THE GTL/CTL/BTL PROCESS

FISCHER-TROPSCH (F-T) FUELS

Historical Review

THE FIRST DISCOVERY

- In 1902, two scientists, P. Sabatier and J.D. Senderens, first observed the primary chemistry involved.
- They managed to produce methane from carbon monoxide and hydrogen.

THE GROUND WORK

- Later, in 1918, the catalytic synthesis and process for manufacturing ammonia was discovered by German scientist Fritz Haber, and developed by the German engineer Carl Bosch.
- Today, this is known as the Haber-Bosch Ammonia Process.

THE GROUND WORK

- Their introduction of recycle processing and the developing German technology to handle high pressure hydrogen, revolutionized the chemical industry.
- 20 years later this achievement earned Bosch a Nobel Prize, the first engineer so honored

THE GROUND WORK

In rapid succession, the Germans developed:

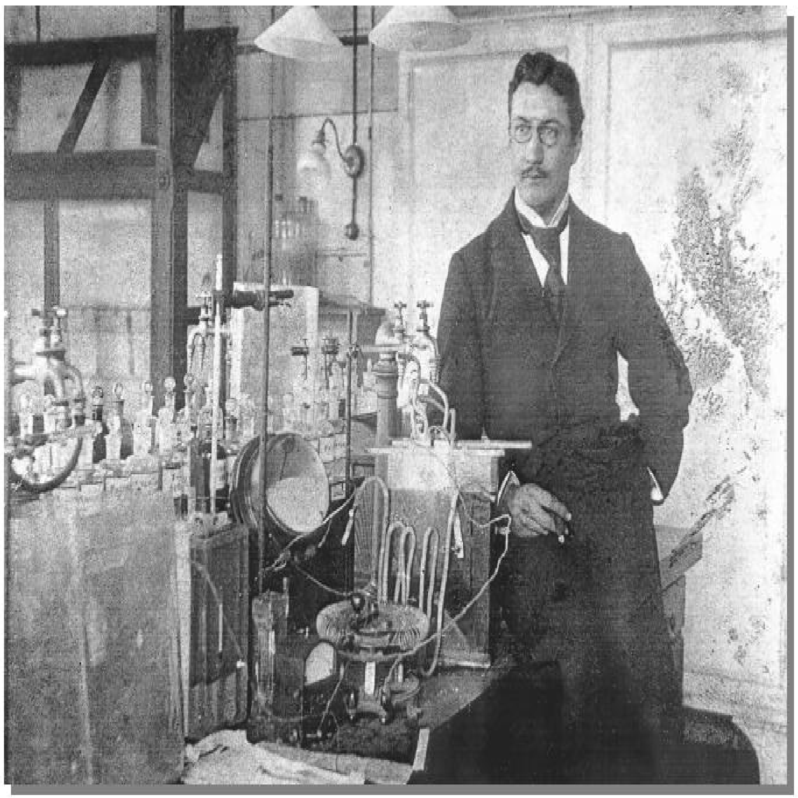
- the high-pressure MeOH synthesis,
- a saltpeter synthesis,
- methods to manufacture synthetic rubber (“buna”), and
- the means to liquefy coal

Germany 1923-1926

In 1923, at the Kaiser Wilhelm Insitut, Franz Fischer, Hans Tropsch, and Helmut Pichler developed a method to hydrogentate carbon monoxide, reacting synthesis gas over an iron or cobalt catalyst to produce gasoline, diesel, middle and heavy oils

