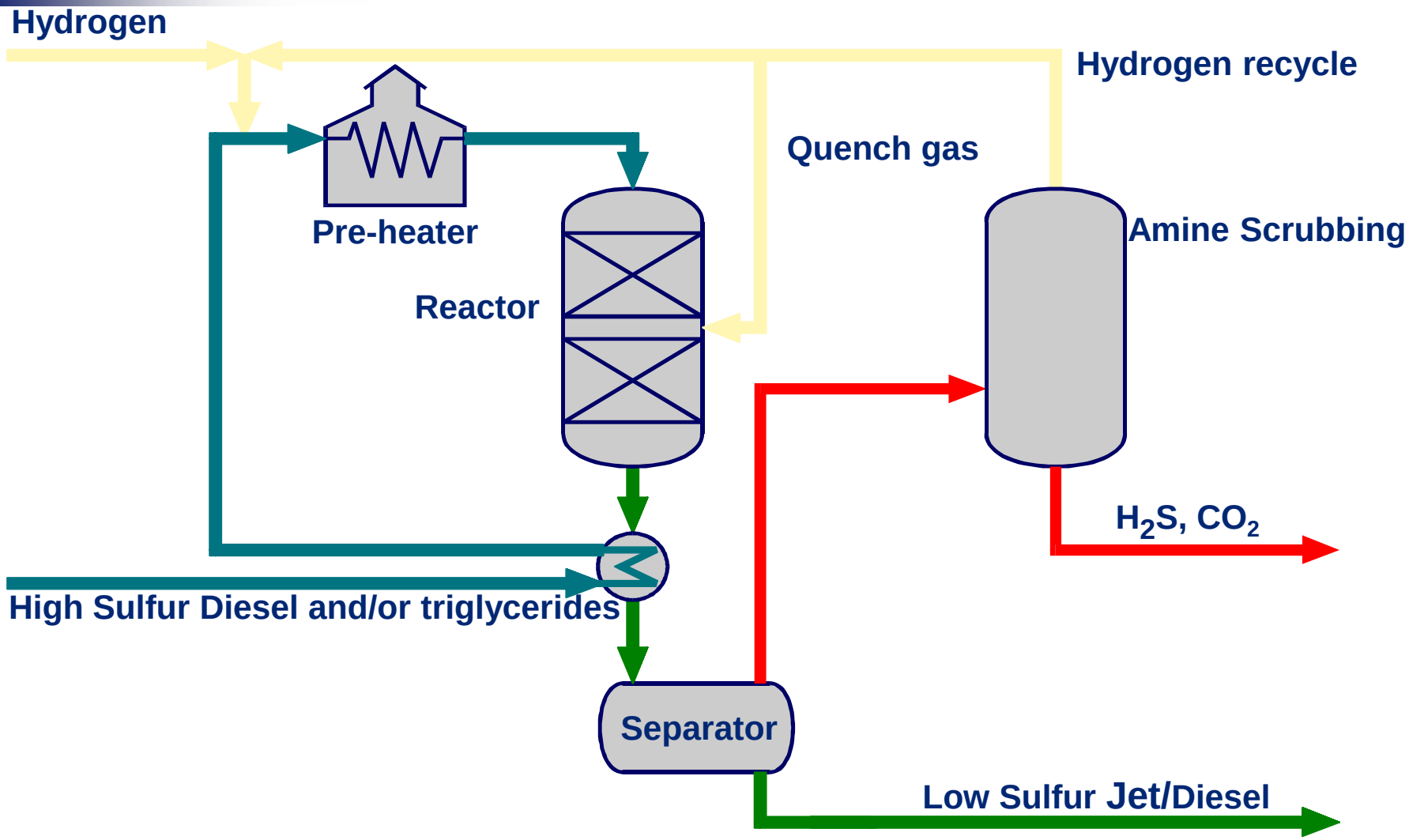
- Preferred fuels are liquid hydrocarbons
  - Compatibility with existing fleet
  - Energy density
- Large alternative carbon sources are solid or gas
  - Natural Gas
  - Coal
  - Biomass (lignocellulosic)
  - Waste
- Contains more than C and H
  - Oxygen
  - Impurities

