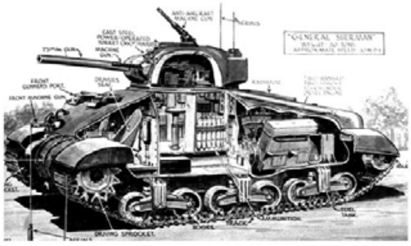
Synthetic Fuels



Synthetic Fuels

Synthetic fuels - liquid fuel obtained from:

- Coal
- Natural gas
- Biomass
- Worldwide production capacity July 2009 240,000 bpd (38,000 m^3/day)

- Direct conversion of coal to synthetic fuel originally developed in Germany
- Bergius process patented in 1913 – production began in 1919
- Indirect coal conversion (gasified then converted) developed in Germany by Fischer & Tropsch 1923
- Number of processes – three broad categories
  - Indirect
  - Direct
  - Biofuel

Synthetic Fuels

Commercialisation

Sasol – leading company based in South Africa

Indirect Fischer Tropsch plants:

- Mossgas and Secunda CTL (160,000 bpd) in South Africa
- Oryx GTL in Qatar – 35,000 bpd
- Shell Bintulu in Malaysia GTL – 14,500 bpd
- Mobil process plant in New Zealand

Mossgas

Shell Bintulu GTL plant

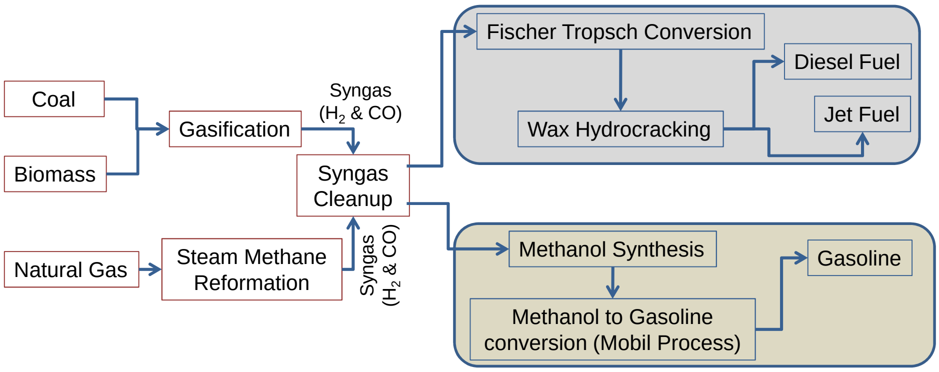
Oryx GTL

Synthetic Fuels

Indirect conversion

- Most widely deployed technology
- Worldwide production 260,000 bpd (41,000 m^3/d) – 2009 figures
- Process in which biomass, coal or natural gas converted into syngas (H_2 + CO) through gasification or steam methane reforming and syngas processed to appropriate transport fuel
- Known as:
  - Coal to Liquids (CTL)
  - Gas to Liquids (GTL)
  - Biomass to Liquids (BTL)
- Primary technologies:
  - Fischer-Tropsch synthesis
  - Mobil process (or Methanol to Gasoline – MTG)
- Can also be used to produce hydrogen for fuel cells

Indirect Conversion to Synthetic Fuels



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Gas to Liquids

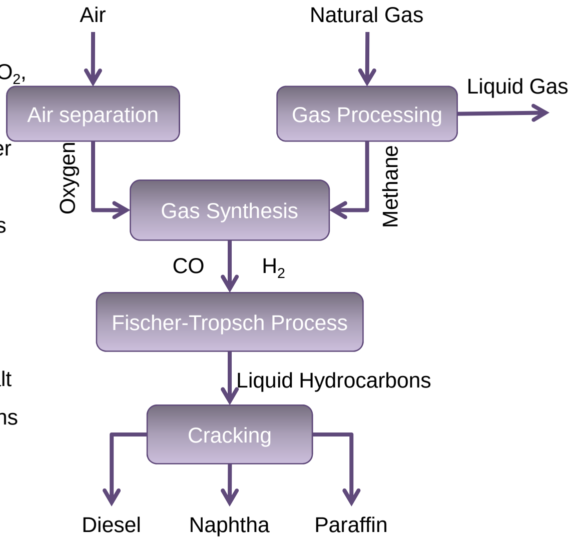
Gas to liquids

- A refinery process to convert natural gas or other gaseous hydrocarbons into longer chain hydrocarbons such as gasoline or diesel fuel
- Methane-rich gases are converted into liquid fuels either via direct conversions or via syngas as an intermediate
  - Fischer Tropsch process
  - Mobil process

