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List of Abbreviations and Definitions

Abbreviation	Definition
ACCR	Annual capital charge ratio
ASF	Anderson Schulz Flory
ASU	Air Separation Unit
ATR	Autothermal Reforming
BTL	Biomass to Liquid
CFB	Circulating Fluidized Bed
CPOX	Catalytic Partial Oxidation
CTL	Coal to Liquid
DMR	Dry Methane Reforming
FFD	Fixed Fluidised Bed Reactor
FT	Fischer-Tropsch
GLAMOUR	Glycerol to aviation fuel via chemical looping with sustainable recovery
GLY	Glycerol
GTL	Gas to Liquid
HER	Heat Exchange Reforming
HP-IP-LP	High pressure, Intermediate Pressure, Low Pressure
HTFT	High Temperature Fischer Tropsch
IM	Inorganic Material
ISBL	Inside Battery Limits
KPI	Key Performance Indicator
LHV	Lower Heating Value
LTFT	Low Temperature Fischer Tropsch
MSR	Methane Steam Reforming

OSBL	Outside Battery Limits
POX	Partial Oxidation
PSA	Pressure Swing Absorber
SAS	Sasol Advanced Synthol
SG	Syngas Generation
SMDS	Shell Middle Distillate Synthesis
TAC	Total Annualised Cost
TFCC	total fixed capital cost
WGS	Water Gas Shift
XTL-FT	Feed (Natural Gas, Biomass, Coal etc.) to liquid via Fischer-Tropsch

1. Executive Summary

This report constitutes the deliverable D2.2 of the WP2, Task 2.3. The object of this task is to identify a benchmark for FT which will be used for further comparison in WP6. Consequently, the current industrial scale GTL-FT and BTL-FT technologies have been reviewed. As to the GTL, it has been assumed that the gas feedstock, whether natural gas or bio-methane, is delivered upgraded at the GTL battery limits.

The analysis of the current GTL-FT and BTL-GTL shows that these facilities are capitally expensive. Indeed, the capital expenditure for the industrial running GTL-FT plants, which benefit of the most favourable technical and economic conditions, ranges from $100,000 per barrel per day to $146,000 per barrel per day. The capital intensive character of these industrial installations calls for large scale production in order to achieve the economy of scale. In fact, the plant capacity spans from 15,000 bld to 146,000 bld.

The key process performance parameters of both GTL-FT (about 8800 bld) and BTL-FT (4400 bld) are detailed in the Part III of this report. The summary of the overall KPI's along with the economic KPI's are shown also here below for the convenience of the reader.

Overall Process KPI

KPI	Unit	GTL-FT	BTL-FT
h_{carbon}	kmol/kmol	0,564	0,321
$h_{products\ (*)}$	MJp/MJf&f	0,513	0,519
h_{el}	MJel/MJf	0,071	0,057
$y_{naphtha}$	kg/kgfeed	0,162	0,059
y_{diesel}	kg/kgfeed	0,345	0,093
c_{I}	MJ/kgprod	92,1	90,2
c_{II}	MJ/kgprod	87,4	86,6
e_{CO2}	tonCO2/tonprod	0,56	5,60
e_{CO2tot}	tonCO2/tonprod	0,559	5,60

(*) Electric power to export factored in as product

GTL-FT Economic Performance

Capital costs [MM$]		**Operating Costs** [MM$]	
Inside Battery Limits	161	Natural Gas	13,7
Outside Battery Limits		Capital Annual Charge	20,6
Combined Cycle Plant	55	Maintenance	4,58
Other outsides	120	Insurance	1,14
EPC contractor fee	26,9	Labor	3,43
Contingency	33,6	Overheads	2,40
Owner Costs	69,9	General Expenses	11,4
Total Fixed Capital Cost	466	Total Annualized Cost	57,3
Break Even COE [$/barrel]	18,8	**Cost of Production** [$/ton]	0,16

Note: values in 1998 currency

BTL-FT Economic Performance

Capital costs [MM$]		**Operating Costs** [MM$]	
Inside Battery Limits	485	Feedstock	50,9
Outside Battery Limits		Capital Annual Charge	69,7
Power Generation	54,4	Maintenance	35,6
Other outsides	102	Insurance	17,8
EPC contractor fee (8% ISBL+OS	51,3	Labor	3,77
Contingency (10% ISBL+OSBL)	64,1	Overheads	2,64
Owner Costs (15% TFCC)	134	General Expenses	12,4
Total Fixed Capital Cost	890	Total Annualized Cost	192,8
Break Even COE [$/barrel]	127,0	**Cost of Production** [$/ton]	1,038

Note: values in 2008 currency

In the Glamour process, the syngas needed to produce FT-synfuel is generated in a sorption-enhanced reformer (*looping reforming*) of glycerin - a liquid biomass co-produced with biodiesel. As glycerin is a liquid by-product of an energy production facility, it does not need the same kind of pre-treatments required by biomasses, and the syngas originated by its gasification is a clean gas that does not need of a gas clean-up operation.

From the above characteristic of the biomass gasification, it can be concluded that the BTL-FT obtained from biomass gasification cannot be taken as the reference technology for Glamour**.**

Moreover**,** as shown above, the breakeven point of the BTL-FT is by far greater than the recent crude oil price. That means that, unless a game-changer technology emerges, only environmental, social and political arguments can give cause to a BTL-FT plants to be applied on an industrial scale.

As opposed to biomass gasification, the production of syngas through a looping reforming is analogue to the production of syngas from natural gas. Indeed, the natural gas used in GTL plant comes from midstream facility where the gas is purified ahead of being admitted in the gas pipeline network for transportation to end-users among which petrochemical facilities. Therefore, a GTL plants are less in need of cumbersome pre-treatment unit and gas clean-up downstream the gasification process. Moreover, the looping reforming is a novel technology for gasification that overcome the thermodynamic limitation of conventional steam reforming, therefore **the benchmark for the Glamour project has to be sought among the natural gas gasification processes.**

PART I

CURRENT FISCHER-TROPSCH TECHNOLOGIES

2. Introduction

The Fisher Tropsch (FT) is an established technology and already implemented on a large scale, although its popularity is challenged by high capital costs, high operational and maintenance costs, and volatile crude oil price.

The synthesis of hydrocarbons from carbon monoxide and hydrogen was discovered by Sabatier and Senderens in 1902 who produced methane by passing CO and H_2 over Fe, Ni, and Co catalyst[I]. In 1923, the synthesis of liquid hydrocarbon and oxygenated derivatives from syngas was discovered by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research (presently Max Plank Institute) in Mulheim, Germany. They observed that carbon monoxide and hydrogen reacted over an iron surface to produce mixtures of hydrocarbons and oxygenated compound termed *synthol*. In their first published work they used alkalized iron turnings as catalyst at high temperature and pressure (about 400°C, 100÷150 atm). By lowering the pressure to 7 atm, they formed increasing amounts of hydrocarbons**.**

Certain iron and cobalt catalysts were later found to be active at atmospheric pressure. Since its inception variations in the synthesis pathways were introduced to produce methanol, mixed alcohols and iso-synthesis products.

Most of the original research on Fischer-Tropsch chemistry was carried out before World War II in Germany, where the lack of crude oil demanded alternative sources for liquid fuels**.** The first commercial catalyst developed in the 1930s was cobalt and thoria supported on kieselguhr (diatomaceous earth) operated in a fixed-bed reactor at about 200° C and atmospheric pressure with an H_2 : CO ratio of 2. The catalyst composition was later changed to include magnesia, which resulted in decreased solid paraffin production.

At medium pressure (0.5÷2.0 MPa) higher hydrocarbon yields with different product compositions could be achieved. Synthesis gas used in Fischer-Tropsch plants originated from coal gasification processes, as coal was available as raw material. The German brown coal, however, is high in sulfur, and consequently it was necessary to develop catalysts that tolerated this component.

The first plant came into operation in 1936 in Oberhausen, and eight others were built until the end of the war in Germany. Plants were also constructed in France and Japan. All plants used the so-called *Ruhrchemie process.*

After World War II the commercial Fischer-Tropsch synthesis was terminated in Germany. Research, however, still continued mainly in the United States at the U.S. Bureau of Mines. This included mechanistic studies, catalysts and process developments**.** A commercial plant with a fluidized-bed iron catalyst was built in 1951 and operated until 1957 (Carthage Hydrocol). At this time cheap Middle East crude oil rendered FT oil synthesis uneconomical.

South Africa, however, facing a worldwide embargo in the 1950s, established a FT industry. The first large-scale plant was operated by the South African Coal, Oil and Gas Corporation's (SASOL I) at Sasolburg. This plant, known as Sasol I, operated on fixed-bed Arge technology reactors, using a precipitated iron catalyst supported on silica and promoted by copper and an alkali. It uses two different reactors. A fixed-bed reactor with a precipitated iron on silica catalyst yields mainly high-molecular-weight saturated hydrocarbons (diesel oil and waxes) at 220÷250°C and 27 atm. The other, a circulating fluidized-bed reactor - aka *Synthol entrained-bed reactor*, produces primarily gaseous hydrocarbons and gasoline rich in olefin utilizing a fused iron catalyst (320÷350°C, 22 atm).

The oil embargo of the 1970s brought about the revival of research and development interest in FT synthesis. Catalyst characterization and chemisorption studies with spectroscopic techniques**,** kinetic and mechanistic studies including the use of labeled compounds, and new ideas originating from coordination and organometallic chemistry resulted in new, deeper insights into the chemistry of the process. Significant, multi-billion-dollar demonstration plants were built and operated. More recent research efforts are aimed at increasing the selectivity of FT synthesis to produce specific products used as chemical feedstock.

Promoted by the extremely cheap domestic coal and the particular state policies in South Africa, two largescale plants (Sasol II and Sasol III) came in operation. These plants initially operated using circulating fluidized-bed (CFB) reactors which were later improved to the Sasol Advanced Synthol (SAS) technology.

Later two FT plants operating on offshore methane were also built in South African and Malaysia. The first one, which was commissioned in 1992, was the Mossgas plant (now known as PetroSA), with a production capacity of 20 000 barrels per day. The second one was the Shell Bintulu[2] plant (Malaysia) which produces 15 000 barrels per day. This plant was commissioned in 1993 and it utilizes the Shell middle distillate synthesis (SMDS) fixed-bed technology.

In 2005 Oryx GTL, which is a joint venture between Sasol and Qatar Petroleum, commissioned another gas-to-liquid plant in Qatar in alliance with Chevron. The plant was strategically constructed at the Ras Laffan industrial city complex (Qatar) which is in close proximity to large natural gas reserves in the North of Qatar. The plant operates on Sasol's slurry phase technology, with a daily production capacity of 34 000 barrels per day. Since 2005 many FT plants have been planned or are being constructed by ExxonMobil, Syntroleum, BP, and Chinese companies. Not only gas to-liquid (GTL) but also coal-to-liquid (CTL) and biomass-to-liquid (BTL) technologies have been developed with FTS as the key step[1]. A summary of other plants that have been commissioned are listed in Table 1.

Table 1 - Current Commercial Fischer-Tropsch operating facilities

Year	Companies/Plant	Technology	Capacity [bpd]	CAPEX MMUSD	Country	Note
1955	Sasol	Sasol I	500		South Africa	
1980	Sasol	Sasol II	11.000	3.200	South Africa	
1982	Sasol	Sasol III	20.000	2.800	South Africa	
1992	PetroSA (Mossel Bay)	Sasol's slurry phase technology	15.000	1.500	South Africa	Gas Processing facilities included
1993	Shell/ Bintulu	Shell middle distillatesyntesis (SMDS) fixed-bed technology	30.000	1.500	Malaysia	Capex refers to the original capacity of 12500 bpd
2005	Sasol & Qatar Petroleum in alliance with Chevron/ORYX	Sasol's slurry phase technology	34.000	1.500	Qatar	Based on Sasol's SSPD technology Two Slurry FT reactors
2007	Chevron Nigeria and NNPC/ Escavros	Sasol's slurry phase technology	34.000	8.400	Nigeria	Gas Processing facilities included
2009	Shell and Qatar Petroleum/ PEARL	Shell middle distillate syntesis (SMDS) fixed-bed technology	140.000	16.000	Qatar	Pearl Plant. Integrated with upstream facilities. Based on Shell's SMDS Snthesis
2011	Exxon Mobil and Qatar Petroleum	Advanced gas conversion for the 21 century (AGC-21) technology	154.000		Qatar	
2016	Sasol, Uzbekneftegaz, and Petronas	OLTIN YO'L GTL	38.000	2.500	Uzbekistan	Based on Sasol's Slurry Phase Distillate Technology
2018	Sasol	Lake Charles Chemical Project	96.000	14.000	USA	Capex refers to the petro-chemical complex

3. The FT-Chemistry

The Fischer-Tropsch synthesis is a nonselective process[3]. The products obtained include alkanes and alkenes with a very broad composition, and oxygen- containing compounds, mostly alcohols, carbonyl compounds, acids, and esters. Alkenes, the main isomeric olefins obtained, as well as alcohols, are considered to be the primary products. Most compounds are linear with only a small amount of branched hydrocarbons. Only methyl branching occurs, with the methyl group distributed randomly along the chains. The fraction of dimethyl-substituted compounds is very small, and compounds with quaternary carbon atoms are not formed. Under industrial conditions primarily linear, saturated hydrocarbons are produced with only little oxygenated compounds. Product compositions, however, may be substantially varied by catalysts and reaction conditions.

The basic transformations of Fischer-Tropsch synthesis may be generally summarized as in Eqs. (3.1) and (3.2):

$$2nCO + nH_2 \rightarrow -[CH_2]_n- + nCO_2 \qquad \Delta H=-39{,}8\ \text{kcal/mol} \qquad (3.1)$$

$$nCO + 2nH_2 \rightarrow -[CH_2]_n- + nH_2O \qquad \Delta H=-48{,}9\ \text{kcal/mol} \qquad (3.2)$$

Both processes are highly exothermic. Iron catalyzes the transformation according to (3.1), whereas the reaction (3.2) represents the chemistry characteristic of cobalt. In fact, (3.2) is the primary synthesis reaction on both metals. Over iron catalyst, however, water reacts further with a second molecule of CO to form CO_2 according to the ***water-gas shift reaction*** (3.3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H=-9.81\ \text{kcal/mol} \qquad (3.3)$$

Reaction (3.1), thus can be considered as the linear combination of (3.2) and (3.3).