Germany 1923-1926

Franz Fischer at Work in 1918



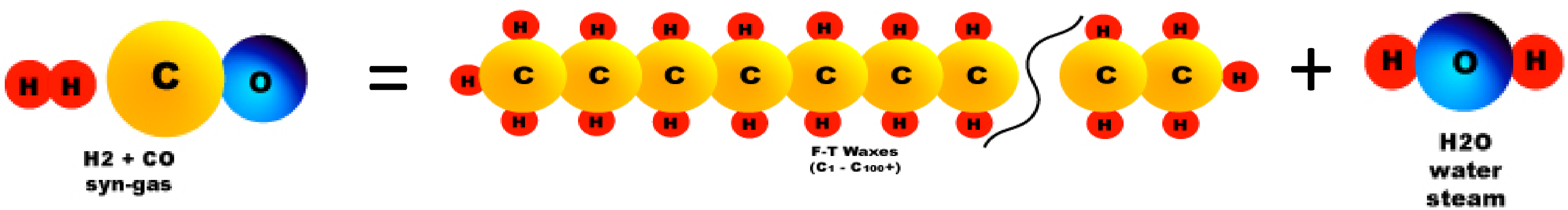
Financial Mail, 2000

Based in part upon the earlier work of Sabatier and Senderens, the process developed by Fischer, Tropsch, and Pichler could be used to manufacture synthetic products from coal and other sources of H_2 & CO

Germany 1923-1926

$$2\,CO(g) + H_2(g) \rightarrow (\text{-}CH_2\text{-})_n(l) + CO_2(g) + H_2O$$

This synthesis reaction would soon become known as the Fischer-Tropsch Synthesis



GERMAN INDUSTRY

- I.G. Farben, a chemical manufacturing cartel formed in 1925, becomes an international industrial giant - the foremost chemical experts
- I.G. Farben controls the patent rights to the Fischer-Tropsch synthesis and other synthetic fuel processes
- I.G. Farben developed a pilot plant for the new F-T process in 1926

1926 ~ Standard Oil of NJ "EXXON"

- In 1926, Frank Howard, head of Standard Oil's R&D visits the IG Farben synthetic fuels pilot plant
- Howard immediately fired off a wire to Walter Teagle, Standard Oil's president:

  "Based upon observations and discussions today, I think that this matter is the most important which has ever faced the company since the dissolution. This means absolutely the independence of Europe in the matter of gasoline supply".

STANDARD OIL
&
IG FARBEN

Walter Teagle, President Standard Oil NJ :

"I had not known what research meant until I saw it [IG Farben's synthetic fuels pilot plant]. We were babies compared to what I saw."

- Standard could not afford to not get involved
- Initial agreement to build a pilot plant in the town of Louisiana, Kansas.

STANDARD OIL
&
IG FARBEN

- In 1929, Standard made an agreement with IG Farben:
  - Standard received the patent rights to all hydrogenation processes, including F-T, outside of Germany
  - IG Farben received 2% of Standard’s stock - worth \$35MM in 1929!
  - IG Farben was now the largest shareholder of Standard’s stock next to Rockefeller

STANDARD OIL
&
IG FARBEN

- Each company agreed to stay out of the other's main fields of activity.
  - As one Standard official said:

  “ *The I.G. are going to stay out of the oil business - and we're going to stay out of the chemical business*”.

The Great Depression

- By the beginning of 1930, The Great Depression brought a surplus of oil and Standard’s plans for synthetic fuels were shelved

The Great Depression Years

- I.G. Farben could not continue to run synthetic fuels production without government help and subsidy. They found no help from the pre-Hitler Brűning government
- I.G. Farben instead looked to the “up and coming” political party of the day…a move that would have dire consequences

The Great Depression Years

- I.G. Farben found support from the Luftwaffe by proving they could produce a high quality aviation fuel. The army, the Wermacht, then lobbied for a commitment to a domestic synthetic fuels industry
- By 1936, I.G. Farben was no longer an independent company, but an independent arm of the German state, and fully Nazified.

The Great Depression Years

- In February 1936, at Germany's annual auto show, the *New York Times* reported Adolph Hitler as saying:

"Germany has effectively solved the problem of synthetic gasoline. This achievement possesses political significance".

The Great Depression Years

With his eye already on war, later in 1936, Hitler was recorded saying:

> *"German fuel production must now be developed with the utmost speed. This task must be handled and executed with the same determination as the waging of a war, since on its solution depends the future conduct of the war. The production cost of these raw materials are of no importance."*

The Great Depression Years

Hitler would use Germany’s synthetic fuel industry for his own ends in the years ahead

THE WWII YEARS

- As Hitler started out on his conquest of Europe, 95% of the Luftwaffe’s aviation fuel was provided by domestic synthetic fuel plants
- By September 1939, when Germany invaded Poland, 14 synthetic fuel plants were operating and 6 more were under construction