EG5066 Energy Technologies: current issues & future directions

GTL Fischer-Tropsch Process

- Partial oxidation of methane to CO_2, CO, H_2, H_2O
- CO to H_2 ratio adjusted with Water Gas Shift Reaction
- Excess CO_2 removed by aqueous solution of alkanolamine
- Water removed
- Produces syngas (CO + H_2)
- Syngas reacted over iron or cobalt catalyst to give liquid hydrocarbons



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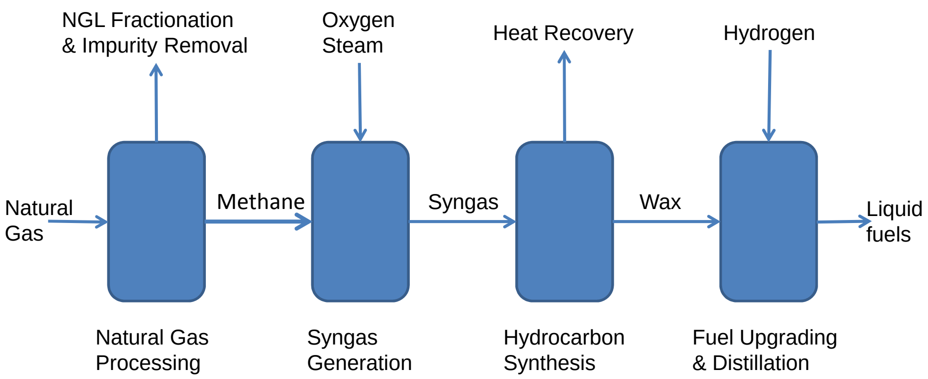
GTL Process



- Treatment to remove impurities
- Reforming of natural gas to give syngas
- Fischer-Tropsch conversion to produce hydrocarbon waxes
- Upgrading to clean diesel fuel
- Typical yield – 70% diesel fuel, 25% naptha
- 10mcf natural gas gives 1 barrel of output

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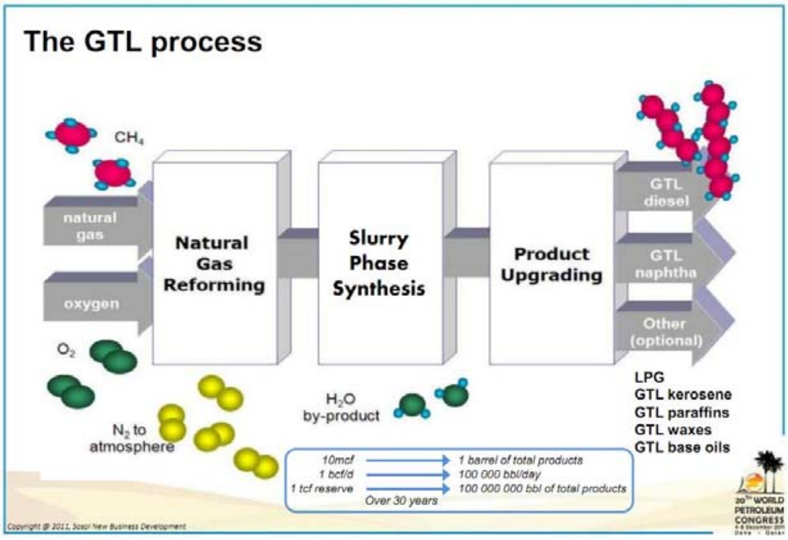
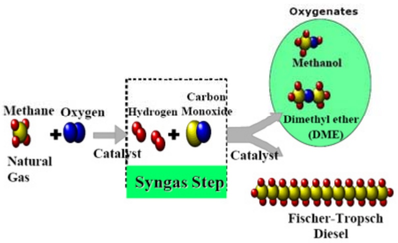
Sasol Slurry Phase Distillate Process[tm]



Source: www.sasol.com

Chevron & Nigerian National Petroleum Corporation

- GTL plant at Escravos – start up 2013
- 325 mcf pd of natural gas converted to 33,000 bpd of low sulphur diesel fuel



Mobil Process

- Developed by Mobil in early 1970s
- Conversion of natural gas to syngas
- Conversion of syngas to methanol
- Methanol polymerised into alkanes over a zeolite catalyst to give gasoline

Methanol from methane (natural gas)

Steam reforming: $CH_4 + H_20 \longrightarrow CO + 3H_2$

Water shift reaction: $CO + H_2O \longrightarrow CO_2 + H_2$

Synthesis: $2H_2 + CO \longrightarrow CH_3OH$

Methanol converted to gasoline by Mobil process

Methanol dehydrated to dimethyl ether

$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$

Dehydrated over a zeolite catalyst to give gasoline

Synthetic Fuels

Direct conversion

Two processes:

- Pyrolysis & Carbonisation
- Hydrogenation

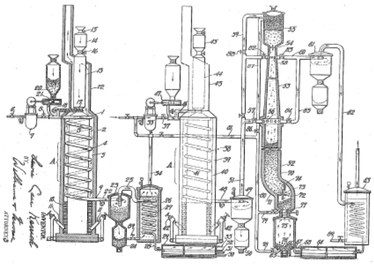
Pyrolysis & Carbonisation Processes

- Carbonisation through pyrolysis or destructive distillation
- Gives ; condensable coal tar, oil and water vapour, non-condensable synthetic gas and char
- Condensable coal tar and oil processed by hydrogenation to remove sulphur and nitrogen
- Processed to fuels

Synthetic Fuels

Karrick Process

- Invented by Lewis Karrick in late 1920s
- Retort based on Nevada-Texas-Utah retort used for shale oil extraction
- Coal heated with superheated steam in absence of air to 360º – 750ºC.
- Coal mainly used but can use oil shale or lignite
- Optimizes production of lighter hydrocarbons
- Generates no CO_2
- Unlikely to yield economically viable volumes of liquid fuel
- 1 tonne coal yields:
  - 0.175 m3 oils
  - 95m3 gas
  - 750kg semi-coke



Coal to Liquids

Hydrogenation processes

Bergius process

- Developed by Friedrich Bergius in 1913 – Nobel Prize for Chemistry 1931
- Synthetic fuel by hydrogenation of high volatile bituminous coal
- Developed before the Fischer-Tropsch method
- One of main methods for Coal-to-Liquids
- Coal liquefied by mixing it with hydrogen gas and heating
- Dry high-volatile bituminous coal is mixed with heavy oil recycled from the process with a catalyst (tungsten or molybdenum)
- Reaction at 400ºC to 500ºC and 20-70MPa hydrogen pressure
- 97% conversion rate
- Used in Germany WWII, now 4000 tpd plant in China
- Basis for a number of different developments

$$nC + (n + 1)H_2 \longrightarrow C_nH_{2n+2}$$

Coal to Liquids

Hydrogenation processes

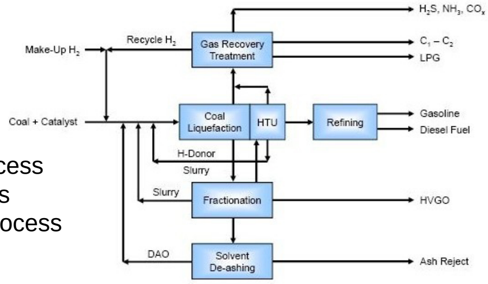
Number of different developments:

Nedol Process

- Developed 1970 – 1980 by group of Japanese companies
- Coal mixed with solvent and iron-based catalyst
- Reactor operates at 430 – 465ºC, 15 – 200 bar
- Produces low quality oil
- Needs upgrading

Other process include:

- Gulf Oil's Solvent refined coal
- Exxon Donor solvent process
- Imhausen High Pressure Process
- Conoco Zinc Chloride Process
- Chevron Coal Liquefaction Process



Gas to Liquids

GTL Jet Fuel

- Shell developed and produced 50-50 blend of synthetic GTL kerosene and conventional oil-based kerosene fuel
- Gives lower SO_2 and particulates emissions than conventional oil-based kerosene

Shell's Pearl GTL plant in Qatar

- 1.6 bcf pd of gas from the North Field converted to 140 kbo/d liquid fuels
- Uses Shell Middle Distillate Synthesis (SMDS)

Aviation Biofuels

Flightpaths for Aviation Biofuels

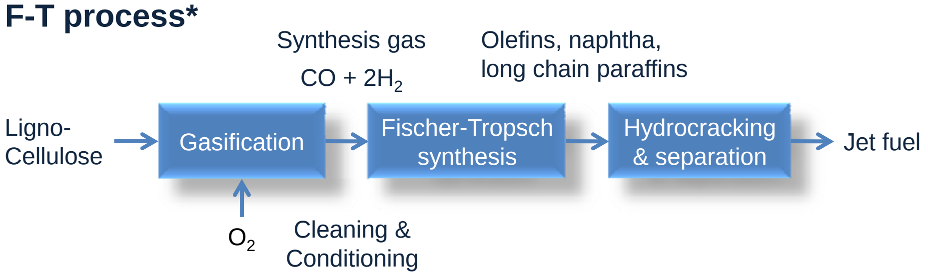
USDA – Farm to Fly programme
- One million gallons of biofuel per year by 2018