Olefins form according to the following reaction:

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad (3.4)$$

Other secondary reactions taking place under operating conditions. These are the alcohol formation (3.5), the Boudouard reaction (3.6), coke deposition (3.7), carbide formation (3.8) and catalyst oxidation/reduction (3.9), (3.10):

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (3.5)$$

$$2CO \rightarrow C + CO_2 \qquad (3.6)$$

$$CO + H_2 \rightarrow C + H_2O \qquad (3.7)$$

$$xC + yM \rightarrow MyCx \qquad (3.8)$$

$$MxOy + yH2 \leftrightarrow yH2O + xM \qquad (3.9)$$

$$MxOy + yCO \leftrightarrow yCO_2 + xM \qquad (3.10)$$

The methane formation is an undesirable side-reaction of the Fischer-Tropsch synthesis.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta=49{,}2\ kcal/mol \qquad (3.11)$$

Depending on a number of factors, primarily the hydrogen to carbon monoxide consumption ratio - *usage ratio* – in relation to the composition of the syngas and the type of catalyst employed, either paraffin formation (3.1)/(3.2) or olefin formation (3.4) predominates the synthesis.

Whereas the formation of paraffins is favored by high H_2/CO ratios and catalysts with strong hydrogenating abilities, the formation of olefins is favored in syngas with low H_2/CO ratios and catalysts with less strong hydrogenating abilities.

Apart from hydrocarbons, H_2O is also a primary product from FT synthesis. The presence of water is undesirable since it affects syngas conversion, hydrocarbon selectivity, FT product distribution and the catalyst longevity due to its influence on the degree of syngas adsorption on the catalyst, chain initiation, chain growth, methanation, hydrogenation to paraffin's and dehydrogenation to olefins.

It is believed that a high H_2O concentration is one factor that leads to oxidation and deactivation of iron carbides; therefore, understanding H_2O formation and desorption is important for enhancing the FT catalyst activity.

The water-gas-shift reaction (3.3) consumes CO and water, formed in the FT synthesis, and converts the reactants to hydrogen and carbon dioxide. WGS activity is normally high over potassium-promoted iron catalysts and it is negligible over cobalt or ruthenium catalysts. This reaction helps to make up the deficit of H_2 in the syngas making iron based catalysts a better choice for coal-based FT Synthesis. Alcohols and oxygenates are also produced during FT synthesis, in particular, for precipitated iron based catalysts.

4. Catalysts

Most Group VIII metals are active in the reduction of carbon monoxide, but they form different products. Methanation, hydrocarbon formation, and methanol formation are the characteristic major transformations. The two classical metals, iron and cobalt, used in commercial Fischer-Tropsch operations are capable of producing hydrocarbons at atmospheric pressure. Nickel is also active in FT chemistry, yielding, however, primarily methane. Moreover, during the reaction nickel carbonyls, a very toxic compound, form. For these reasons, it is generally not desirable for liquid synthetic fuels production[3].

Cobalt-based catalysts feature higher hydrogenation activity, hence they produce higher yield of middle-distillate products and much less oxygenated relative to iron based catalysts. They show higher selectivity for paraffinic derivatives at low temperature; at high temperature, however, undesired quantity of methane forms. Thus this type of catalyst is not suitable for high temperature Fischer-Tropsch (HTFT) process. Compared to Fe-based catalyst, those based on Co show less water gas shift (WGS) activity, thus they produce more water according to Eq. (2), and small amounts of CO_2 can be found in the reactor at any given time.

Cobalt-based catalysts are much more expensive than iron-based ones, hence they are only used industrially as supported catalysts. Commonly used supports include SiO_2, TiO_2 and Al_2O_3. Generally, Co catalysts are about 3 times more reactive than Fe catalysts in FT synthesis, yet they are about 250 times more expensive. Nonetheless, Co catalysts have a longer lifetime, usually over five years' time on stream. This is because they are not susceptible to deactivation by carbide or oxide formation as found for Fe catalysts.

Both iron and cobalt are sensitive to the presence of S species in the syngas and can be poisoned by S compound. The sensitivity to S is higher for Co than for Fe. Hence, generally, Co-based catalyst is preferred for FT synthesis with syngas derived from natural gas, which has a relatively low S content and higher usage ratio that does not require the water-gas-shift activity. Generally, the sulfur content of the syngas is kept below 0,02 mg/m^3. Alkali metal of the Group 1 are poisons for the Co-based catalyst. Co-based catalyst can only be operated at low temperature regime (220÷270°C).

Fe-based catalysts are the catalyst of choice for many industrial applications because not only are they relatively inexpensive to prepare, but they also tolerate flexible operation conditions, and they give a good turnover with a broad product spectrum.

This type of catalysts preferentially produces CO_2 according to the reaction (7). They have a relatively higher WGS activity and are preferred for FT synthesis with the low H_2/CO ratio syngas typically derived from low quality feedstock as coal or biomass, although it produces significant quantity of non-paraffinic derivatives as by products.

Alkali metal of the Group I (K or Na) are used as promotors for the Fe-based catalyst in order to increase the average molecular weight and the olefinity of the hydrocarbons produced, as well as promote the water-gas-shift reaction. A typical catalyst also contains copper to enhance catalyst reducibility, along with some silica or zinc oxide to improve the amount of iron atoms interacting with the synthesis gas

Fe-based catalyst can be operated both at low temperature and at high temperature (300÷350°C). In comparative terms, coke deposition rate is higher for Fe-catalysts than for Co-based catalyst, thus the lifetime of this latter is higher.

Iron catalysts used in FT synthesis are very sensitive to conditions of their preparation and pretreatment. Metallic iron exhibits very low activity. Under FT reaction conditions, however, it is slowly transformed into an active catalyst. Iron used in medium-pressure synthesis required an activation process of several weeks at atmospheric pressure to obtain optimum activity and stability**.** During this activation period, aka *carburization,* phase transformation takes place, and surface carbon, carbides, and oxides are formed. The catalyst undergoes additional slow structural changes during its lifetime with parallel changes in activity and selectivity, and even the breakdown of the catalyst.

All in all, it can be concluded that for a given operating temperature, a Co-containing catalyst shows a higher selectivity for heavier hydrocarbon relative to Fe-containing catalyst. Hence, in order to maximize production of kerosene fraction, a slurry reactor with a Co-based catalyst is the most appropriate choice. On the other side, for maximizing the production of naphtha fraction, it is best to use Fe-based catalyst at high temperature in a fixed bed reactor.

Iron nitrides are an interesting class of FT catalysts**.** They exhibit high mechanical stability and yield increased amounts of oxygenated compounds, mainly alcohols.

Ruthenium is very active in methane formation at temperatures as low as 100°C and moderate pressures, whereas high-molecular-weight hydrocarbons are formed at higher pressures. In the range of 1000÷2000 bar forms a product termed polymethylene, equivalent to high- density polyethylene. Ruthenium is very expensive catalyst, thus in commercial operations is often used in low concentration as a promoter.

Although discovered in the 1930s, the process was never commercialized probably because of the low activity of the catalyst used and the very severe reaction conditions. Iron nitrides are an interesting class of FT catalysts**.** They exhibit high mechanical stability and yield increased amounts of oxygenated compounds, mainly alcohols.

Rhodium is a unique metal since it can catalyze several transformations. It is an active methanation catalyst and yields saturated hydrocarbons on inert supports. Methanol is the main product when supported on $Mg(OH)_2$. Transition-metal oxides as supports or promoters shift the selectivity toward the formation of C_2 and higher oxygenates.

Catalyst preparation is crucial in successful FT synthesis. Appropriate catalyst composition and delicate pretreatment and operating conditions are all necessary preconditions to achieve the desired results. Catalyst disintegration due to oxidation and carbide formation is a serious problem that can be prevented only by using catalysts with adequate chemical and mechanical stability under appropriate operating conditions[3].

Promotors

Both cobalt and iron require chemical promotion to exhibit steady activity and selectivity. These are achieved by adding an optimum amount of potassium to iron. Electron donation from potassium to iron is assumed to weaken the carbon-oxygen and iron-hydrogen bonds, and strengthen the iron-carbon bond. These changes result in increased CO adsorption, increased probability of chain growth, and decreased hydrogenation ability. The overall effect on products distribution is decreased methane and increased oxygenate production. Paraffin formation is also decreased, resulting in enhanced alkene selectivity. The product has a higher average molecular weight. Other possible factors include the enhanced dissociation of CO due to its direct interaction with adsorbed potassium and enhanced migratory insertion in propagation brought about by surface K.

It is worth mentioning that oxygenate formation increases with potassium content, but there is an optimized potassium content for oxygenate yield over precipitated iron catalysts. Moreover, K suppresses the formation of methanol and increases the formation of higher molecular weight alcohols.

Besides alkali, in FT synthesis other promoters can be used. Among these, it is worth mentioning Cu and Mn. The main function of Cu, particularly when bubble column slurry reactors are employed, is to decrease the temperature required to reduce iron oxides. Mn has also been widely used to promote the production of $C_2 \div C_4$ olefins and also increase the sulfur-tolerance property of iron catalysts.

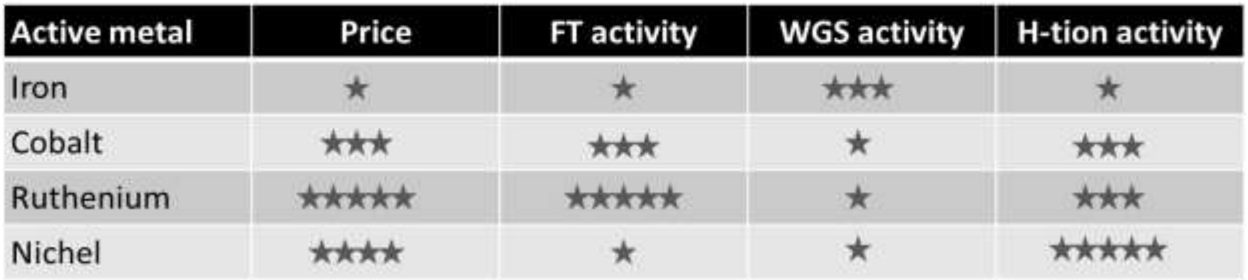
Catalyst activation is done by reducing the catalysts with either H_2 (eq. 9), CO (eqn. 10) or syngas. A cobalt catalyst is usually activated with H_2 and the metallic cobalt produced is believed to be the active phase for FTS in these catalysts. However, it has been reported that the reducing pre-treatments with H_2, CO or syngas often have significant effects on catalytic activity and selectivity for iron-based catalysts.

The choice of the catalyst and its composition also depends on the type of reactor to be used. Fixed-bed iron catalysts are prepared by precipitation and have a high surface area. A silica support is commonly used with added alumina to prevent sintering. Catalysts for fluidized-bed application must be more attrition-resistant. Iron catalysts produced by fusion best satisfy this requirement. The resulting catalyst has a low specific surface area, requiring higher operating temperature. Copper, another additive used in the preparation of precipitated iron catalysts, does not affect product selectivity, but enhances the reducibility of iron. Lower reduction temperature is beneficial in that it causes less sintering.

For a given operating temperature, a Co-containing catalyst shows a higher selectivity for heavier hydrocarbon relative to Fe-containing catalyst, it can be concluded that in order to maximize production of kerosene fraction, a slurry reactor with a Co-based catalyst is currently the most appropriate choice. On the other side, for maximizing the production of naphtha fraction, it is best to use Fe-based catalyst at high temperature in a fixed bed reactor[3].

The main characteristics of the Fischer Tropsch catalysts are wrapped up in Table 2.

Table 2 – Characteristics of today's FT catalysts



Active metal	Price	FT activity	WGS activity	H-tion activity
Iron	★	★	★★★	★
Cobalt	★★★	★★★	★	★★★
Ruthenium	★★★★★	★★★★★	★	★★★
Nichel	★★★★	★	★	★★★★★

Catalysis Mechanism

The FT synthesis can be considered as the polymerization of carbon monoxide under reductive conditions. The CH_2 units, formed by the hydrogenation of CO are taken as the "monomers" in a stepwise oligomerization process. At each stage of growth, the adsorbed hydrocarbon species has the option of desorbing or being hydrogenated to form the primary FT products or of adding another monomer to continue the chain growth.

If it is assumed that the probability of chain growth is independent of the chain length, then it is a simple matter to calculate the product distribution. The agreement between the calculated and observed results, with the exception of the C_1 and C_2 products is good and this supports the concept of a stepwise growth process. Therefore, product distributions may be predicted by assuming that chain growth occurs via the addition to the growing chain of one carbon atom at a time.

The statistics of chain length distribution usually give a linear correlation between the carbon number n and the mole fraction of molecules containing n carbon atoms when an appropriate mathematical formula is used. ***Schulz-Flory*** or ***Schulz-Flory-Anderson distribution*** describes the distribution the carbon number distribution in the syncrude by linking the probability of chain growth to the fraction of each carbon number by the following equation:

$$Wn = n(1-\alpha)\alpha^{n-1}$$

Where Wn is the weight fraction of HC molecules containing n carbon atoms, α (growth probability) is the probability a radical continues to growth to form a longer chain.

The growth probability α depends on i) the feedstock gas composition; ii) the catalyst type; iii) the catalyst composition; iv) the reactor design; v) and operating conditions (T and P).

The above distribution equation suggests that methane will always be the largest product. Since in the FT synthesis methane is regarded as an undesired by product, the operating conditions and the catalyst have to be chosen so as to increase α to the maximum possible extent. Indeed, with α close to 1 the amount of methane would be very low relative to the total of heavier HC. However, increasing α increases the length of the hydrocarbon chains with formation of waxes (solid material) as well. To produce transportation fuel, therefore, it is necessary to crack in the refining part of a FT facility those long HC chains by means of a hydrocracker, which generally makes the synthetic fuel production less economically attractive.

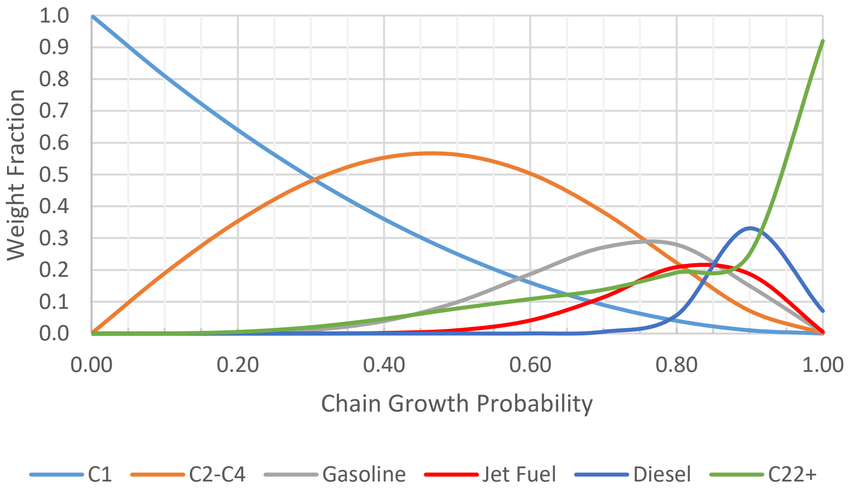


Figure 1 - FT product distribution

Some have proposed the use of catalyst substrate featuring fixed pores sizes like zeolite to limit the chain length so that the methane formation is minimized while avoiding the formation of significant quantity of heavy HC not directly usable as transportation fuel.