Biodiesel vs. Renewable Diesel

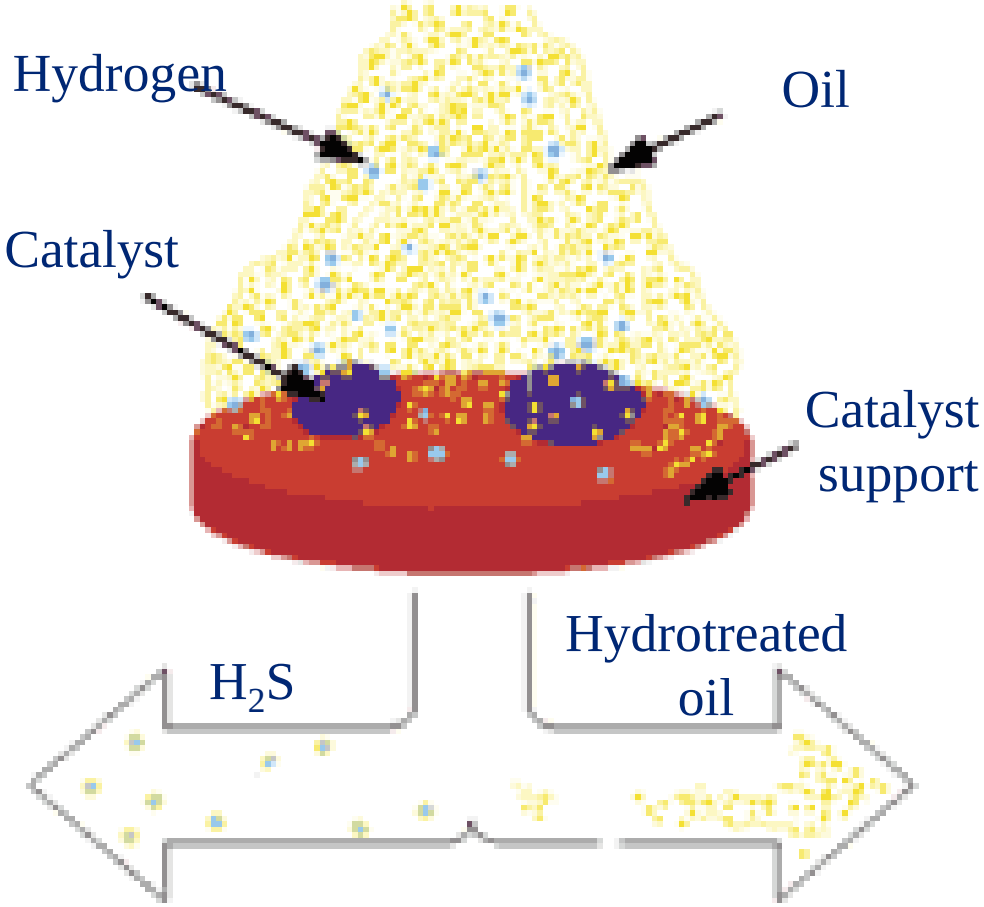


Freely from: Knothe, G. Biodiesel and renewable diesel: A comparison, Progress in Energy and Combustion Science 36 (2010) 364 - 376

Hydrotreating Process Layout



Hydrotreating Fossil Fuels



Temp: 300-400 °C
Pressure: 20-100 bar

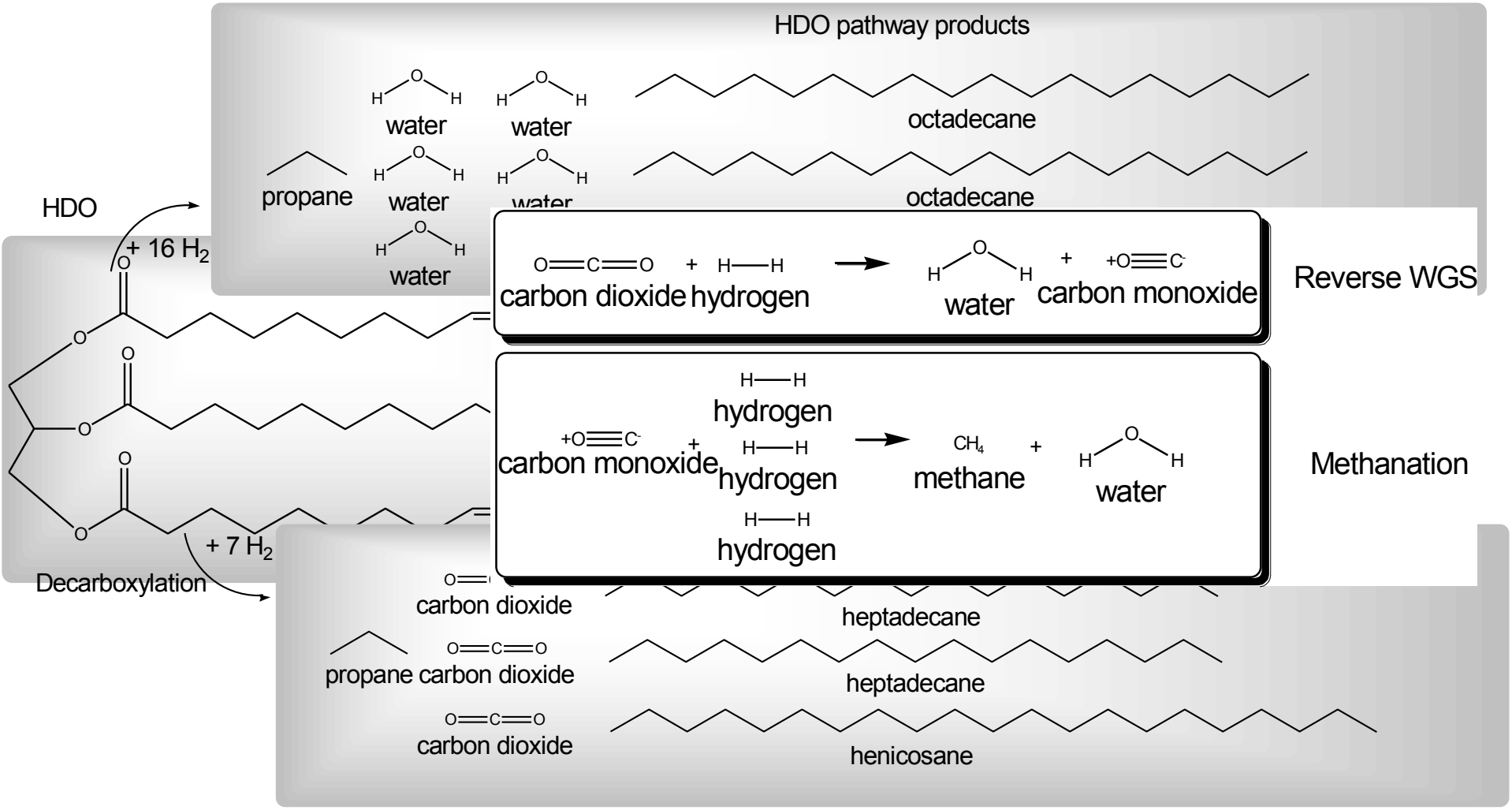
Catalyst:

Surf. area: 200 m^2/g

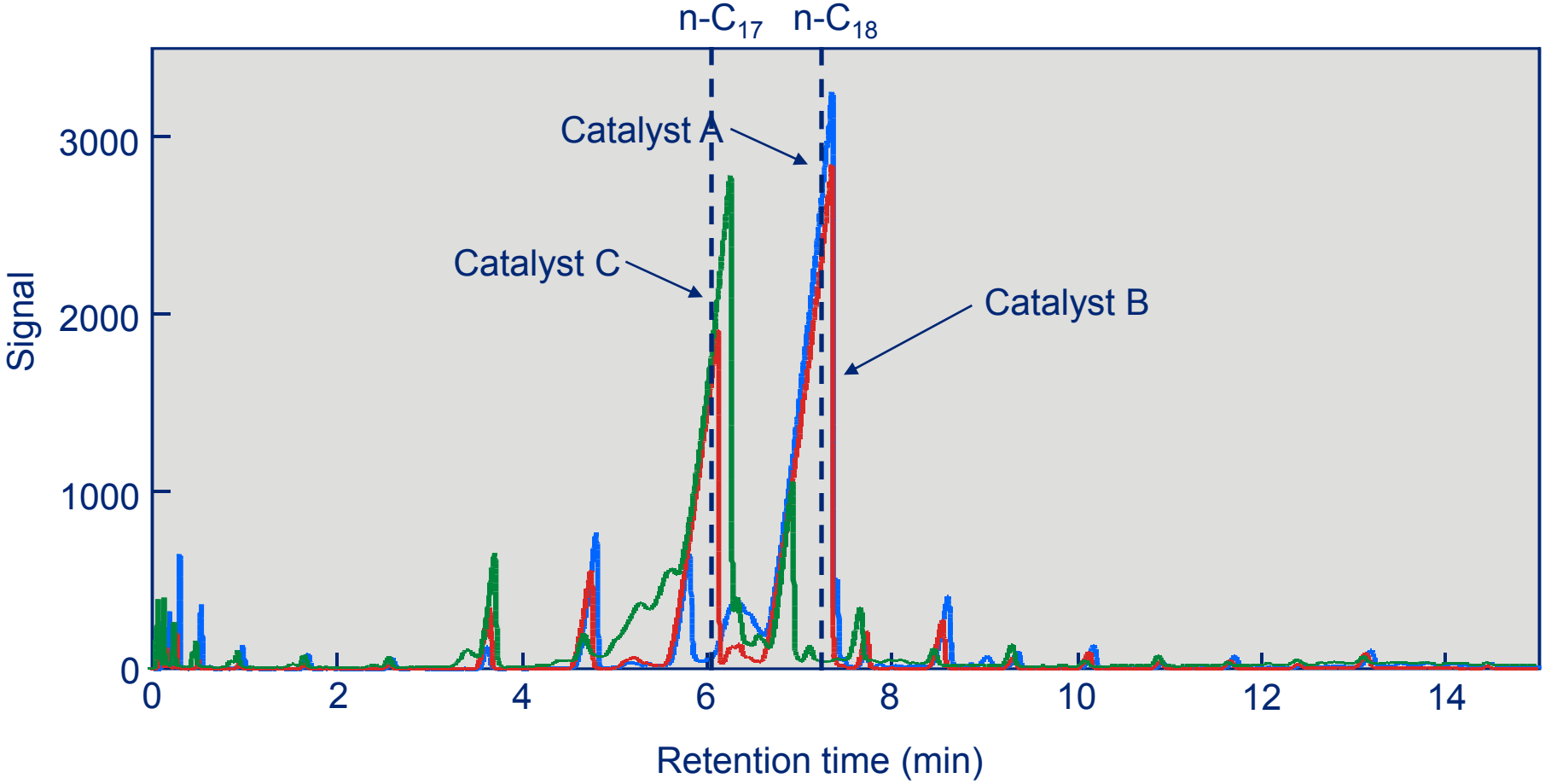
NiMo / CoMo

Carrier: Al_2O_3

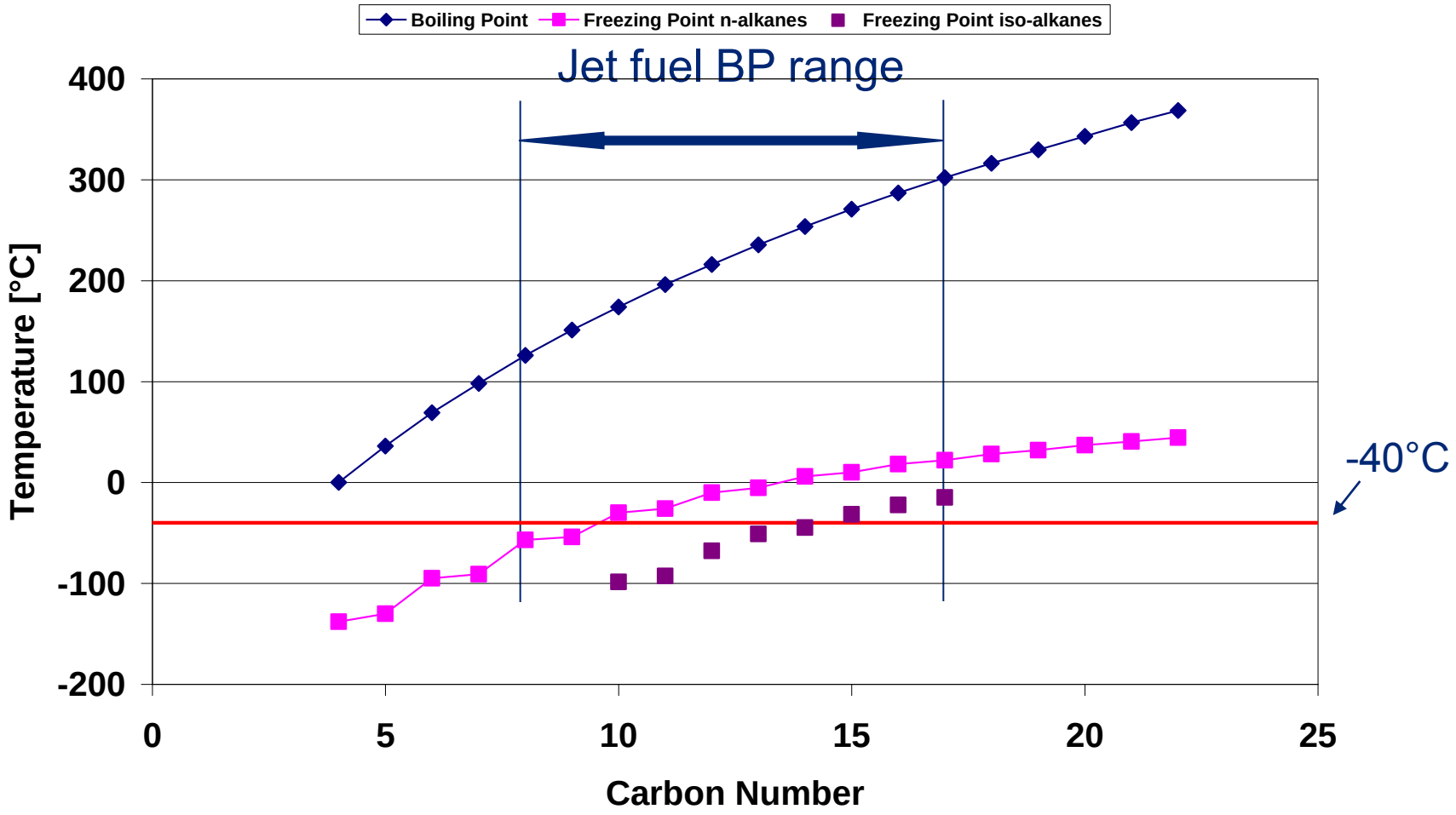
Hydrotreating of Triglycerides