The WWII Years

- By 1940, synthetic fuel production reached 72,000 barrels per day (BPD), providing 46% of Germany's war time fuel requirements
- From 1940 to 1943 synthetic fuel nearly doubled from 72,000 BPD to 124,000 BPD, now over 57% of the total fuel supply and 92% of the aviation fuel supply

"High Priority Targets"

- In preparation for the Normandy Invasion, American and Allied bombers specifically targeted Germany's synthetic fuels plants.
- In May 1944, Germany's synthetic fuels plants averaged 92,000 BPD. By September 1944, Allied bombing reduced the output to just over 3,000 BPD, effectively grounding the German airforce.

After the War

- By 1945, Franz Fischer had retired. Hans Tropsch had died in 1937. Helmut Pichler remained as the acting head of the Kaiser Wilhelm Institut.
- WWII moved the Fischer-Tropsch process from the laboratory into full scale multiple plant operations. New production technologies and better catalysts had been developed.

After the War

- In 1945, Allied intelligence officials initiated a full investigation into Germany’s synthetic fuels industry. U.S. Army Intelligence, British Intelligence, and Canadian Intelligence detailed the industry until 1948. Russian intelligence did likewise.
- Their findings would remain “classified”until the late 1970’s.

After the War

- During and after WWII, US officials recognized the potential limits of petroleum crude
- Major efforts were directed toward developing the F-T process in the U.S.A

1945 - 1950

- A commercial scale F-T plant was built in Brownsville, Texas. This plant utilized fluidized bed reactors similar to what Standard Oil had recently developed for catalytic cracking

- It also led to the development of large scale O_2 production plants

1945 - 1950

- Smaller scale pilot plants were built and operated by the U.S. Bureau of Mines in Louisiana and Kansas in 1950. Other plants were built as well.
- The F-T pilot plants utilized a version of a slurry-bubble column reactor that was being tested in Germany, primarily by Herbert Kolbel.

1955 ~ South Africa

- In 1951 the South African Coal, Oil and Gas Corporation (now known as Sasol) began construction on South Africa's first coal to synthetic fuels plant using F-T technology.
- By 1955 this operation was marketing petrol as well as a full range of specialty chemicals.
- By 1978, Sasol had over 200,000 bbl/d of F-T
- Sasol's plants are still in operation today

SASOL F-T REFINERIES SOUTH AFRICA

Secunda 150,000 BPD Coal to Liquids (CTL)

The 50's and 60's

Ibd Saud

In the early 1950's enormous oil reserves were discovered in the Middle East. This discovery had a profound impact on the economics and politics of fuel production and usage.

The 50's and 60's

- Even though the amount of oil U.S. refiners could import was limited, to encourage U.S. production, U.S. crude had a production cost of $4.50 per barrel.
- Middle East crude was being imported for $2.00 per barrel.
- This prevented the F-T plant in Brownsville, Texas and the other F-T pilots from being a commercial success.

The 50’s and 60’s

- The U.S. economy was booming and our cars were the hot topic of the day. Cheap gasoline was the name of the game!
- By 1953, all U.S. F-T plants had been shut down.

The 50’s and 60’s

In effect, the short-term political and economic interests of the time were helping to create the oil dependency we are experiencing today.

1970’s

- The Middle East oil embargo in the late 1970’s renewed interest in Fischer-Tropsch and other alternative fuels.
- The WWII F-T documents were “de-classified”
- Major oil companies and universities began intensive research and development programs in the Fischer-Tropsch process.

1970's

- Standard Oil (now Exxon) brushed off the data from IG Farben in WWII and started on their own F-T process.
- Many companies followed suit, including:
  - Mobil
  - Texaco
  - Statoil
  - Sasol
  - and others

1970's

- One oil company that invested research and development in Fischer-Tropsch synthetic fuel technology was Gulf Oil.
- Gulf Oil R&D, Pittsburgh PA, developed an advanced F-T process utilizing cobalt catalysts.
- Gulf teamed with Badger Engineering and their process is still often referred to as "The Gulf-Badger Process"

1980’s

- Chevron purchased Gulf Oil in the mid 1980’s and sold the Gulf-Badger F-T process to Shell Oil.
- Shell added the Gulf-Badger knowledge to their “Shell Middle Distillate Process” and began engineering efforts for a full scale plant.