To attain a desired selectivity of some product, kerosene for example, it is necessary to get deep insights into the correlation between the chain growth probability and the reaction conditions so that mathematical expressions can be developed in order for proper process modelling[4].

The FT Synthesis is not a simple polymerization, since the “monomer” itself forms in a multistep pathway. Further complications may arise from the heterogeneous nature of the process. The deviation of the higher-molecular-weight products, for instance, was explained by invoking the participation of two types of active site with different chain growth probability factors**.**

Transport limitations may also contribute to this phenomenon. Retarded diffusion, for example, enhances the re-adsorption of olefin products. As a result, they may initiate new chains, eventually leading to the formation of heavier products and a higher fraction of paraffins.

The question of the mechanism of FT reaction is of considerable controversy. Three principal routes for product formation have been proposed: i) carbide mechanism; ii) hydroxymethylene mechanism; iii) and CO insertion mechanism.

The carbide mechanism was first suggested by Fischer and Tropsch themselves in their first publications. They proposed that a carbide-rich intermediate was the source of the products. This was later elaborated by Craxford and Rideal[3] in a model assuming that surface carbide is hydrogenated to methylene groups that polymerize to form a $-(CH_2)_n-$ macromolecule on the catalyst surface. Cracking would lead to gaseous products and other hydrocarbons. Inconsistent with this model is the small fraction of monomethyl-substituted products and the significant difference between product distributions of FT synthesis and hydrocracking. This mechanism does not explain the formation of oxygenated products, either.

An important subsequent observation seemed to indicate that carbides are not reactive under FT conditions. When carbon was deposited on a surface by the decomposition of CO, labeled carbon was not incorporated into the products. This and other evidence accumulated against the carbide mechanism by the 1950s led to the formulation of other mechanisms.

The hydroxymethylene or enolic mechanism assumes the formation via the hydrogenation of carbon monoxide of a surface-bound hydroxymethylene species. A strong argument in favor of this mechanism is that alcohols can initiate chain growth. They do not participate in propagation, however, although they should do so through dehydrocondensation. Additionally, no convincing evidence has been found to support the existence of the suggested enolic surface species.

By invoking certain analogies with coordination complexes and organometallic chemistry, a carbon monoxide insertion mechanism was later proposed. Initiation takes place via CO insertion into a metal-hydrogen bond either through a metal hydrocarbonyl intermediate or as adsorbed carbon monoxide. Propagation occurs through CO insertion into a metal-carbon bond (alkyl migration) to form an acyl intermediate, which then undergoes further product-forming transformations

The revival of interest in FT chemistry in the 1970s resulted in new observations that eventually led to the formation of a modified carbide mechanism - the most widely accepted mechanism at present. Most experimental evidence indicates that carbon-carbon bonds are formed through the interaction of oxygen-free, hydrogen-deficient carbon species. Ample evidence shows that carbon monoxide undergoes dissociative adsorption on certain metals to form carbon and adsorbed oxygen

The bond strengths of the metal-carbon and metal-oxygen bonds play an important role in the reduction of CO**.** If these bonds are too strong, stable oxides and carbides are formed. Metals that do not dissociate CO easily (Pt, Pd, Ir, Cu) are inactive in the FT synthesis and yield methanol instead of hydrocarbons. Metals that are the most active in CO dissociation (Fe, Co, Ni, Ru) are the most active. Supports and promoters may strongly affect activities and selectivity. Adsorbed oxygen is removed by reacting with CO at low pressure, and by adsorbed hydrogen at high pressure.

Carbon may exist in different forms, of which carbidic surface carbon is the most reactive species. It is readily transformed to carbenic species, which participates in chain growth. This is supported by revaluation of earlier labeling experiments. New studies showed that certain surface carbon species may be very reactive and do incorporate into products mainly into methane. Hydrogenation of adsorbed CO without previous dissociation may also lead to surface carbenic species.

Oxygen-containing compounds are suggested to be formed with the participation of non-dissociated CO in a parallel pathway**.**

Efforts have been made over the years to advance a unified concept of FT chemistry. The basic problem, however, is that most information comes from studies of different metals. Considering the specificity of metals, it is highly probable that different mechanisms may be operative on different metals. The numerous mechanistic proposals, therefore, may represent specific cases on specific surfaces and may be considered as extremes of a highly complex, widely varied reaction network. A unified concept should include multiple active sites and several surface species participating in parallel product-forming reactions**.**

Indeed, it is very probable that both carbon species such as elemental C, CH_x, etc. (forming carbided metal sites) and oxygenated species such as O, OH, H_2O, etc. (forming oxydised metal sites) are chemisorbed on the surface of the metal catalyst. The process involves rapid cycling, that is, at any instant a particular surface metal atom could be in the oxidised, carbided or reduced state. This chemical cycling should enhance sintering and so loss of active surface area.

The metal in the oxidized state can also chemically interact with the support forming inert aluminates, silicates, etc. The smaller the supported metal particles, i.e. the higher the proportion of exposed surface metal atoms, the higher the likelihood of these processes occurring. This could mean that a very highly dispersed metal may well have a high initial FT activity but could rapidly decline with time-on-stream. For similar reasons high H_2O/H_2 ratios within the reactor should not exceed some critical value.

High conversions can nevertheless be achieved by recycling a portion of the tailgas after water and heavy product knock-out. This is common practice in FT operations. For iron-based catalysts bulk phase oxidation occurs in addition to the above factors. At high temperatures aromatics are formed which lead to fouling of the surface by aromatic coke. Large amounts of elemental carbon are also formed which results in catalyst break up and subsequent physical loss of the low density carbide and alkali rich fines from the fluidized bed reactors. The deposition rate of elemental carbon increases with the alkali promoter content of the catalysts and correlates with the value of pCO/p^2H_2 at the reactor entrance. The latter factor means that if the syngas pressure is increased then the rate of carbon deposition is lower.

The FT synthesis to produce hydrocarbons for use as motor fuels is allegedly not economical at present (except as mentioned use in South Africa). A significant drawback of the FT synthesis is its low selectivity due to the Schulz-Flory polymerization kinetics. This sets a serious limitation to produce specialty chemicals since a wide distribution of products is always formed. For example, the maximum obtainable quantity (in w%) of C_2-C_4 hydrocarbons, gasoline (C_5-C_{11}), and diesel fuel (C_{12}-C_{17}) is 56%, 27%, and 32%, respectively.

In the 1970s and 1980s improved selectivity of specialty chemical production was achieved through catalyst manipulation and process modifications. The proper choice of metal loading, dispersion, promoters and supports, alloying, careful control of reaction conditions, and the use of gaseous additives can significantly alter product compositions resulting in higher selectivity.

The direct synthesis of low-molecular-weight olefins and the synthesis of LPG to produce ethylene and propylene by subsequent cracking are the most promising processes. Promoted iron-manganese catalysts are highly active and selective in alkene production.

Iron and iron-manganese supported on silicalite promoted with potassium yield C_2-C_4 olefins with high selectivity. One paper has reported the selective synthesis of 1-alkenes over highly reduced zeolite-entrapped cobalt clusters. Mixed metal-zeolite catalysts, in general, produce higher amounts of aromatics and gasoline-range hydrocarbons through the interception of intermediates. Liquefied petroleum gas, principally ethane and propane, can be produced with a molybdenum-based alkali promoted catalyst.

The unique selectivity of rhodium to catalyze the formation of oxygen-containing compounds is a potentially promising possibility for practical utilization. When promoted by transition metal oxides, rhodium is highly selective in the formation of C_2 oxygenates (ethanol, acetaldehyde). An even more attractive transformation is the direct synthesis of ethylene glycol from synthesis gas. The reaction was demonstrated using rhodium, cobalt, and ruthenium carbonyls. Although highly economical, it is far from practical application.

Of the technological modifications, FT synthesis in the liquid phase (slurry process) may be used to produce either gasoline or light alkenes under appropriate conditions in a very efficient and economical way.

The slurry reactor conditions appear to establish appropriate redox conditions throughout the catalyst sample. The favorable surface composition of the catalyst (oxide and carbide phases) suppresses secondary transformations (alkene hydrogenation, isomerization), thus ensuring selective a-olefin formation.

5. Fischer Tropsch related processes

A modification of the FT synthesis is the Kolbel-Engelhardt reaction, which converts carbon monoxide and water to hydrocarbons by combining the following reaction

$$3nCO + nH_2O \rightarrow -(CH_2)_n- + 2nCO_2$$

with the water-gas shift reaction. This latter produces hydrogen, which then reacts with carbon monoxide in the normal FT reaction (1) to yield hydrocarbons. All metals that are active in Fischer-Tropsch synthesis may be employed in the Kolbel-Engelhardt reaction as well.

Iron, cobalt, and nickel were found to be the best catalysts. Product composition in the Kolbel-Engelhardt reaction differs significantly from that of FT synthesis. Since the hydrogen partial pressure is much lower in the former process, all hydrogen-consuming transformations are retarded. As a result, olefins and alcohols are not reduced and formed in much larger amounts in the Kolbel-Engelhardt reaction. Even methanation on nickel is suppressed to only about 25% of hydrocarbons produced. Reaction in the liquid phase in a slurry reactor provides the best operating conditions.

Methanation, that is, the transformation of CO to methane, was developed in the 1950s as a purification method in ammonia synthesis. To prevent poisoning of the catalyst, even low levels of residual CO must be removed from hydrogen. This is done by methanation combined with the water-gas shift reaction. In the 1970s the oil crises spurred research efforts to develop methods for substituting natural-gas production from petroleum or coal via the methanation of synthesis gas.

The same catalyst compositions used in the more important methane steam reforming may be used in methanation too. All Group V in metals, molybdenum and silver exhibit methanation activity. Ruthenium is the most active but not very selective since it is a good FT catalyst as well. The most widely used metal is nickel usually supported on alumina or in the form of alloys operating in the temperature range of 300-400 °C. A bimetallic ruthenium-nickel catalyst shows excellent characteristics.

The methanation reaction is a highly exothermic process (ΔH =-49.2 kcal/ mol). The high reaction heat does not cause problems in the purification of hydrogen for ammonia synthesis since only low amounts of residual CO is involved. In methanation of synthesis gas, however, specially designed reactors, cooling systems and highly diluted reactants must be applied. In adiabatic operation less than 3% of CO is allowed in the feed. Temperature control is also important to prevent carbon deposition and catalyst sintering. The mechanism of methanation is believed to follow the same pathway as that of FT synthesis.

Isosynthesis is a potentially important variation of the FT synthesis since it yields mainly branched C_4-C_8 paraffins**.** Most of the pioneering work was carried out by Pichler[3] and coworkers. They observed that certain non-reducible tetravalent oxides (thoria, zirconia, ceria) exhibited activity in the reaction producing primarily isobutane. The optimum operating conditions for isosynthesis on thoria are 375÷175°C and 300÷600 bar. Alcohols are the main products at lower temperature, whereas methane and dimethyl ether predominate at higher temperature. Alumina produces only a minor amount of branched hydrocarbons but enhances the activity of thoria. A 20% alumina-thoria catalyst with 3% K_2C0_3 gave the best results.

Rare-earth oxides (La_2O_3, Dy_2O_3) have been shown to be active in isosynthesis**.** It was also observed that zirconia may catalyze the highly selective formation of isobutylene under appropriate conditions**.** Two chain growth processes, CO insertion into aldehydic Zr-C bonds and condensation between methoxide and enolate surface species, were invoked to interpret the mechanism on zirconia. Acidity of the catalyst was found to correlate with C4 selectivity. This results from the enhancement of condensation through the stabilization of the enolate species on Lewis acid sites.

Isoalkanes can also be synthesized by using two-component catalyst systems composed of a FT catalyst and an acidic catalyst. Ruthenium- exchanged alkali zeolites and a hybrid catalyst (a mixture of RuNaY zeolite and sulfated zirconia) allow enhanced isoalkane production.

On the latter catalyst 91% isobutane in the C_4 fraction and 83% isopentane in the C_5 fraction were produced. The shift of selectivity toward the formation of isoalkanes is attributed to the secondary, acid-catalyzed transformations on the acidic catalyst component of primary olefinic FT-products.

6. Effect of operating conditions on the product distribution

Different catalysts yield different product distribution for a given operating condition (T, P and the feed H_2/CO ratio). The influence of these conditions on the product distribution can be assessed through the study of the thermodynamic equilibrium analysis based on the minimization of the Gibbs free energy assuming: i) the product distribution can be characterized by the ASF distribution model, irrespective of the catalyst type; ii) complete conversion of H_2 and CO; iii) that all products are vapor phase.

Effect of temperature and pressure

The effects of changing temperature on the distribution of Fischer–Tropsch products is shown in Figure 2a wherein the logarithm of the mole fraction of the total organic products is plotted against the number of carbon atoms. The plot refers to three temperature levels: 510 K (237 °C), 525 K (252°C) and 540 K (267 °C) at 1,5 MPa with H_2/CO ratio set at 0,7.

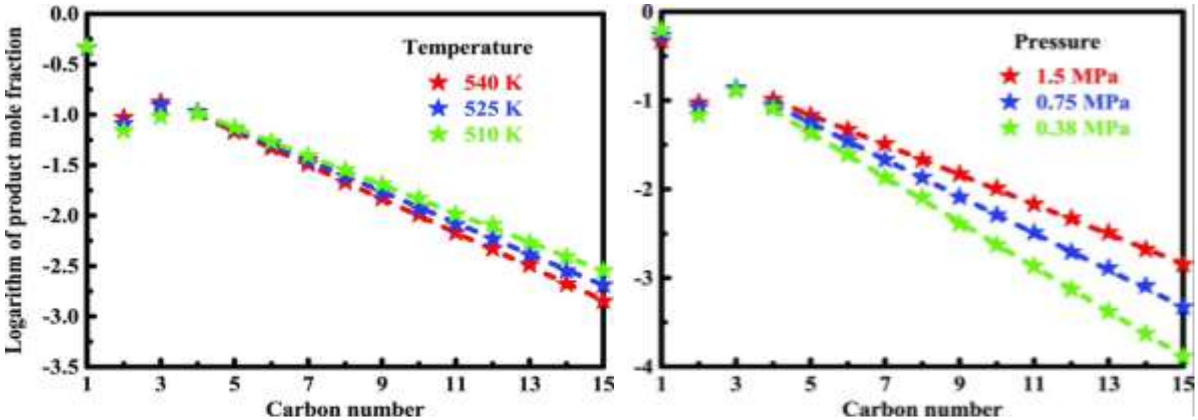


Figure 2 - Effects of temperature and pressure on FT distribution products[5]

At each temperature of the thermodynamic equilibrium system, there is a linear relationship between the number of carbon atoms and the concentration of the C_4 plus products. An increase in reaction temperature results in a shift in selectivity towards low carbon number hydrocarbons. This shift in selectivity is due to the increase of the desorption rate and thereby chain termination to less hydrogenated products (alkenes and oxygenates).