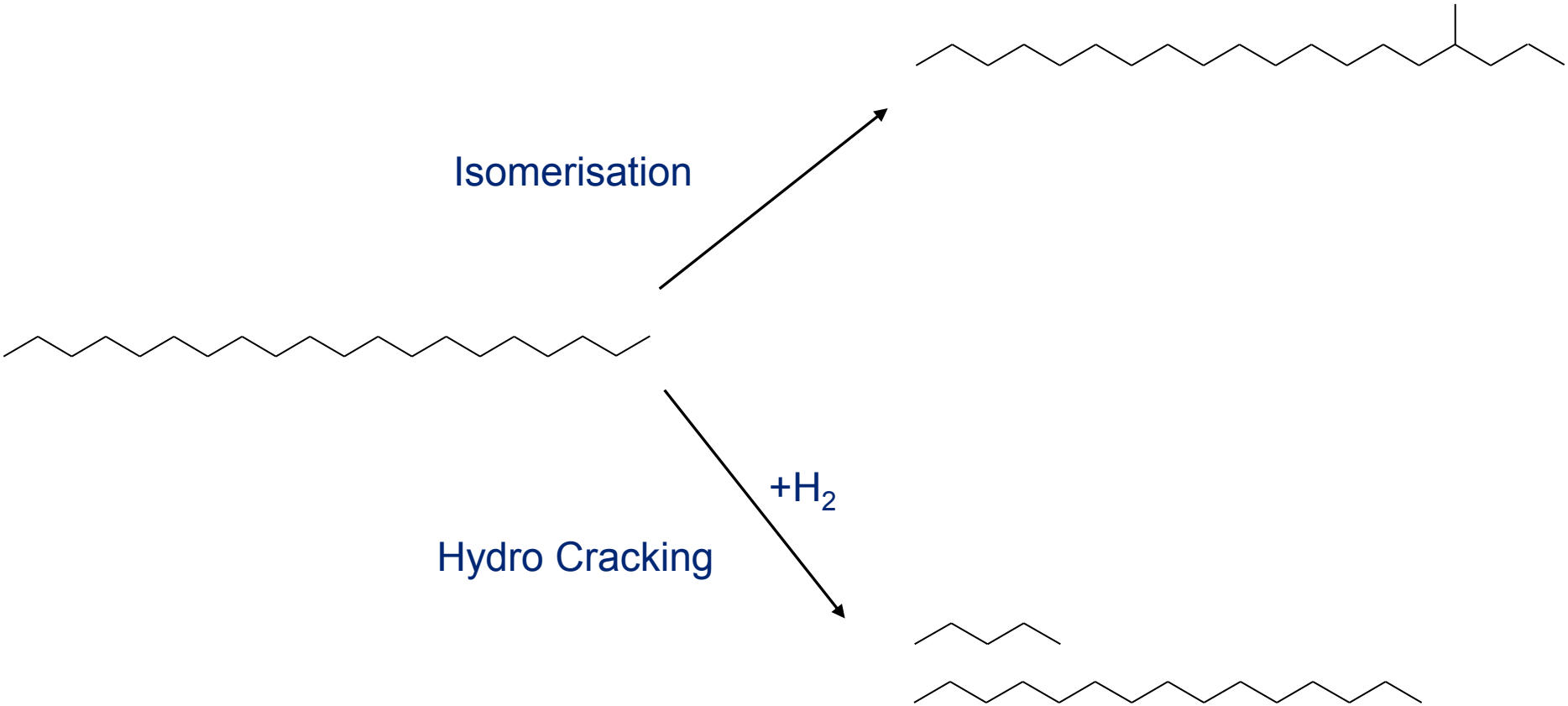
Controlling the Reaction Pathway



Boiling Point vs. Chain Length

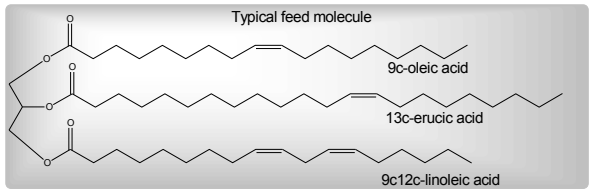


Isomerisation + Cracking of n-alkanes