1980’s

- The Middle East oil embargo resolved. But a world wide recession and a severe down turn in the oil business in the early 1980’s with the exception of Sasol put most efforts in Fischer Tropsch development back on the shelf.

1980’s

- In 1987, amidst boycotts surrounding apartheid policies and the discovery of a domestic natural gas field, the So. African government announced the Mossgas project for the production of synthetic fuels from natural gas to reduce their dependence on imported oil.
- The Mossgas Plant, in Mossel Bay, S.A. is still running and produces 47,000 BPD of petrol, diesel and other chemicals.

MOSSGAS F-T REFINERY SOUTH AFRICA

The World's Cleanest Refinery 47,000 BPD Gas to Liquids (GTL)

1990’s

- In 1993, Shell completed construction and began operating their “Shell Middle Distillate Process” in Bintulu, Malaysia.
- The Bintulu Plant produces 12,500 BPD and in 2000 increase that capacity to 15,000 BPD. This F-T plant has effectively captured the world specialty wax market.

SHELL F-T REFINERY BINTULU MALAYSIA

15,000 BPD Gas to Liquids (GTL)

2000

- While Saudi Arabia produced about 8 million barrels of oil per day in 2000, the world flared (burned) or re-injected associated gas equivalent to 7.2 million barrels per day of clean synthetic fuels.
- World wide environmental legislation requiring ultra low sulphur and aromatic levels in fuel will cost billions in oil refinery upgrading.

Sasol’s Optimized – Cost Effective F-T GTL Plant*

Thermal Efficiency	Constructed Cost	Project Schedule
1995 **45-50%**	**1995** **25K-30K $/bbl**	**1995** **36-42 months**
2000 **60-65%**	**2000** **17K-30K $/bbl**	**2000** **30-33 months**

* Presented by Sasol in Sun City, South Africa November 2000 – Design, Engineering and Construction of a Sasol SPD Plant

2001

- Science and Engineering have come a long way since Fischer & Tropsch pioneered the path in 1923
- Engineering break-throughs and new advances in catalysis have led to cost reductions making the F-T process viable

2002

- Nearly every major oil company is either developing their own F-T technology, forming joint ventures, or scrambling to do so.
  - Exxon/Mobil and has spent over $500 MM
  - Chevron formed a joint venture with Sasol
  - Statoil has formed a joint venture with Mossgas
  - Conoco built a $400MM test plant in Oklahoma
  - BP completed its pilot/test plant in Alaska
  - Shell has announced 7 new projects

2004

- As of July 2004, 50 new Fischer-Tropsch projects have been announced.
- These projects total over 900,000 BPD capacity
- Some of these projects are pilot plants, some are feasibility studies for clients, and some have started construction.

2005

- These projects include:
  - Chevron/Sasol: 100,000 BPD GTL Qatar *
  - Shell: 140,000 BPD GTL Qatar
  - Conoco/Phillips: 130,000 BPD GTL Qatar *
  - Exxon-Mobil : 150,000 BPD GTL Qatar *
  - Chevron/Sasol: 33,000 BPD GTL Nigeria
  - Shell: 6 projects worldwide @ 72,000 BPD each
  - Sasol 2 - 80,000 BPD CTL China *
  - Shell 70,000 BPD CTL China *

* these projects with executed agreements are now on hold

2005-09

Sasol – 35,000 bbl/d

ORYX GTL Plant Qatar

(two additional 35,000 bbl/d expansions planned)

2008-12

Shell Oil 140,000 bbl/d

PEARL GTL Plant Qatar

SASOL F-T REACTOR 17,000 BBL/D

33’ Diameter, 196’ Tall, 2,200 tons can only be delivered via ship/barge at a tide water location