The rate of hydrogenation, which can also cause chain termination to more hydrogenated products, is increased by an increase in temperature too. The net effect is lower the α-value and increase the desorption rate, resulting in a carbon number distribution that favors shorter chain products. The relative increase in desorption rate without hydrogenation and hydrogenation leading to desorption determines whether the product will become more olefinic or not. The reaction rate of oxygenates by re-adsorption and interconversion also increases with temperature.

As mentioned earlier, the chain growth probability is sensitive to the reaction temperature. More specifically, this parameter decreases from 0.72 to 0.68 when the temperature of the thermodynamic equilibrium system increases from 510 to 540 K. Thus, the Chain growth probability decreases with increasing temperature. Moreover, the ratio C_3/C_2 product increases with increasing temperature.

In conclusion in a FT-process high temperatures tend to favor the formation of products with lower carbon number and more hydrogenated products. Moreover, high temperature increases branching and the formation of secondary products like ketones and aromatics. By contrast, low temperature favors yielding high molecular mass linear waxes. The result is that the ratio naphtha/kerosene decreases with decreasing temperature.

Since different temperature levels determine different product distribution, in the current industrial practice, the FT processes are grouped into two categories defined by two FT operating temperature regimes: low temperature FT (LTFT) process or a high temperature FT (HTFT) process depending on the products required.

HTFT utilizes iron-based catalysts at temperatures varying from 300 °C to 350 °C for the production of gasoline and linear hydrocarbons. LTFT operates on both cobalt and iron-based catalysts for the production of waxy materials. The main advantage of HTFT over LTFT is that there is no liquid phase around the catalyst particles in the HTFT process. The typical product distributions for the Sasol's LTFT and HTFT processes are shown in Figure 3.

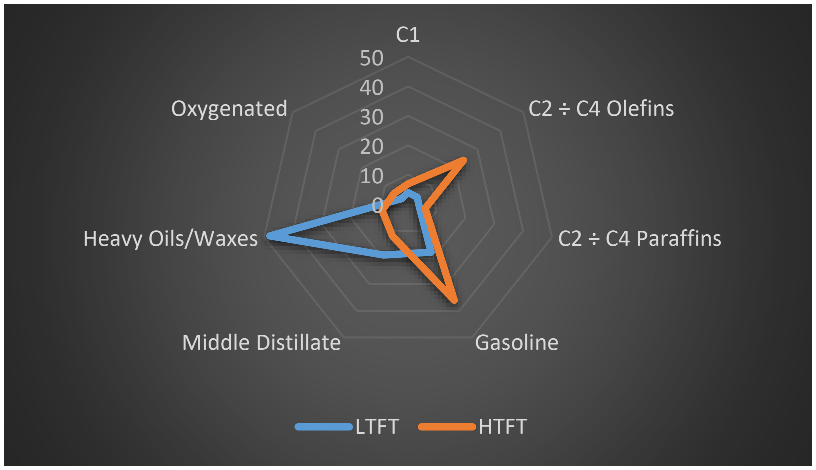


Figure 3 - Typical product distribution (%w) for LTFT and HTFT processes

The pressure, in combination with the syngas composition, determines the partial pressure of the reactants (H_2 and CO). Since CO is more strongly adsorbed onto the catalyst than H_2, the concentration of CO onto the catalyst surface increases when the pressure increases. High CO concentration promotes chain growth and increases the α-value of the catalyst. A high CO concentration also favors CO incorporation and consequently the production of oxygenates.

Indeed, the effect of the pressure on the FT product distribution is illustrated in the right side of Figure 2 wherein the logarithm of the mole fraction of the total organic products is plotted against the number of carbon atoms for 0.38, 0.75, and 1.5 MPa pressure levels at 540 K, and with the H_2/CO set at 0,7.

Figure shows that high carbon number hydrocarbons are thermodynamically favored at high pressures. Chain growth probability is sensitive to pressure too. More specifically, this parameter varies from 0.56 at a pressure of 0.38 MPa to 0.68 at a pressure of 1.5 MPa.

Olefin formation.

Figure 4 shows the predicted mole fractions of olefins at each carbon number as a function of the number of carbon atoms for 525 and 540 °K at 1.5 MPa, and with H_2/CO ratio is 0.7. It can be seen that that under the specified conditions, the FT syncrudes contain a certain amount of olefins. An increase in reaction temperature results in a shift of selectivity towards more hydrogenated products. This shift is consistent with the relative stability of the products.

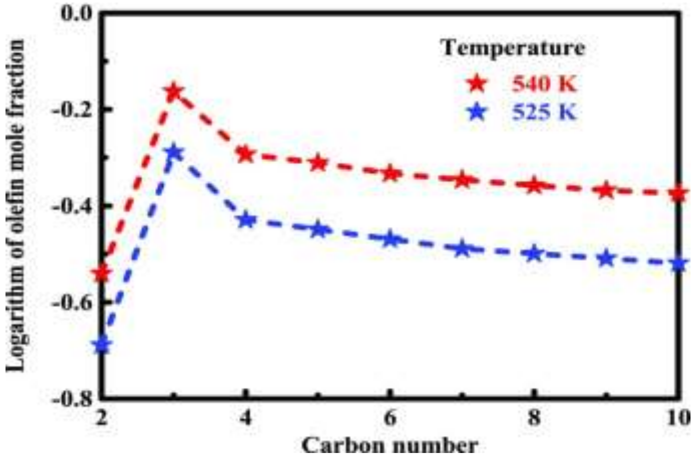


Figure 4 - Olefins formation in FT process[5]

Figure 4 also show that the concentration of C_2 olefin products is low. By contrast, the concentration of C_3 olefin product is high, and the concentration of high-molecular-weight olefin products in the C_4–C_{10} range is essentially constant. On the other hand, the amounts of olefins decrease with decreasing temperature. Therefore, it can be concluded that higher temperature operation favors olefin products.

Effect of H_2/CO ratio in the syngas

Generally, during the FT synthesis, H_2 and CO are consumed in a ratio that is dependent on the products being formed. As the products became heavier, the usage ratio approaches 2, irrespective of the compound class being formed. It is important that the syngas composition matches the usage ratio. Indeed, if it does not, the H_2/CO ratio is going to change during the synthesis. By and large, if H_2/CO ration increases, the probability of chain growth decreases, as well as the selectivity to alkenes and oxygenates. The usage ratio for the different products is shown in the following Table 3.

Table 3 - Usage Ratio for the production of different FT primary products[6]

Product	**H2:CO**	**H_2:CO usage ratio based on product carbon number**					
		C_1	**C_2**	**C_4**	**C_{10}**	**C_{25}**	**C_{50}**
Alkane	(2n+1)/n	3,00	2,50	2,250	2,10	2,04	2,02
Alkenes	2	-	2,00	2,000	2,00	2,00	2,00
Alcohols	2	2,00	2,00	2,000	2,00	2,00	2,00
Carbonyls	(2n-1)/n	1,00	1,50	1,750	1,90	1,96	1,98
Carboxylic Acids	(2n-2)/n	-	1,00	1,500	1,80	1,92	1,96

The effect of H_2/CO ratio on the FT performances is illustrated in Figure 5, wherein the distribution of the product is depicted for 0.6, 0.7, and 0.8 ratios at 540 °K and 1.5 MPa.

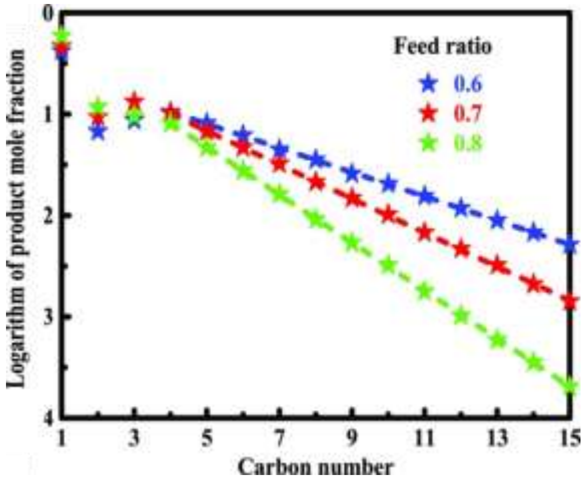


Figure 5 - Effect of syngas (H_2/CO ratio) composition[5]

For each feed ratio of hydrogen to carbon monoxide, there is a linear relationship between the number of carbon atoms and the concentration of the C_4 plus products. It can be seen that an increase in the feed ratio of hydrogen to carbon monoxide results in a shift in selectivity toward low carbon number hydrocarbons, especially towards methane.

When the whole system is at thermodynamic equilibrium at the specified temperature and pressure, the selectivity to methane is between 0.4 and 0.6 in the FT product stream. In other words, higher feed ratios of hydrogen to carbon monoxide tend to favor the methanation reaction, most notably when Ni catalyst is uses, and this is generally undesirable for industrial synthetic liquid fuel production.

For Co-based catalyst feed ratio of hydrogen to carbon monoxide is typically set at 1.8÷2.1; whilst Iron-based catalysts can tolerate lower feed ratios due to intrinsic water-gas shift reaction activity of iron-based catalysts.

Moreover, Figure 4 suggests that α is significantly sensitive to feed ratio. Indeed, it decreases from 0.76 to 0.58 when the ratio is increased from 0.6 to 0.8.

Formation of water and alcohol

When the conditions for thermodynamic equilibrium are satisfied for the reaction system, the thermodynamic analysis shows that no alcohols at high degrees of conversion form. Therefore, alcohols are not favored as products, and the product distribution is mostly constituted of normal paraffins and primary olefins. Since low space velocities enable the distribution of the products to approach chemical equilibrium, the amount of alcohol formed in the FT process decreases with decreasing space velocity. In fact, by increasing the space velocity, secondary reactions are reduced because the re-adsorption and reaction probability becomes less. This reduce hydrogenation of alkenes and oxygenates.

As mentioned earlier, iron-based catalysts preferentially follow the global reaction (1), thus only a small amount of water forms over this kind of catalyst due to water–gas shift reaction (3), which becomes thermodynamically less favored with increasing temperature.

Effect of Ethanol and Ethylene in the feed gas

There exists evidence that some species such as olefins and alcohols may become incorporated into growing chains, but the extent to which this occurs seems to vary greatly with reaction conditions. The distribution of the total products formed in the FT reactions of added ethylene or ethanol is represented in Figure 6a (T = 540 °K, P = 1.5 MPa, and $H_2/CO = 0.7$).

High carbon number hydrocarbons become more thermodynamically favorable after the addition of ethylene to the feed, which suppresses the conversion of carbon monoxide to methane through hydrogenation. It is worth mentioning that the presence of ethylene affects the chain growth probability (α). In fact, this parameter varies from 0.68 in the absence of ethylene to 0.8 with a molar ratio of ethylene to carbon monoxide 0.2 to 1. Moreover, the addition of ethylene to the feed of carbon monoxide and hydrogen enhances the formation of propylene. Overall, ethylene acts as an effective chain initiator, and enhances the formation of high carbon number hydrocarbons.

On the other hand, the effect of the addition of ethanol to the feed on the distribution of the total products is depicted in the right side of Figure 6. Low carbon number hydrocarbons become more thermodynamically favorable after the addition of ethanol to the feed, and the presence of ethanol enhances the conversion of carbon monoxide to methane through hydrogenation. In addition to this, the presence of ethanol also affects the chain growth probability. More specifically, this parameter varies from 0.68 in the absence of ethanol to 0.56 with a molar ratio of ethanol to carbon monoxide 0,2:1.

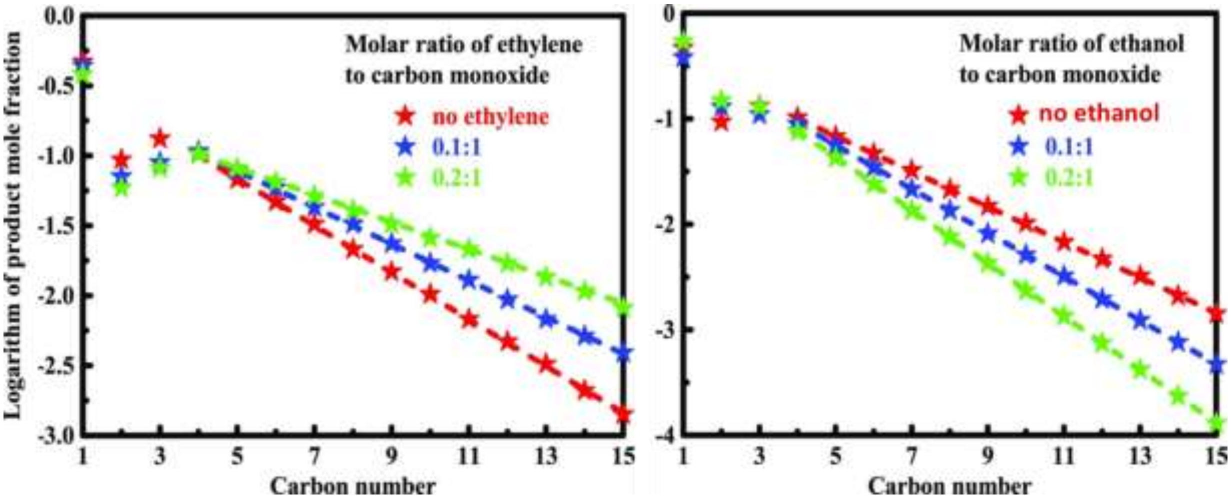


Figure 6 - Effect of ethylene and ethanol in the FT feed[5]

After the addition of a small amount of ethanol to the feed of carbon monoxide and hydrogen, however, the formation of alcohols with more than two carbons is enhanced in the FT process. This is because ethanol also acts as a chain-growth initiator. Overall, the distribution of the total products is greatly affected by the addition of ethylene or ethanol to the feed.

A summary of the effect of various parameter on the FT process is highlighted in the synoptic of the Table 4.