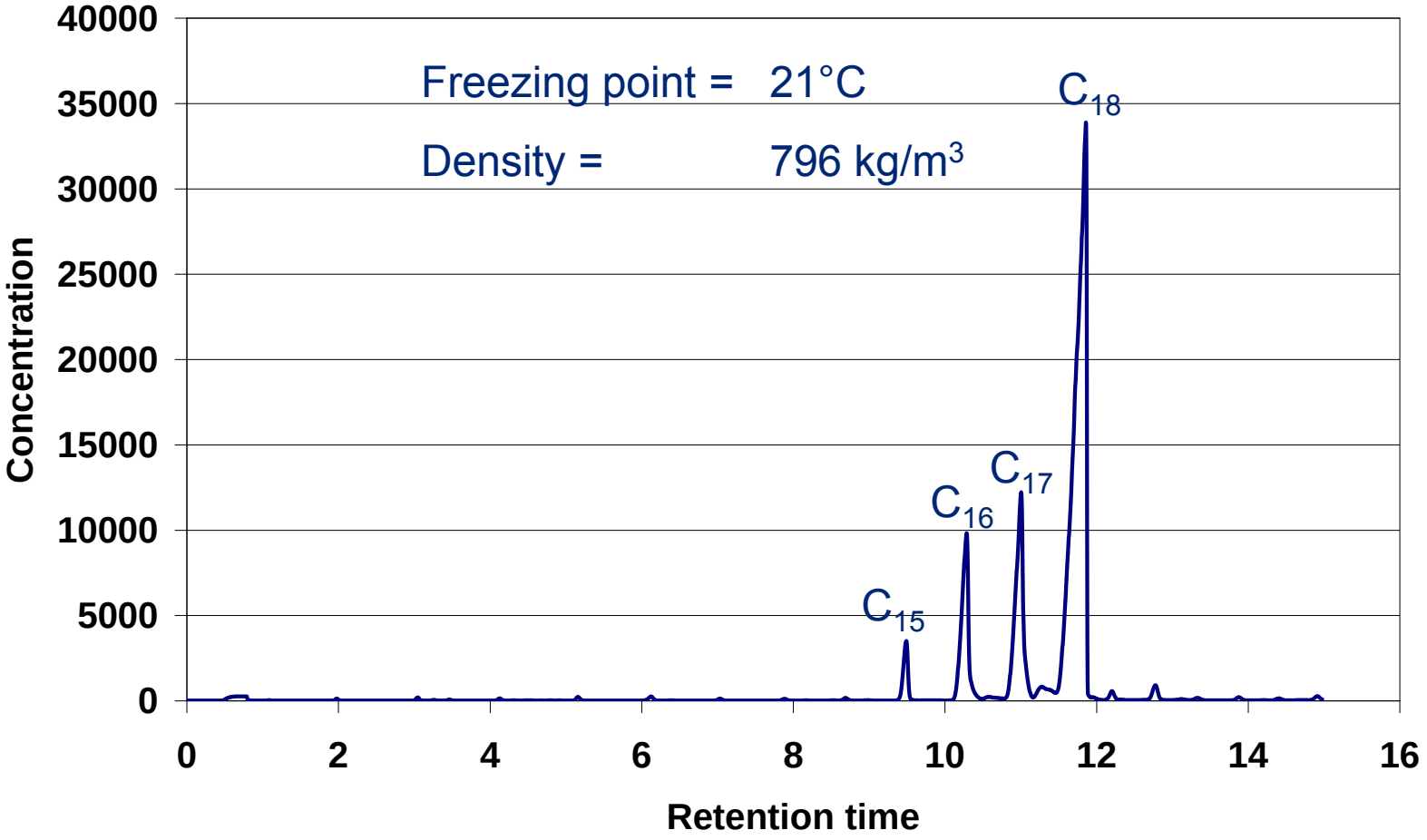


Crude Corn Oil to Jet Fuel (HEFA SPK)

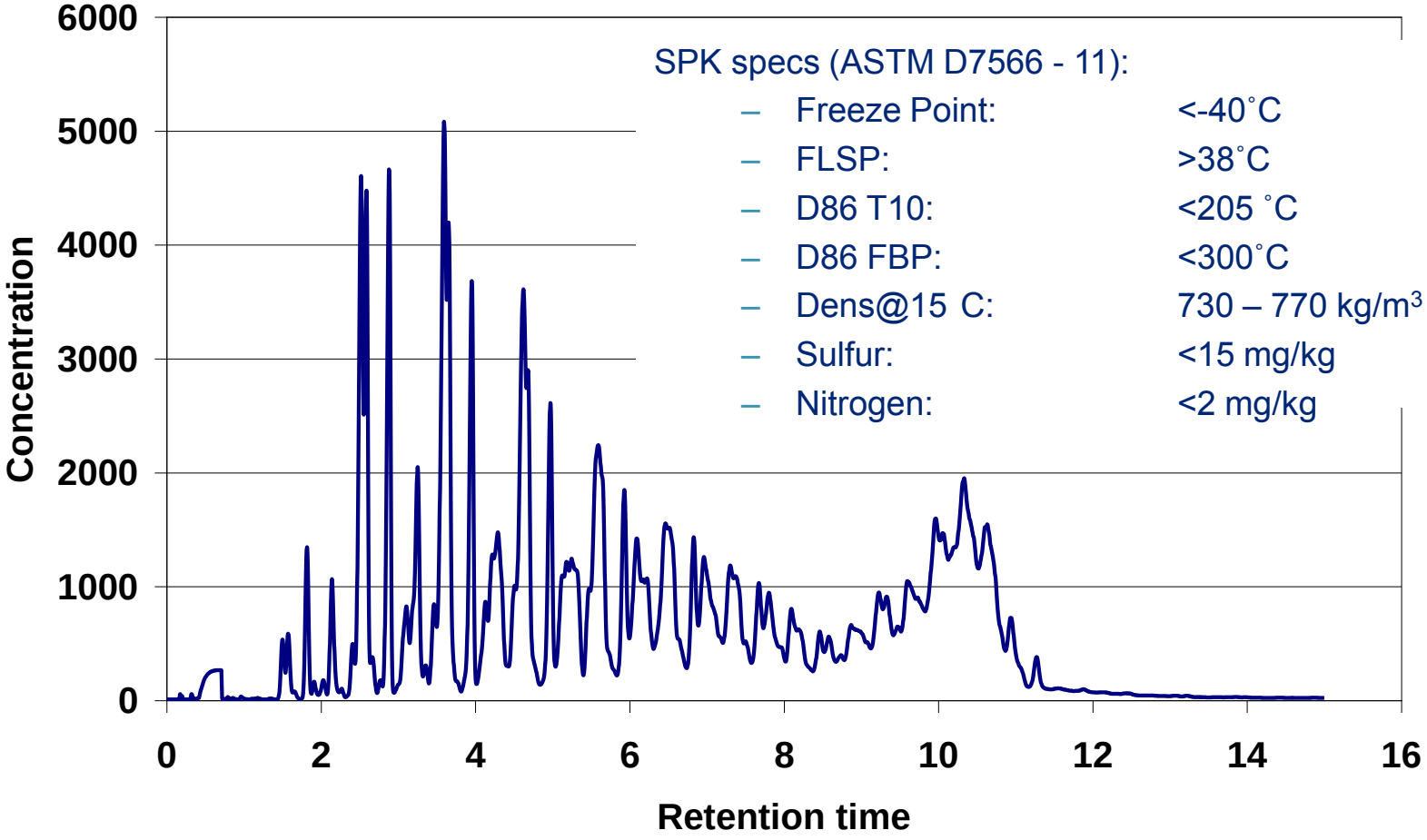
- HEFA SPK = Hydroprocessed Esters and Fatty Acids Synthetic Parafinnic Kerosene
- Large freezing point improvement of product needed
- Yields Based on %wt Fresh Feed
  - Hydrocarbons 91%
  - Water 10%
  - $CO+CO_2$ 2%