Shell F-T Reactors at Pearl

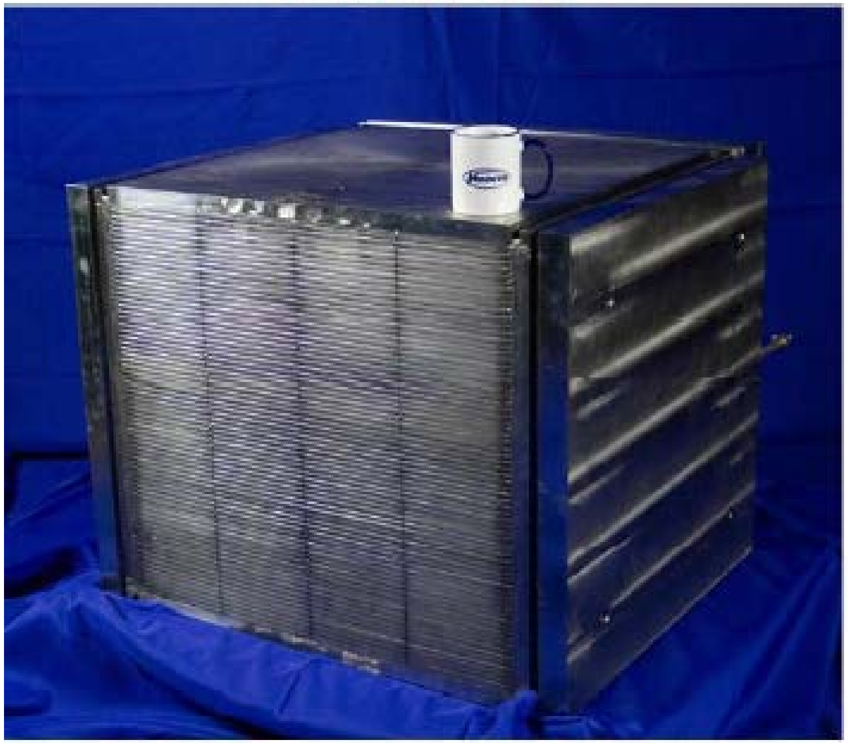
7,500 BBL/D

2010-14

Velocys PLC Micro-Channel F-T Reactor

3 core 125 bbl/d F-T reactor
less than 23 tons

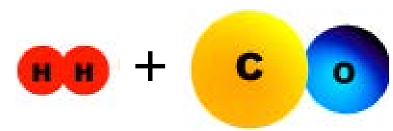
FT Reactor Core



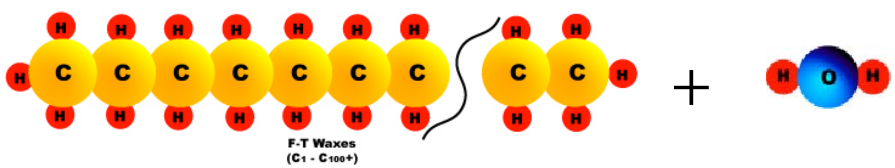
The F-T Process

Three Steps in GTL/CTL/BTL Refining to make F-T Fuels

GTL/CTL/BTL Processes use 3 distinct steps, all commercially proven to convert a gas, liquid or solid into synthetic transport fuels:

- Step 1 - Syn-Gas generation (H_2 & CO) 

- Step 2 - The F-T reaction (long paraffin chains ➡ wax)



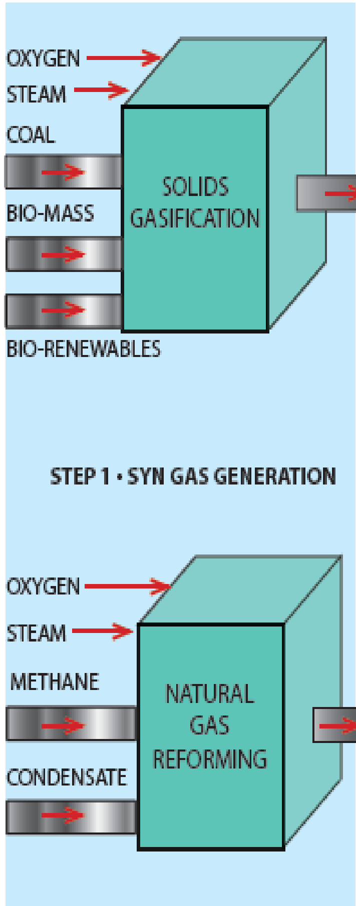
(water)