Table 4 - Summary of the impact of some variables on the FT-process

	Chain length	Chain branching	Olefin Selectivity	Alcohol Selectivity	Carbon Deposition	Methane Selectivity
Temperature	↓	↑	*	↓	↑	↑
Pressure	↑	↓	*	↑	*	↓
H_2/CO ratio	↓	↑	↓	↓	↓	↑
Conversion	*	*	↓	↓	↑	↑
Space Velocity	*	*	↑	↑	*	↓
Alkali Content	↑	↓	↑	↑	↑	↓

The FT reactions are highly exothermic - ΔH°/n=-154 kJ/mol, it is thus important to rapidly remove the heat of reaction from the catalyst particles in order to avoid overheating of the catalyst which would otherwise result in an increased rate of deactivation due to sintering and fouling and also in the undesirable high production of methane. Consequently, providing sufficient heat transfer area is a major consideration in the design of a FT reactor. The effectiveness of heat transfer determines the temperature profile in the reactor as well as the temperature profile within each catalyst particle. As shown earlier, the temperature profile in turns affects the selectivity with significant impact on the downstream product refinery and, all in all, on the plant economy.

In most industrial application, the reaction heat is removed by steam production. In the HTFT synthesis high pressure steam at 320÷340 °C is produced, whereas in the LTFT synthesis medium (intermediate) pressure steam is produced at 220÷230°C.

7. Fischer Tropsch Products

The FT synthesis output is a synthetic crude oil. There are three syncrude types that currently are produced commercially, which constitute the base to classify the FT synthesis. The three types of syncrude are iron-based high temperature FT, (Fe-HTFT), iron-based low temperature FT, (Fe-LTFT), and cobalt-based low temperature FT. In general, a syncrude produced by a FT plant includes five groups of hydrocarbons: i) light components – C_1 to C_4; ii) naphtha-light and heavy-C_5-C_{10}; iii) distillate-C_{11}-C_{22}; iv) waxes- C_{22+}, v) and aqueous products.

The syncrude that are representative of each type are given in the following Table 5

Table 5 - Range of hydrocarbons in the raw FT products[6]

Product Fraction	Carbon Range	Compound class	Syncrude Composition [w%]		
			Fe-HTFT	Fe-LTFT	Co-LTFT
Tail Gas	C_1	Alkane	12,7	4,3	5,6
	C_2	Alkene	5,60	1,00	0,10
		Alkane	4,50	1,00	1,00
LPG	C_2-C_4	Alkene	21,2	6,00	3,40
		Alkane	3,00	1,80	1,80
Naphtha	C_5-C_{10}	Alkene	25,8	7,7	7,8
		Alkane	4,30	3,30	12,00
		Aromatic	1,70	0,00	0,00
		Oxygenate	1,60	1,30	0,20
Distillate	C_{11}-C_{22}	Alkene	4,80	5,70	1,10
		Alkane	0,90	13,5	20,8
		Aromatic	0,80	0,00	0,00
		Oxygenate	0,50	0,30	0,00
Redidue/Wax	C_{22+}	Alkene	1,60	0,70	0,00
		Alkane	0,40	49,2	44,6
		Aromatic	0,70	0,00	0,00
		Oxygenate	0,20	0,00	0,00
Aqueous product	C_1-C_5	Alcohol	4,50	3,90	1,40
		Carbonyl	3,90	0,00	0,00
		Carboxylic Acid	1,30	0,30	0,20

Within each syncrude type, there is variation caused by reactor technology, operation, catalyst, and catalyst deactivation. In this respect, syncrude is analogous to crude oil, where the composition of a specific crude oil may vary not only between sources but also within a source between locations and with time.

It is pointed out that the analogy with the crude oil is limited to the above consideration. In fact, in the same token of the crude oil, the selection of the feedstock and the syncrude production technology is addressed to yield a syncrude that provides the most feed material to refine the desired product slate. Indeed, it is only by a refining step that the syncrude can be turned into saleable liquid fuel.

It is noteworthy noticing that the diesel produced in a X-TL plant is superior to conventionally refined diesel: it is sulfur free, almost completely paraffinic, and with acceptable high cetane rating. Recent efforts to improve the Fischer-Tropsch process tend to focus on increasing selectivity for the diesel fraction and minimizing the naphtha fraction. With certain modifications and modest post-processing, the Fischer-Tropsch process can currently claim selectivity for the diesel fraction with the distribution of the hydrocarbon fraction as diesel (kerosene) 75% v/v, naphtha (gasoline) 20% v/v, and LPG 5% v/v.

High-temperature circulating fluidized-bed reactors (*Synthol* reactors) have been developed for gasoline and light olefin production, and these reactors operate at 350 °C and up to 2.8 MPa. Branched paraffin series like iso-octane cannot be directly produced in Fischer-Tropsch synthesis, thus any gasoline produced is low in octane rating (<85). Consequently, when Fisher-Tropsch synthesis has been used to produce gasoline, it has been blended with conventionally refined petroleum to achieve the desired octane number.

8. FT Reactors and Operation Conditions

Currently four FT reactors are used commercially. These reactors can be categorized into: i) Multitubular Fixed bed reactor; ii) Slurry Reactor; and iii) Fluidized bed reactor.

The fixed-bed tubular reactor (aka ARGE reactor) is one of the most competitive reactor technologies and it occupies a special position in FTS industrial practices, as exemplified by the large-scale commercial operations of Sasol and Shell. ARGE reactors were first commissioned at Sasol I in 1955. The original reactors consisted of a shell containing 2050 tubes, 12 m long, 5 cm in diameter, packed with an iron based catalyst. Sasol also designed a 5000 tube fixed-bed reactor that was not eventually used following the development of a more efficient slurry bed reactor.

Fixed bed reactors (see Figure 7 a) operate at a temperature of about 220 °C and reactor pressures in the range 25÷45 bar g. Heat removal from the FT process is achieved by the boiling water in the shell side of the reaction and rising steam at high pressure. However, this heat removal finds a limitation in the axial and radial temperature profiles in the tubes.

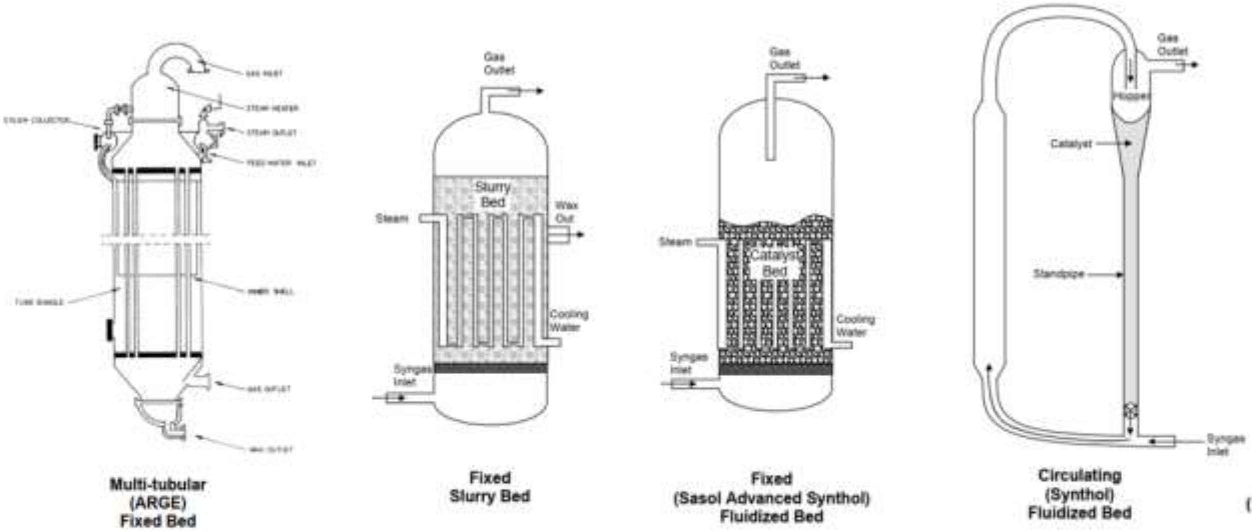


Figure 7 - Fischer-Tropsch Reactors. *Source: Berkshire, Energy Laboratory, LLC*

Typical industrial FT processes with fixed-bed reactors normally produce complex mixtures consisting of hydrocarbons ranging from methane to wax. For reducing pressure drop and facilitating heat removal, catalyst particles of a few millimeters in size are generally needed to be used in fixed-bed reactors, contributing to intra-particle pore-diffusion limitations. As a result of diffusion limitations and capillary condensation, the catalyst pores are often filled with a stagnant phase formed by the heavy waxy products. The major problems associated with fixed bed reactors are that they are expensive to assemble and they do not readily permit on-line catalyst replacement which may be necessitated by catalyst poisoning. The latter results in long shut-down compromising the overall plant availability.

In this reactor design the synthesis gas flows downward though the tubes and exit the reactor through the bottom outlet nozzle. The heat of reaction is being removed from the reaction environment by boiling water at high pressure in the shell. Therefore, the reactor temperature (250°C), which a fundamental process parameter, is controlled by controlling the pressure of the steam exiting the steam drum of the reactor assembly.

In Slurry reactors the catalyst is suspended as small particles in the liquid reaction media and moves around together with the reaction components. Currently this type of reactor is preferred over the multitubular fixed bed reactor in the low temperature Fischer Tropsch (LTFT) processes because it offer better temperature control and higher conversion. Belonging to the slurry reactor category is the *Sasol slurry phase distillate reactor*, which gained the most market favor for commercial production of synthesis fuels.

The idea of a slurry bed reactor (Figure 7) was first tried out during the Second World War and up to the late 1970's by Kölbel and co-workers[4]. Sasol's involvement in the development of slurry reactors dates back to the early 1980's, even though it was on a small scale.

A commercial-scale slurry reactor (5 m diameter, 22 m high) was commissioned in May 1993 at Sasol and this reactor has been operated successfully since that time. In these three-phase reactors syngas is distributed from the bottom and it rises through the slurry that consists of a high thermal capacity liquid (predominantly the FT wax product), with the catalyst particles suspended in it. As the FT synthesis proceeds in the reactor, the heavy hydrocarbon products form part of the slurry phase while the lighter gaseous products and water diffuse through the gas bubbles and then to the gas outlet.

Unlike tubular fixed bed reactors which have a tendency of developing hot-spots in the catalyst bed, hot-spots are non-existent in slurry systems because of the churning nature of the slurry and controlled slurry mixing. As a consequence, the slurry phase is sufficiently well mixed to give isothermal operation, giving a different perspective to temperature control in the highly exothermic FT system. The heat transfer coefficient for the cooling surfaces in a slurry phase reactor are five times higher than those for fixed bed reactors. Furthermore, the average synthesis temperature can be higher than that used in a tubular reactor without the risk of catalyst degradation. Higher reactor temperatures lead to higher CO conversions to products.

The advantages of slurry over multitubular reactors are as follows:

- The cost of a reactor train is only 25% of that of a multitubular system
- The differential pressure over the reactor is about four times lower which results in lower gas compression costs
- The lower catalyst loading translates to a four-fold lower catalyst consumption per ton of product
- The slurry bed is more isothermal and so can operate at a higher average temperature resulting in higher conversions
- On-line removal/addition of catalyst allows longer reactor runs.

Fluidized reactors consist of two phases (gas and solid) and they can either have a fixed or a circulating bed. The distinguishing feature between the two types of reactors is that in the fixed fluidized bed reactor (FFD) the catalyst bed remains stationary and the gases pass upward through the bed (Figure 7c) while in the circulating fluidized bed reactor (CFB) the catalyst is entrained in the fast moving gas stream (Figure 7d).

A commercial plant utilizing FFD reactor technology was erected in Brownsville, Texas, by Carthage Hydrocol in the 1950's. This reactor was 18 m high and 4 m in diameter with a nominal capacity of 180,000 tons per year. It operated at 300 °C and 2 MPa. In this type of reactor, the reaction heat is removed by vertical bundles of cooling tubes submersed in the bed.

In a CFB system a fine catalyst bed (between 40 and 150 mm diameter) is entrained by a high velocity (1÷2 m/s) gas stream through a riser reactor. In this latter design, catalyst moves down a standpipe in dense phase while it is transported up the "reaction" zone in lean phase. To avoid the feed gas going up the standpipe, the differential pressure over the standpipe must always exceed that over the reaction zone.

At high operating temperature carbon is deposited on the iron-based catalysts and this lowers the bulk density of the catalyst and thus the differential pressure over the standpipe. In this scenario it becomes more difficult to raise the catalyst loading in the reaction section in order to compensate for the normal decline of catalyst activity with time-on-stream.

The catalyst is separated from the effluent by cyclones and is then returned to the reactor inlet.

Two cooling zones in the riser are used for removing the reaction heat. The improved version of this CFB reactor was named as *Synthol reactor* at Sasol.

The main disadvantage of the two fluidized bed reactors is that should any poison enter the reactor the entire catalyst bed is poisoned whereas in the fixed bed tubular reactor, the poison is adsorbed preferentially on the top layer of the catalyst leaving the rest of the bed intact.

The FFB reactor shows several advantages over CFB reactors, more specifically:

- The construction cost is 40% lower. For the same capacity the FFB reactor is much smaller
- Because of the wider reaction section more cooling coils can be installed increasing the reactor production capacity (more fresh gas can be fed by either increasing the volumetric flow or by increasing operating pressure. Pressures up to 4MPa are feasible.)
- At any moment, all of the catalyst participates in the reaction, whereas in the CFB only a portion of it does.
- For the reasons previously discussed the lowering of the bulk density by carbon deposition is of less significance in the FFB and thus a lower rate of on-line catalyst removal and replacement with fresh catalyst is required to maintain high conversions. This lowers the overall catalyst consumption.
- Because the iron carbide catalyst is very abrasive and the gas/catalyst linear velocities in the narrower sections of the CFB reactors is very high these sections are ceramic lined and regular maintenance is required. This problem is absent in the lower linear velocities FFB reactors and this allows longer on-stream times between maintenance inspections.

In fact, from 1995 to 1999, the Sasol's 16 CFB at Secunda were replaced by eight FFB reactors (Sasol Advanced Synthol reactor).

Eventually it is emphasized that should any catalyst poison such has H_2S enter the reactor all of the catalyst is deactivated, whether FFB or CFB. Whereas in a fixed bed reactor all the H_2S is adsorbed by the top layers of catalyst, leaving the balance of the bed essentially unscathed.

Recent FT commercial reactor development

Microchannel Reactors Recent has recently been developed by Velocys plc (USA). These reactors consist of a large number of parallel channels with diameters below 1 mm and with the catalyst on a thin layer inside the channel walls constructed immediately adjacent to water-filled coolant channels.