EU programme
- 2 million tonnes of aviation biofuels by 2020:
  - Mainly based on Neste hydrogenated vegetable oil technology
  - Potential 400,000 t/a F-T SPK by 2020
  - Potential 100,000 t/a HPO
  - Potential 160,000 t/a from algal oil
  - Gives 1% replacement of global aviation kerosene by 2020

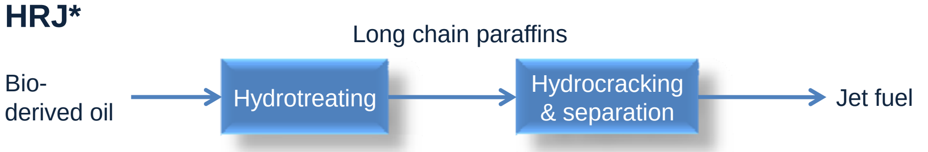
HRJ/HEFA – Hydroprocessed esters & fatty acids
FT-SPK – Fischer Tropsch synthetic paraffinic kerosene
ATJ – Alcohol to Jet
PTJ/HPO – Pyrolysis oil to jet/Hydrogenated pyrolysis oil
FRJ – Fermented renewable jet

Routes to SPK

F-T process*



HRJ*



*ASTM Approved as 50:50 mix with Jet-A

Alcohol to Jet

Utilises **Oligomerization** – process of "***building C chains"***

Alcohol → Ethanol Dehydration → Oligomerization → Distillation → Hydrogenation → Jet Fuel

Aviation Biofuels

Emerging Processes – Alcohol to Jet (ATJ)

Cobalt Technology with Albemarle Corp & NAWCWD

Bio *n*-Butanol to JP-8
Tested 50:50 in A-10 Thunderbolt II Engine

Woody biomass → Fermentation → *N*-butanol → 1-butene → Oligomerization → Distillation → Hydrogenation → Jet Fuel

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Aviation Biofuels

Emerging Processes – Alcohol to Jet (ATJ) Thermo-biological processes

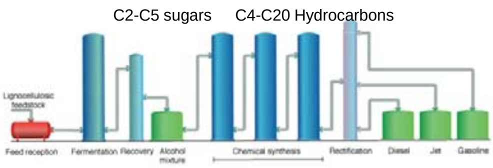
LanzaTech with Swedish Biofuels

Lanza Tech

- CO from SynGas (CO & H2) or offgas from steel works
- Fermentation (*Clostridia sp*) to alcohols (ethanol, butanol, propanol)

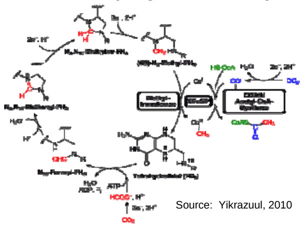
Swedish Biofuels technology

- Alcohols to Jet Fuel



Source: Swedish Biofuels AB

Wood Ljungdahl Pathway

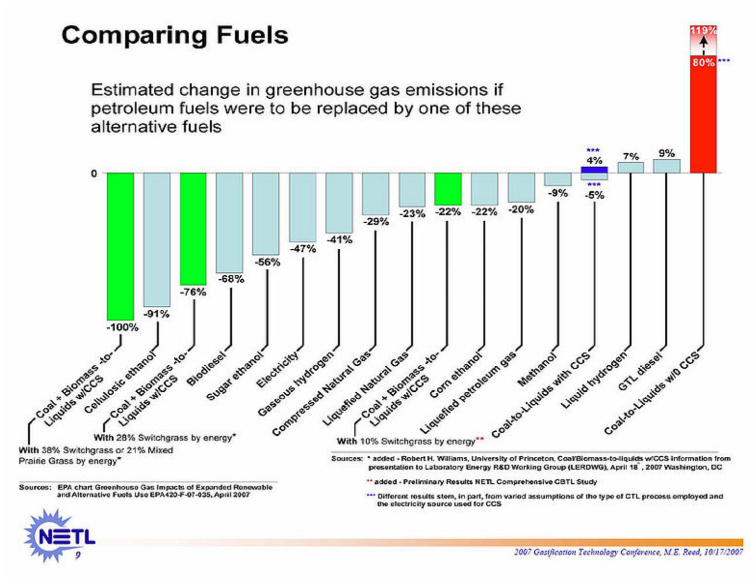


Reductive acetyl-CoA pathway

Methanogens or acetogenic organisms

- H_2 as electron donor (**Energy Source**)
- CO_2 as electron acceptor (**Carbon Source**)
- CO_2 reduced to CO
- CO converted to acetyl coenzyme A

Life cycle analysis of different fuels



Synthetic Fuels

Methanex, New Zealand. A Mobil process plant producing 5,200 t methanol a day