Pilot Test – Feed to Isomerisation/Cracking



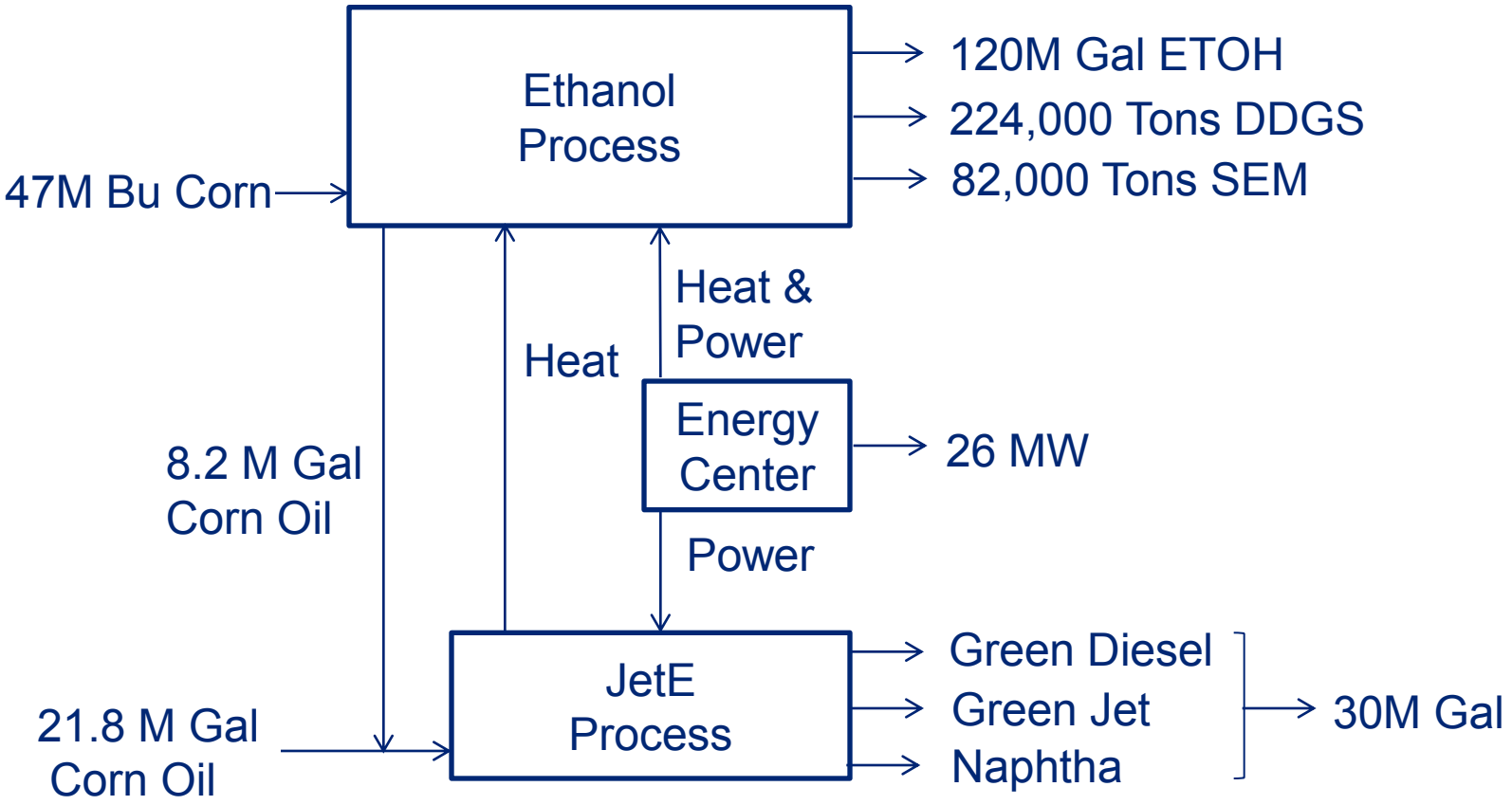
Pilot Test – HEFA SPK cut



SPK specs (ASTM D7566 - 11):

- Freeze Point: <-40˚C
- FLSP: >38˚C
- D86 T10: <205 ˚C
- D86 FBP: <300˚C
- Dens@15 C: 730 – 770 kg/m^3
- Sulfur: <15 mg/kg
- Nitrogen: <2 mg/kg

JetE: Integration of ETOH and Green Jet



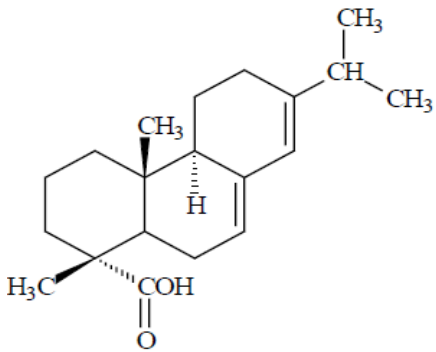
Preem AB Gothenburg: Revamp to co-process 30% bio component derived from tall oil

- Tall oil is a non-edible, low value paper mill by-product
  - *Ca.* 500,000 t/y processed in Scandinavia
- Preem co-processes 30% of this material along with LGO
- Basic revamp design by Topsøe had to overcome several challenges to deal with unconventional feed

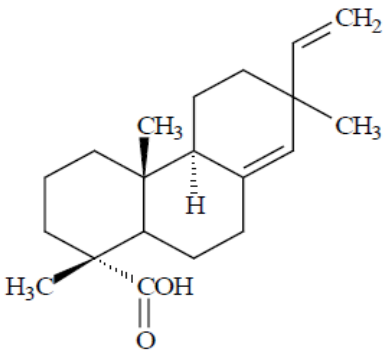
- Preem has since May 2010 been producing a renewable and clean diesel meeting all EN 590 specifications

Preem Process Feed flexibility

- Resin acids



abietic acid

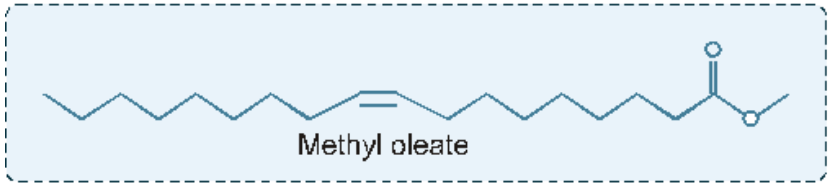


pimaric acid

- Fatty acids (oleic, linoleic, palmitic)

Oleic acid

- FAME/RME



Challenges in hydrotreating of biofeeds

- High hydrogen consumption and exotherm
- Impurities in feed