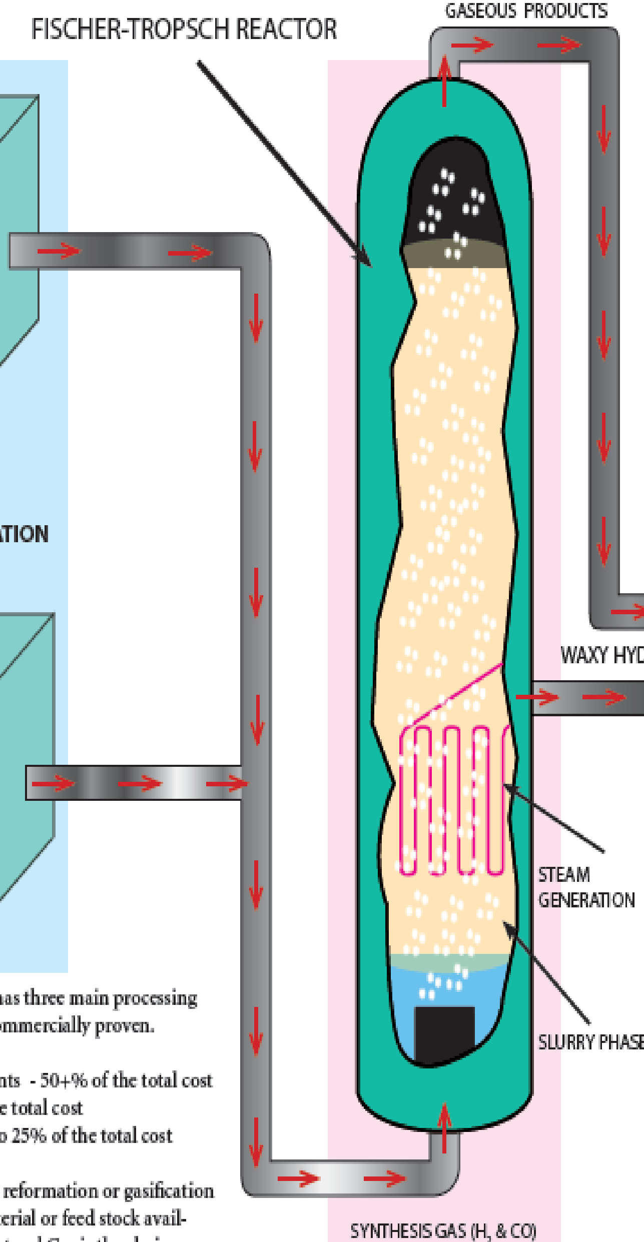
- Step 3 - Product upgrading (hydrocracking of the long chain F-T paraffin to produce the desired end product – similar to a crude oil refinery)
  - Kerosene – Diesel – Gasoline - Jet Fuel – Naphtha

    C_{10}-C_{13} C_{14}-C_{20} C_5-C_{10} C_{10}-C_{13} C_4-C_{10}

F-T FUELS THE ONE FUEL FOR OUR FUTURE

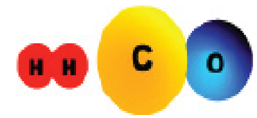
Note: Although the Sasol F-T reactor is illustrated here, the Shell F-T technology (SMDS) is also commercially proven





STEP 2 • F-T CONVERSION

The first step converts natural gas, coal or bio-mass into synthesis gas, a mixture of carbon monoxide (CO) and hydrogen (H_2) - syngas.

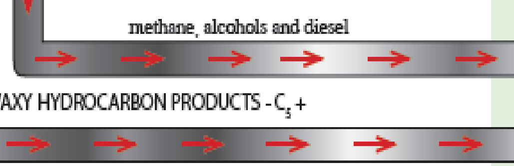


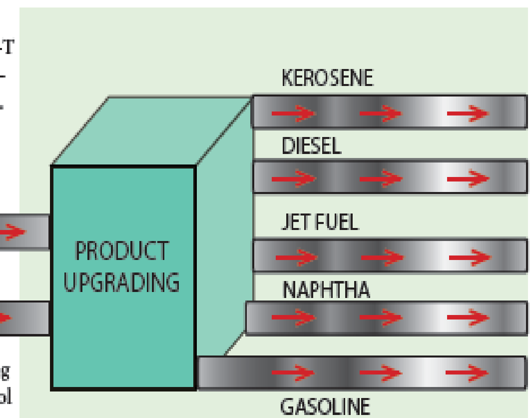
F-T FUELS - THE SENSIBLE SOLUTION FOR A NEW GENERATION OF ULTRA CLEAN ENVIRONMENTALLY FRIENDLY DIESEL FUELS