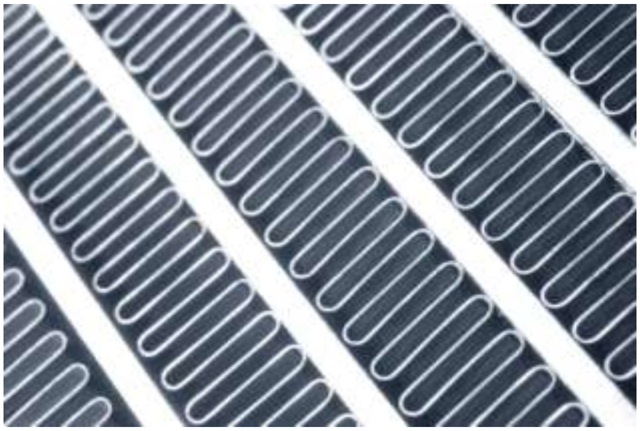


Figure 8 – Channels in an FT microchannel reactor*. Source: Velocys plc*

This design allows for isothermal operation even for highly exothermic reactions and improves mass and heat transfer, compared with conventional fixed-bed reactors. Allegedly, in the microchannel reactor, the catalyst is submitted to a uniform temperature profile due to a high heat transfer coefficient between the bed and wall, large transfer surface area, and short transfer distance in the microchannel. Even at a GHSV of 60,000 h^{-1} and temperature of 230 °C, the temperature gradient of the reactor remained in a narrow range. Also, the microchannel reactor seems to offers the best catalyst utilization and thus a high productivity. The main challenges of this reactor type are the difficulty in changing the catalyst and the significant investment required (almost no scale-up advantage regarding costs because for scaling up several microchannel reactors have to be operated in parallel). Therefore, the Velocys' microchannel FT technology is commercially viable at capacities up to 1,400 bpd.

Currently only few small Velocys FT processes have been implemented in USA.

The following Table 6 summarizes the main features of the Fischer Tropsch reactors.

Table 6 - Main characteristic of the FT reactor type[6]

Description	Fixed bed		Slurry Bed	Fluidized bed	
	Multitubular	**Microchannel**		**Fixed fluidized**	**Circulating**
Nature of Reactor	PFR	PFR	CSTR	CSTR	CSTR
Reaction phase	g or (g+l)	g or (g+l)	(g+l)	(g+l)	(g+l)
Catalyst particles sixe (mm)	>2	< 0,1	< 0,1	< 0,1	< 0,1
Mass transfer limitation	High	Low	Medium	Medium-low	Medium-low
Heat transfer limitation	High	Low	Low	Medium-low	Medium-low
On-line catalyst replacement	No	No	Possible	Possible	Possible
Catalyst mechanical strenght	Low	Low	Medium	High	High
Catalyst-product separation	Easy	Easy	Difficult	Fearly easy	Fearly easy
Scale-up risk (lab to plant)	Low	Low	Medium	Medium	Medium
Scale-up economy of scale	Medium-low	Low	High	Very High	High
Feed poisoning	Local	Low	Global	Global	Global
Feed turn down limitation	none	None	Catalyst Settling	Defluidization	Defluidization

9. FT Product refining

In the previous section it has been shown that the Fischer-Tropsch synthesis is a nonselective process. Indeed, the FT effluent reactor is a mixture containing alkanes and olefins with a very broad composition, oxygen-containing species, mostly alcohols, carbonyl compounds, acids, and esters. Moreover, most hydrocarbon produced are linear with only a small amount of branched hydrocarbons. Thus, these products, for being used as transportation fuel, require further treatment in the refining section of the facility.

The composition of a FT product depends on the operating conditions, the catalyst used and the design of the FT reactor. When fluidized bed reactor operating at relatively high temperature and iron-based catalyst is selected, α-olefins are the prevailing component of the FT-reactor effluent. The olefin content of the C_3, C_5÷C_{12} and C_{13}÷C_{18} cuts are typically 85, 70 and 60%, respectively.

Ethylene goes to the production of polyethylene, polyvinylchloride, etc. and propylene to polypropylene, acrylonitrile, etc. The extracted and purified C_5÷C_8 linear α-olefins are used as co-monomers in polyethylene production. The longer chain olefins can be converted to linear alcohols by hydroformylation. The alcohols are used in the production of biodegradable detergents.

By contrast, the LTFT processes produce predominantly longer chain linear paraffins. Since the objective of the Glamour project is the production of jet-fuel and marine bunkering fuels, only the treatment and separation of the paraffins will be described afterwards as these are suitable for producing liquid transportation fuels.

The FT-reactor effluent can be upgraded by means of a two stage recycle hydrocraking process, which consists in a mild hydrotreating combined with and hydrocraking (Figure 9)

In the hydrotreating reactor, oxygen, as well as nitrogen and sulfur, are removed[7]. In the same time olefins and aromatics become saturated, hence preventing secondary reactions (such as polymerization) which lead to catalyst deactivation in the following hydrocraking reactor.

Furthermore, phenolic constituents are completely deoxygenate depending on the severity of the operation, and some cracking takes also place in the first stage. Typical catalysts are sulfided CoMo or NiMo supported on alumina or aluminosilicates.

Ketones and aldehydes can be hydrogenated to alcohols under mild conditions over Raney nickel catalyst. After mild hydrotreatment, the linear oils and various grades of linear waxes may be sold at high prices.

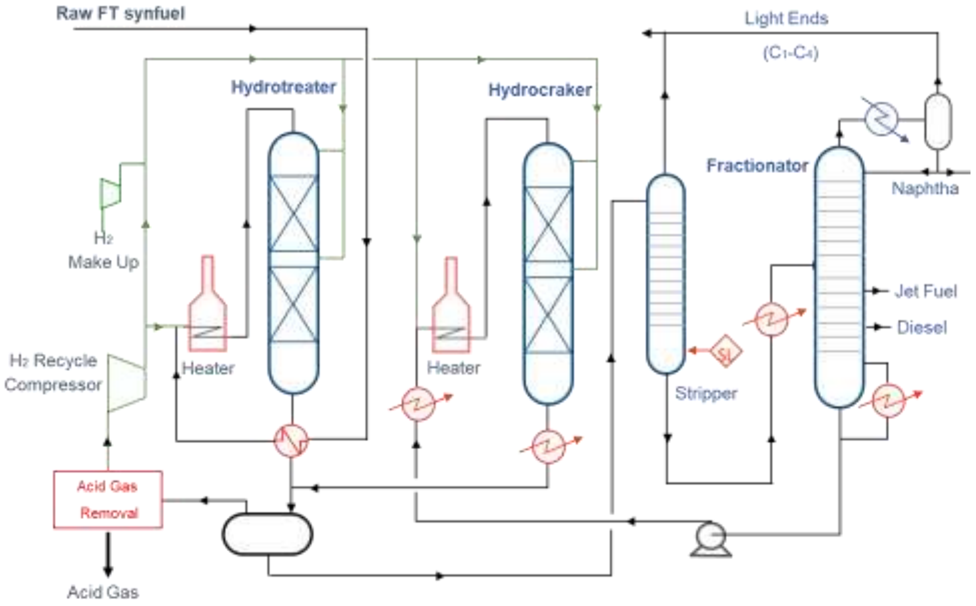


Figure 9 - Simplified two stage recycled hydrocraker process scheme

The effluent from the first stage is fractionated in a common refinery separation unit, with the unconverted oil going to the second stage – the catalytic hydrocracker operating at more severe conditions relative to the mild hydrotreatment reactor. The unconverted oil from the second stage reaction section goes back to the common fractionator

Catalytic hydrocracking accomplishes deoxygenating through simultaneous dehydration, decarboxylation, and decarbonylation reactions occurring in the presence of zeolite catalysts.

The second reactor operates at greater severity than the first; it uses higher temperatures and/or lower space velocities to achieve low levels of oxygen (<1% w/w). Since the catalyst in the second stage will be operating in near absence of ammonia, and depending on the particular design, in the absence of hydrogen sulfide it allows the use of either noble metal or base metal sulfide hydrocracking catalysts.

The process is typically high pressure and moderate temperature (up to 400 °C) and produces a naphtha-like product that requires orthodox refining to derive conventional transport fuel. Typically, a part of this naphtha stream is converted by isomerization from normal paraffins to isoparaffins to boost the gasoline blendstock octane value. The other fraction of the naphtha is catalytically reformed to provide some aromatic content to (and further boost the octane value of) the final gasoline blendstock.

10. General FT process set up

The FT process is a series of catalyzed chemical reactions that convert a mixture of CO and H_2 (syngas) into hydrocarbon derivatives. Since the conversion of said reactants into liquid synfuels is not complete, the outlet of a FT reactor is a mixture of unconverted gas, light gases, and the syncrude produced by the conversion of the syngas.

The quantity of unconverted syngas and light gases (collectively defined as *tailgas*) depends on the per pass conversion, which affects the syngas conditioning requirement as well. When the per pass conversion is low, it is not so much important to adjust the syngas composition to match the usage ratio as the H_2:CO ratio at the reactor outlet does not change significantly with the CO conversion. The importance of providing conditioned syngas close to the usage ratio increases as the CO conversion increases. Thus at high conversion, the feed composition becomes important as it affects the product selectivity and the kinetic of the FT reaction.

The condensable species contained in the tail gas can be recovered by cooling and phase separation in the refining front end. At 45°C both propane and butane can be recovered at a pressure around 20 barg. C_1-C_2, which may be exported as *synthetic natural gas*, can be recovered by means of a cryogenic separation. After cooling and separation the exhausted tail gas can be used somewhere else (as fuel or in a combined cycle power generation system) or recycled to the FT synthesis. In the former case the process is configured as an open loop design – which involves a once-through flow of the syngas - in the latter as a closed loop design.

The open loop configuration may be considered when:

- the syngas is produced by air blow gasification or autothermal reforming. In such a case often the design may consider one or more FT reactor in series with intermediate product recovery
- the FT plant is integrated with an electricity generation system
- the per pass conversion is high.

The closed loop design can be either internal recycle or external recycle. In the internal recycle, the FT reactor effluent is cooled down, the condensed liquid phase separated and the gas phase recycled directly to the FT synthesis without any further treatment. On the contrary, in the external recycle the tail gas is kicked back in the FT synthesis after having submitted to one or more separation step, reformed in a steam reformer or in a autothermal reformer where the methane and the heavies are converted back into syngas.

It should bear in mind that the closed loop design requires a purge gas stream in order to avoid the buildup of inert species in the recycle loop. The loss of the valuable syngas contained in the purge gas, hydrogen can be recovered passing the purge through a pressure swing adsorber.

In principle the syngas can be produced from any carbonaceous feedstock including bio-mass, natural gas, naphtha, Tar, and coal. Varied feedstock entails varied process set ups. Nonetheless, a general process scheme can be spotlighted regardless the feedstock used to generate the syngas.

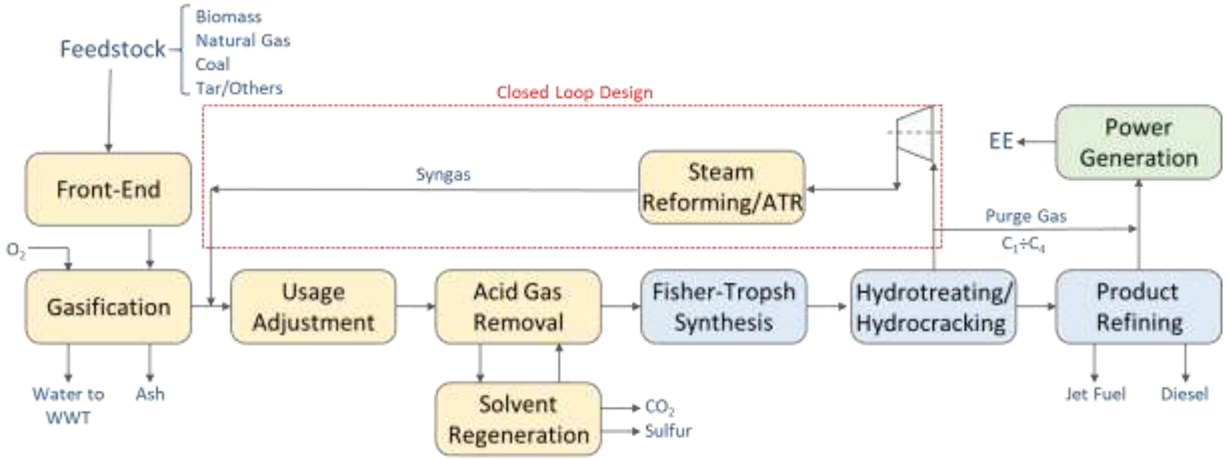


Figure 10 - General Process Lay-out of a Synthetic Liquid Fuel Production complex

Figure 10 is a simplified generic process block diagram representing the foundational manufacturing steps leading to the production of synthetic liquid fuel for the transportation sector. The feedstock is first pre-treated in the front end section, then is gasified in oxygen (air) and steam, with subsequent gas conditioning that includes waste heat recovery, cleaning of the raw syngas and in some cases adjusting, by water gas shift reaction, the composition of the syngas in preparation for downstream synthesis of Fischer-Tropsch liquids (FTL).

Prior to synthesis, CO_2 and sulfur compounds are removed in the acid gas removal step. The CO_2 may be vented or captured and stored underground, while sulfur is recovered as liquid or granulated and sold out. Since the syngas conversion is not complete, the unreacted can be recycled for additional conversion. The light ends ($C_1 \div C_4$) from the FT products separation and treatment section can be converted again into syngas by means of a steam reformer or an autothermal reformer and recycled back along with the unreacted syngas.

Alternatively, these light components can be used to generate electric power for export to grid after meeting inside power needs; or part of them recycled back for further conversion in synthetic fuel and the remaining part used for power generation.

Following the FT-synthesis, the crude FTL product (syncrude) is refined products.

PART II

SYNTHESIS GAS PREPARATION

11. Syngas generation

In the Part I it has been seen that the FT consists of three main steps. The first is the conversion of feedstock to synthesis gas (a mixture of CO and H_2), the second step is the FT synthesis which converts the syngas to waxy hydrocarbons, and the third step is synfuel upgrading which converts the waxy hydrocarbons into petroleum products analogues: naphtha and sulfur free diesel.

Therefore, the syngas generation is a fundamental step in synthetic liquid fuels production, and it is the costliest stage and the more energy-intensive of the production chain. Indeed, the syngas generation section of an FT complex represents 50÷60% of the total cost (hence, this is the stage which requires further development, even in a well-established process in order to reduce capital expenditure), while FT conversion accounts for around 25% and product upgrading accounts for 15÷25% of the total cost.

The synthesis gas can be manufactured by:

- Pyrolysis, in which carbonaceous materials are gasified by heat in the absence of oxidants.
- Partial oxidation. This is a thermochemical process wherein a gas, a liquid, or a solid carbon-containing feedstock (biomass, coal, heavy oil, refinery residues etc.) is converted into a gas mixture containing H_2, CO, CO_2 and water in the presence of oxidants (air, pure/enriched air, or oxygen) without combustion[8].
- Steam reforming, a catalytic process that converts liquid hydrocarbon (naphtha) or natural gas into syngas. The autothermal reforming (ATR) is a particular steam reformer that combines a partial oxidation process with a traditional steam reformer).