- Coking and dP build-up
- Risk of corrosion
- CO, CO_2, CH_4 and C_3H_8 in recycle gas
- Possible inhibition of HDS/HDN catalyst
- Poor cold flow properties
  - Optimize Yields

Topsøe Catalyst technology for bio material

- Extended grading
  - dP control
  - Contaminant adsorption
- Specialty catalysts for biofuels hydroconversion
  - TK-335, TK-337, TK-339,TK-341, TK-351
  - Allows for complete conversion of oxygenates and control of exotherm with long cyclelengths
  - May be combined with highly active BRIM^{TM} catalysts for co-processing
- Isodewaxing catalysts TK-928 and TK-932
  - Improves cold flow properties by n-paraffin isomerisation/cracking

Recent Commercial References Renewable Diesel

Customer	Type of renewable feed	% biofuel co-processing
Undisclosed refinery, Australia	Bio fuels and animal fat	0-5%
Undisclosed refinery, Europe	Bio fuels and animal fat	2-5%
Cetane energy, NM, US	Animal fat/algae	100%
Preem, Sweden	Tall oil	20-30%
Undisclosed, LA, US	Chicken fat	100%
Undisclosed, US WC	Chicken fat	10-20%
Undisclosed, Canada	Tallow	100%
Undisclosed, Scandinavia	Undisclosed	100%

Thank you for listening

- Questions?