This mature process technology has been used in many commercial facilities as the first step for producing ammonia, hydrogen, methanol.

Sasol and Shell, the recognized world leaders in F-T technology use both gas reformation and coal gasification to produce syngas for its F-T production. called Gas-to-Liquids (GTL) and Coal-to-Liquids (CTL) respectively

STEP 3 • HYDROCRACKING - PRODUCT WORKUP





The Fischer-Tropsch Process (F-T) has three main processing steps shown here, all of which are commercially proven.

STEP 1, SynGas Generation represents - 50+% of the total cost
STEP 2, F-T Conversion - 25% of the total cost
STEP 3, Product Upgrading - 15% to 25% of the total cost

The type of SynGas Generation, gas reformation or gasification of solids, depends upon the raw material or feed stock available. Around the world stranded Natural Gas is the choice; however, in the US with the exception of North Slope Natural Gas, coal, bio-mass (garbage), bio-renewables (trees and plants) represent the majority of available feedstock for a US based F-T program!

CHOREN, a German company has been operating a bio-mass gasifier to produce syngas for methanol and electric production since 1998. This plant is considered the worlds first bio-renewable energy gasifier and has the distinction of producing fuels and electricity with a net zero impact on the worlds CO_2 and called Biomass-to-Liquids (BTL)

Step two, the Fischer-Tropsch conversion, discovered by the Germans in the 1920's, upgrades the syngas into a waxy hydrocarbon. Simplified this reaction is :

$$xCO + 2xH_2 \longrightarrow xCH_2 + H_2O$$

The length of the hydrocarbon chain (x) is determined by the composition (or ratio of H_2 to CO) of the syngas, the catalyst selectivity and the reaction conditions.

Sasol has pioneered several types of F-T conversion technologies to produce over 150 different products from their F-T plants in South Africa alone. The hydrocarbon stream (xCH_2) is sent to product workup and the water (H_2O) is sent to the water recovery unit.

The third step, Product Upgrading:

Upgrading can produce a wide range of commercial products from gasoline to diesel to candle wax. For a US based F-T program we would recommend middle distillate fuels: kerosene, diesel and naphtha.

This process makes use of standard hydrocracking and hydroisomerisation processes commonly found in the refinery world. As with the First Step of syngas production, suitable technology is widely available from several licensors around the world.

The F-T process produces sulfur free fuels that contain essentially no aromatics or ring chain hydrocarbons that are toxic and harmful to the environment. The CTL/GTL/BTL process does produce CO_2 but it is in a pure stream and is easily contained for sale to third parties or can be sequestered for injection into underground wells.

F-T Fuels, clean fuels for our future that will reduce US dependence on foreign crude oil and products.

GTL/BTL/CTL is really a clean technology because all of the impurities listed below, if present are captured and disposed of:

Impurities that are removed from Syngas before it enters the F-T reactor in step two. This is the main reason F-T fuels cost so much and are so clean

- CO_2
- Catalyst Poisons:
  - H_2S
  - COS
  - HCN
  - HCl
  - $Fe(CO)_5$
  - $Ni(CO)_4$
  - Hg
  - Traces of Cd, Se and other metal vapours

SYNTHETIC DIESEL

F-T DIESEL
AS CLEAN AS CNG

U.S. EPA* APPROVED

NON-TOXIC

FDA APPROVED

ZERO SULFUR

ZERO AROMATICS

>70 CETANE

$PM_{10} \leq$ CNG

*EPA Water Docket, EB 57 located at 401 M Street SW Washington DC, 20460 Reference Docket No. W-98-26 in UNOCAL data file 4.A.a.3, Vol 13