11.1 Syngas from biomass

In principle a biomass is carbon neutral feedstock. Indeed, it uses the sun's energy to absorb the same amount of carbon from the atmosphere as it releases into the atmosphere. The main sources of biomasses include:

- wood, including sawdust, wood chips, wood pellets, bark, logs, and briquettes
- high-yield energy crops, such as wheat grown specifically for energy applications
- agricultural crops and residues (e.g., straw)
- wood pulp or paper pulp, and other industrial wastes.

The presence of high levels of moisture in biomass reduces the temperature inside the gasifier, which in turn reduces the efficiency of the gasifier performance. Many biomass gasification technologies therefore require the moisture content be reduced prior to feeding into the gasifier process. The moisture reduction is typically achieved in a *torrefaction* process in which, in absence of oxygen, the biomass is heated at 250÷300°C. In addition, since biomasses can come in a range of sizes, they may require to be processed to a uniform size or shape before being fed into the gasifier.

In the gasification process, the biomass feedstock is first dried and size reduced to yield particles of uniform size, with a moisture content no higher than 15%[9]for optimal results. The pretreated biomass is sent to the gasifier, where it is mixed - generally under pressure - with oxygen and water. Part of the biomass fed to the gasifier is burned to generate the heat necessary for the gasification process. Part of the heat released by the combustion can be used to dry the plant feedstock before the gasification. The produced flue gas (CO_2 and H_2O) also react with the rest of the biomass to produce CO and H_2. In doing this, no external heat is necessary.

Since the production of syngas from biomasses in a single-step operation by partial oxidation is troublesome, their gasification is generally accomplished in two steps. In the first stage the dried biomass is gasified in a pyrolysis (aka *destructive distillation*) process where it is heated to 400÷600°C in an atmosphere too deficient of oxygen to allow complete combustion. The pyrolysis gas contains H_2, CO, CO_2, H_2O, CH_4, and volatile tar; the residue, which is about 25% of the original fuel mass, is charcoal. In the second stage of gasification, charcoal is let react with oxygen at 1300÷1500°C to produce CO.

Before being sent to the downstream process, the produced syngas has to be purified, in particular, tar has to be removed as it is a source of operational troubles. Indeed, tar is composed mainly by oxygenated compound and higher molecular weight hydrocarbons. These species condense in pipes and equipment leading to flow restriction, blockage, clogging, and other operational difficulties.

Moreover, the quantity of biomass needed to feed an industrial-scale plant would be very large and the biomass would have to be collected from vast areas. However, transporting bulky biomass product with relatively low energy density – about one-tenths that of liquid hydrocarbons - over long distance is in most cases not economical. To keep these costs at reasonably level, small/medium scale plants have to be operated in the center of biomass collecting areas with limited range: 50÷100 km. In recent development, the gasification economics might significantly be enhanced by processing biomass into biocrude, a black liquid intermediate much easier to store and to transport, in small *fast pyrolysis* (*flash pyrolysis*) plants (Figure 11).

In fast pyrolysis, the biomass is swiftly heated up to 400÷600 °C at atmospheric pressure to yield oxygenated hydrocarbon gases. The produced gas is then immediately quenched to avoid their decomposition by cracking. The product of the fast pyrolysis is a black liquor that resemble crude oil.

The fast pyrolysis also originates combustible gas and char, part of which can be finely ground and added to the biocrude to form a slurry. This slurry can be handled, transported in much the same way as crude oil today, facilitating greatly the handling of biomass feedstock; thereafter the biocrude can be gasified in a centralized unit.

Although this technology still need of further development, it holds promise as a domestically available synfuel alternative to petroleum. The concept of decentralized production of biocrude produced by fast pyrolysis has been implemented in the Bioliq process developed by Karlsrubhe Institute of Technology[10].

The process chain of this pilot project include: fast pyrolysis for pretreatment of biomass to obtain an energy dense, liquid intermediate fuel; high-pressure entrained flow gasification providing low methane synthesis gas free of tar; hot synthesis gas cleaning to separate acid gases, and contaminants as well as methanol/dimethyl ether; and gasoline synthesis. First production of synthetic fuel was successfully achieved in 2014.

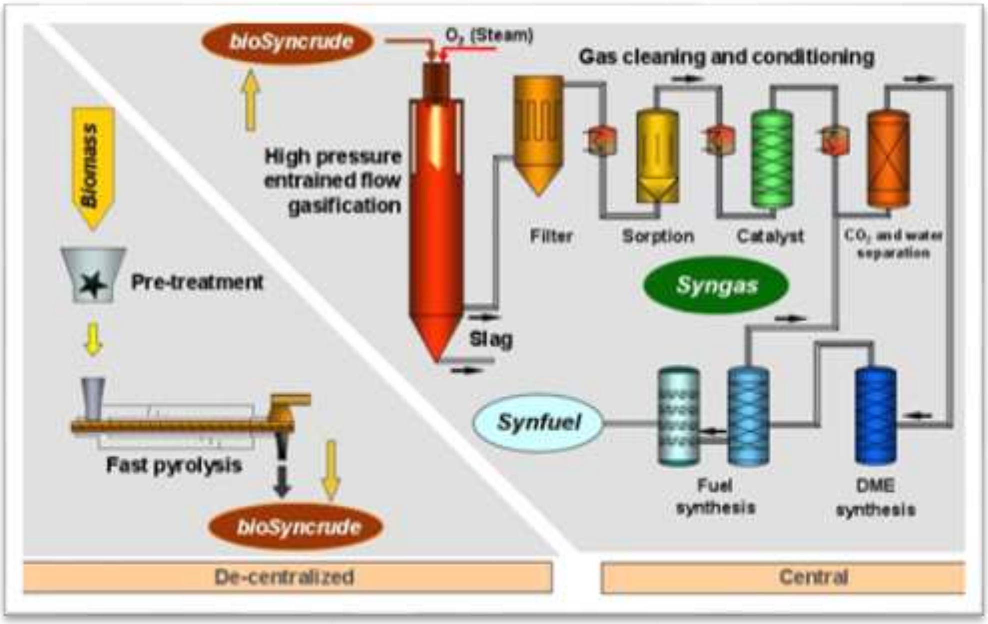


Figure 11 – Decentralized Biomass Gasification Model[10]

Glycerin, a byproduct of biodiesel production included as part of biomass category, was used to produced methanol in the BioMCN large scale BTL in Netherland. However due to some economical and technical reasons, the production using syngas obtained by reforming glycerin was discontinued in 2013, and the bio-methanol produced at the site is now based on biogas.

Gasification of biomass produce a syngas mixture with a low H_2/CO ratio (ranging from 0,45 to 1,5) [8] and a high CO_2/CO ratio. For FT synthesis, the hydrogen to carbon ratio should be close to

2:1. To adjust the ratio, part of the CO_2 has to be separated after gasification.

In most cases, the separated CO_2 has to be vented to the atmosphere, or preferably used for some other process.

An attractive option to dispose of CO_2 is to react the excess CO_2 with CH_4 in a steam reformer and using the high H_2/CO syngas from the reformer to adjust the ratio of the syngas produced by gasification just by blending the two syngas[11]. Alternatively, the excess CO_2 can be reacted with the hydrogen produced by renewables: solar energy, wind etc., to increase the overall yield of synfuel from biomass.

Since biomass could be regarded as "young coal", coal gasification can be taken as the reference technology. For coal gasification the minimum temperature required is about 900°C. Indeed, in the old water-gas process the temperature was allowed to drop from 1300°C to 900°C. To gasify the most refractory part of almost any biomass a temperature range of 800÷900°C is required; this temperature range is comparable with coal gasification. Moreover, the relatively high temperature in combination with the adverse effects on the gasifier materials of impurities - whether sulfur or ash components – keeps indirect heating through a metal surface away from commercial operations.

On the other hand, there are a number of significant differences between coal gasification and biomass gasification, which are directly attributable to the nature of the feedstock. For one, the biomass ash. It has a comparatively low melting point; however, in the molten state the biomass ash is very aggressive. Secondly, biomass has fibrous characteristic, and tar production is particularly high at low temperature range.

Although an entrained-flow process might have an apparent attraction in being able to generate a clean, tar free gas, and the low melting point of the ash would keep the oxidant demand low, the aggressive quality of the molten slag speaks against such a solution, whether using a refractory or a cooling membrane for containment protection. Furthermore, the short residence time of entrained-flow reactors require a small particle size to ensure full gasification of the char. No method of size reduction has yet been found, which will perform satisfactorily on fibrous biomass.

A number of fixed-bed process have been applied to lump wood, but they are limited to this material. They would not work on straw, miscanthus or other materials generally considered for large-scale biomass production unless these were previously bricketted. Furthermore, in a counter-flow gasifier, the gas would be heavily laden with tar. The alternative of co-current flow could reduce the tar problem substantially, but the necessity to maintain good control over the blast distribution in the bed restricts this solution to unit of very small size. With this background it is probably not surprising that most processes for biomass gasification use fluid beds and aim at finding a solution to the tar problem outside the gasifier. In co-firing applications where the syngas is fired in an associated large-scale fossil fuel boiler, the problem can be circumvented by maintaining the gas at a temperature above the dew point of tar. This has the added advantage of bringing the heating value of the tar and the sensible heat of the hot gas into the boiler.

There are many biomass processes at various stages of development. The selection chosen here represents generally those that have reached some degree of commercialization.

To wrap up, the complex structure of biomass makes it more difficult to gasify. As a result, several types of gasifier took hold. The Table 1 provides a list of the most known gasification processes.

Biomass available for gasification include charcoal, wood and wood waste (branches, twigs, roots, bark, wood-shavings and sawdust) as well as a multitude of agricultural residues (maize cobs, coconut shells, coconut husks, cereal straws, rice husks, etc.) and peat.

Because those fuels differ greatly in their chemical, physical and morphological properties, they make different demands on the method of gasification and consequently require different reactor designs or even gasification technologies. It is for this reason that, during a century of gasification experience, a large number of different gasifiers has been developed and marketed, all types geared towards handling the specific properties of a typical feedstock.

Table 7 Commercial Gasification Processes[9]

Fixed-Bed Processes	Foster Wheeler stoic process Lurgi process Wellman Galusha process Woodall-Duckham process
Fluidized-Bed Processes	Agglomerating Burner process Carbon Dioxide Acceptor process Coalcon process COED/COGAS process Exxon catalytic gasification process Hydrane process Hygas process Pressurized fluid-bed process Synthane process U-gas process Winkler process
Entrained-Bed Processes	Bi-gas process Combustion engineering process Koppers-Totzek process Texaco process

Molten Salt Processes	Atgas process Pullman-Kellogg process Rockgas process Rummel single-shaft process

The range of designs includes up-draught, downdraught, cross-draught, fluidized bed as well as other biomass gasification systems of less importance. All systems show relative advantages and disadvantages with respect to biomass type and applications. For this reason, each will have its own technical and/or economic advantages in a particular set of circumstances. By and large, four types of gasifier configurations are currently available for commercial use:

- fixed-bed gasifier, which is subdivided into the countercurrent fixed-bed gasifier and the co-current fixed-bed gasifier
- fluid-bed gasifier
- entrained-flow gasifier
- processes involving the use of molten salt(s) or molten metal(s).

It worth mentioning that, each type of gasifier may be designed to operate either at atmospheric pressure or at high pressure. In the latter type of operation, the reactor size may be reduced. High-pressure systems may have problems associated with the introduction of the feedstock into the reactor. Furthermore, low pressure or atmospheric pressure gasification reactors are frequently designed with a syngas compressor located after the gas clean-up processes.

Before choosing a gasifier for any individual feedstock, it is important to ensure that the biomass meets the requirements of the gasifier or that it can be treated to meet these requirements.

The quantity and quality of the gas generated in a gasification reactor is influenced not only by the feedstock characteristics but also predominantly by the gasifier type and configuration, as well as by the amount of air, oxygen, or steam introduced into the system, which, in turn also sway the gasifier configuration. The nitrogen and sulfur in a gasification process has environmental consequences. Instead of being converted to the respective oxides, the biomass-bound nitrogen is predominantly converted to molecular nitrogen and hydrogen cyanide while the sulfur turns into hydrogen sulfide and carbonyl sulfide.

The major chemical reactions taking place into a gasifier break and oxidize hydrocarbons to give a product gas of carbon monoxide, carbon dioxide, hydrogen, and water. Other important components include hydrogen sulfide, various organic compounds of sulfur and carbon, ammonia, low molecular weight hydrocarbons, and tar. This latter is one of the main barriers for the application of biomass gasification at industrial scale as it may cause severe problems for downstream equipment. Indeed, it is the condensable fractions of the organic gasification products that largely consists of a complex mixture of condensable hydrocarbons, such as single (benzene) to multiple ring aromatic compounds, other oxygen-containing hydrocarbons, and complex PAHs.

The removal of tar from the gasification gas is critical in biomass gasification in order to produce high quality gas fuel. It is thus necessary to recover the tar and to transform it in lighter combustible gas species such as CH_4, CO and H_2. Tar is typically converted by means of cracking (thermal or catalytic) or reforming processes, which decomposes tar products and high-boiling hydrocarbon products into hydrogen and carbon monoxide. Without this removal, tars and heavy hydrocarbons in the synthesis gas will condense, given rise to operational problems, as the synthesis gas is cooled in the downstream process equipment.

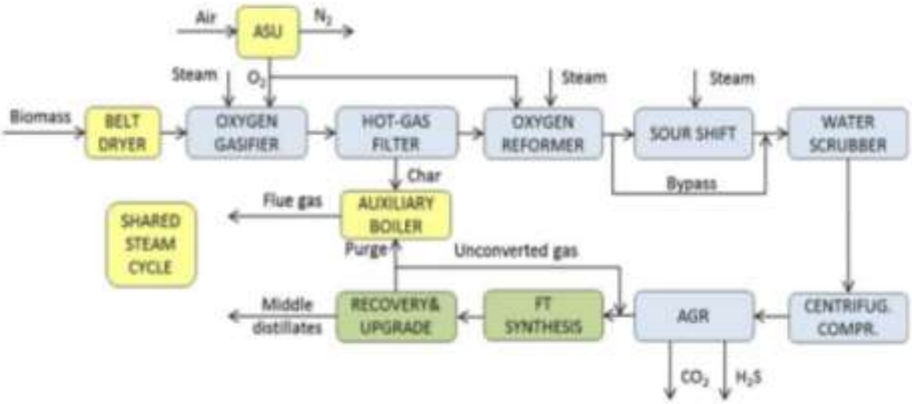


Figure 12 - Biomass to synfuel through Fischer Tropsch process

Thus, tar cracking or reforming technologies, which can be thermally driven and/or catalytically driven, are utilized to break down or decompose tar products and high-boiling hydrocarbon products into hydrogen and carbon monoxide. This reaction increases the hydrogen/carbon monoxide ratio of the syngas and reduces or eliminates tar condensation in downstream process equipment. Thermal tar reformer designs are typically fluid-bed or fixed-bed type. Catalytic tar reformers are filled with heated loose catalyst material or catalyst block material and can be fixed- or fluid-bed designs.

Figure 12 shows a general process diagram of a BTL-FT plant, which includes a pre-treatment section (size reduction, torrefaction), a gas cleaning section (particles filtration, tar reforming, water gas shift, etc.), and an acid gas removal followed by the FT synthesis. It closely recalls the general scheme of a coal-to-liquid process.

In the Glamour process, the syngas needed to produce FT-synfuel is produced in a sorption-enhanced reformer (*looping reforming*) of glycerin - a liquid biomass co-produced with biodiesel. As glycerin is a liquid by-product of an energy production facility, it does not need the pre-treatments described above, and the syngas originated by its gasification is a clean gas that does not need of a gas clean-up operation.

From the above characteristic of the biomass gasification, it can be concluded that the BTL-FT obtained from biomass gasification cannot be taken as the reference technology for Glamour.

As opposed to biomass gasification, the production of syngas through a looping reforming is analogue to the production of syngas from natural gas. Indeed, the natural gas used in GTL plant comes from midstream facility where the gas is purified ahead of being admitted in the gas pipeline network for transportation to end-users among which petrochemical facilities. Therefore, a GTL plants are less in need of cumbersome pre-treatment unit and gas clean-up downstream the gasification process. Moreover, the looping reforming is novel technology for gasification that overcome the thermodynamic limitation of conventional steam reforming, therefore **the benchmark for the Glamour project has to be sought among the natural gas gasification processes.**

The Table 8 reports the tabular description of the main characteristics of the various feedstock eligible for gasification for synthetic fuel production.

Table 8 – Relevant features of various feedstock in relation to glycerine.

	FEATURES	Carbon neutral	Waste / low cost feedstock	Feedstock transportation complexity	Pre-treatment requirements	**Sub-products / contaminants requiring specific treatment**	**Producing quality liquid fuels in the range of gasoline-diesel, ready for massive use**	Producing specific fuel gas for dedicated power generation	Producing liquid fuels for dedicated use (methanol, ethanol, ecc)	Integration with other processes with environmental advantage
FEEDSTOCK										
Glicerol (GLAMOUR)		**Yes**	**Yes**	**Yes (limited)**	**Yes**	**No**	**Yes**	Yes (*)	Yes (*)	**Yes** (with biofuel plants)
Biomass (wood, municipal waste, residue, ecc)		**Yes**	**Yes**	**Yes (ample)**	**Yes**	**Yes**	**Yes**	Yes	Yes	**Yes** (with relevant specific production processes)
Natural gas		**No**	**No**	**No**	**No**	**No**	**Yes**	No (not the purpose)	Yes (if necessary)	**Yes** (potential use of flare gas in case of combined reforming processes)
Coal		**No**	**No**	**Yes (ample)**	**Yes**	**Yes**	**Yes** (*)	Yes	Yes (*)	**No**
Heavy oils, refinery residues		**No**	**Yes**	**Yes (ample)**	**Yes**	**Yes**	**Yes** (*)	Yes	Yes (*)	**Yes** (in combination with refinery processes)

(*) Technical capability. Economics advantage apart, if applicable.

GREEN FEATURES: BONUS

RED FEATURES: MALUS

BLUE FEATURE: BENCHMARKING PARAMETER

11.2 Syngas from natural gas

In methane steam reforming (MSR), methane is reacted in a highly endothermic reaction with steam over a catalyst, typically based on Ni, at high temperature (800÷1000°C) and under pressure (20÷40 barg) to form CO and H_2. Part of the formed CO reacts thereafter with steam in the WGS reaction to yield more H_2 and CO_2. The overall result is a mixture of H_2, CO, and CO_2.

The most important reactions in *steam reforming(SR)* of methane are:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H° = 206$ kJ/mol (11.2.1)

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H° = -41$ kJ/mol (11.2.2)

$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ $\Delta H° = 247$ kJ/mol (11.2.3)

The reaction (11.2.2)is the *Water Gas Shift* reaction, the

(11.2.3)

is the *Dry Methane Reforming*[11] (DMR) because it can be used to produce a CO-rich syngas without steam as reactant.

The operation of a MSR can be affected by the thermal coking process. It involves the formation of carbon, which may deposit in the form of soot, whiskers, or coke on the catalyst as well as all the internal part of the reformer and downstream equipment, resulting in possible clogging.

Carbon may be formed by methane decomposition or CO disproportion (Boudouard reaction) according to:

$CH_4 \leftrightarrow C + 2H_2$ $\Delta H° = 75$ kJ/mol (11.2.4)

$2CO \leftrightarrow C + CO_2$ $\Delta H° = -173$ kJ/mol (11.2.5)

At temperatures above 650 ºC, also the higher hydrocarbons contained in natural gas may crack into coke. In MSR operating at high pressure and temperature higher than 950°C, the carbon deposition on the catalyst due to the heavy's is particularly dangerous because in the zones of the catalytic tubes where soot built up, the heat transferred through the catalytic tube walls is not absorbed by the steam reforming reaction (11.2.1)with hazardous superheating (*hot spot formation*) of the tubes materials. In this cases, an *adiabatic pre-reformer* has to be installed upstream a MSR so that the steam reformer of the heavy hydrocarbons:

$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2$ (11.2.6)

can takes place at a relatively low temperature without soot formation.

By and large, the undesired carbonation, or soot formation, is largely prevented by the use of excess steam, short residence time in the reactor, and by installing a pre-reformer upstream the primary reformer as a safeguard.

The pre-reformer is a just an adiabatic fixed catalytic bed accommodated in a pressure vessel.

The overall heat of reforming reactions depends upon the process conditions. At low steam/carbon (S/C) ratios, and at low catalyst exit temperatures, the overall reaction is only slightly endothermal or even exothermal, if the feed contains high concentrations of higher hydrocarbons. This is because the CO reacts back into CH_4 according to the reverse reaction of (11.2.1). In this case, the process may be carried out without external heating, as is the case of the adiabatic pre-reformer. However, when a syngas with a low methane (*low methane slip*) content is desired, a high reformer exit temperature is required and the overall heat of reaction will be endothermal, and external heat is required.

It is worth noting that the WGS reaction (11.2.2) is exothermic. Therefore, with increasing T the chemical equilibrium shifts to the left, and the residual CO_2 is increasingly consumed by the endothermal reforming reactions, which in turn, are favored by high T.

The methane reforming reactions (11.2.1) and (11.2.3) take place with increasing number of moles. Thus, a higher pressure shifts the steam reforming equilibrium towards the reactants. At 30 barg, a theoretically temperature of 1125°C is needed to reach the equilibrium in which only CO and H_2 exist. In practice, the maximum temperature used in industry for steam reforming is restricted to 1050°C due to reactor material constraints.

Since most syngas applications, such as methanol and ammonia synthesis, require high pressures, the syngas production is often performed at high pressure in order to both avoiding compression costs in the downstream unit and to take advantage from the gas volume reduction, which implies an overall reduction of the reformer capex. However, since the high pressure shifts the chemical equilibrium towards the reactants, a high temperature and excess steam is used to make up with the yield reduction due to the high pressure.

Steam reforming (tubular reforming)

At high temperature (T > 900 ºC) a steam reforming process is highly endothermic. Typically, it is operated at pressures between 15 and 40 bar over a Ni/Al_2O_3 catalyst.

The composition of the gas at the reactor outlet reflects the equilibria of reactions (11.2.1) and (11.2.2). In some cases, CO_2 is added to natural gas to improve the syngas yield and to decrease the H_2/CO ratio in the produced syngas - this is the case of the steam reformer of the 2200 t/day methanol plant in Bandar Imam (Iran), for example.

The CO_2 can be sourced from outside battery limits, or recycled from the acid gas removal unit located downstream the steam reformer.

In a MSR, two parts can be set apart: the convection section, where process streams are heated against the hot flue gas originated in the radiant section; and a radiant section, where heat is supplied to the chemical system (Figure 13) mainly by the radiation.

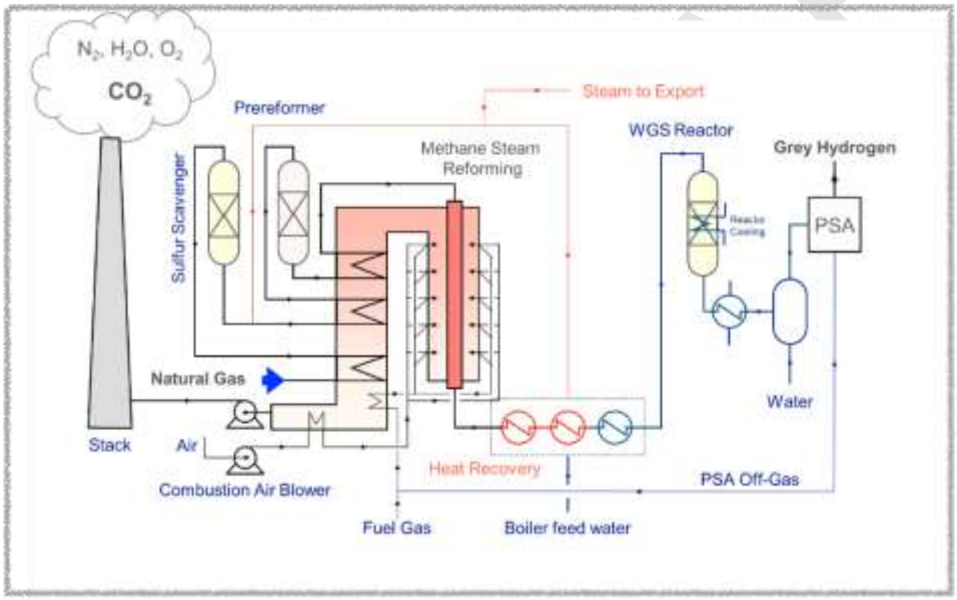


Figure 13 - Methane Steam Reforming Process Flow Diagram

The radiant section of the reformer is where the reforming reactions take place. It consists of a number catalytic tubes, made of high Cr and Ni alloy, arranged in rows in one or two fire boxes with burners placed at the bottom (KT), the top (Toyo), in terrace (Wood Group), or at several elevations in the side wall (Haldor Topsoe), as shown in Figure 14.

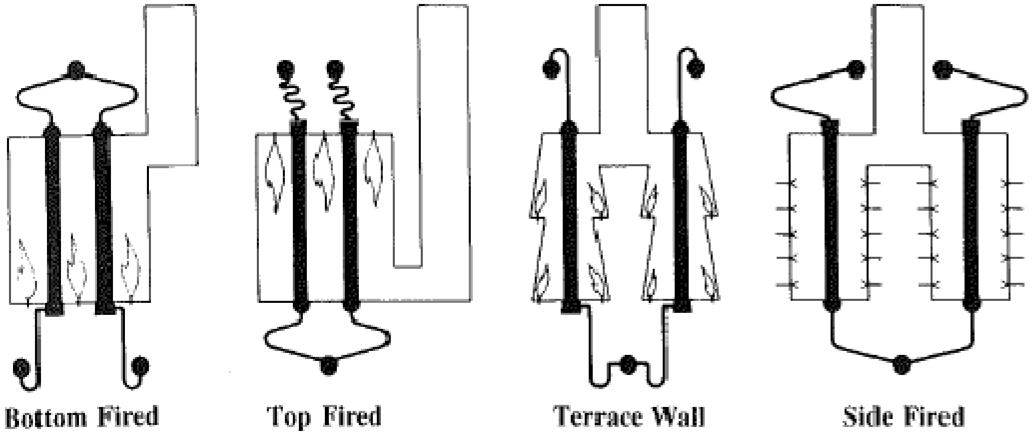


Figure 14 - Burners Arrangements in MSR[12]

A key issue in steam reforming design is the heat balance of the catalytic tubes, whereby the heat input through the tube must equals the heat absorbed by the endothermic reforming reaction. At the same time the maximum tube skin temperature - which is typically 100÷150°C higher than that of the reaction environment - has to be as low as possible in order to limit the mechanical stress on the tubes material. The side-fired reformer was conceived to solve this complex interrelation.

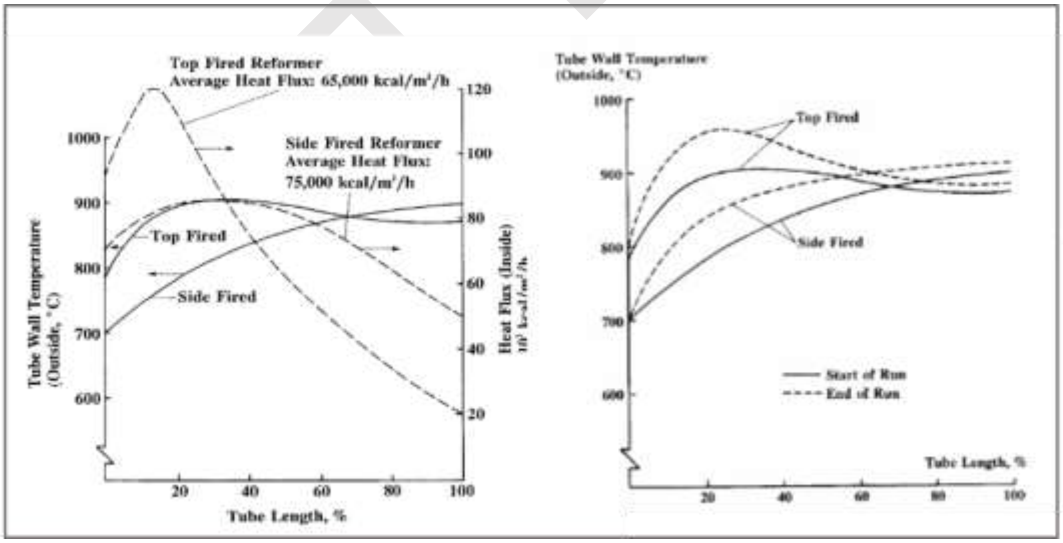


Figure 15 - Temperature and Heat Flux profile along MSR catalytic tubes[12]

In the side arrangement the burners are designed to direct the flames backward against the furnace wall in order to eliminate any risk of flame impingement against of the tubes - this impingement would lead to their rapid collapse. In this configuration, the heat flux along the tube axis's is comparatively smooth (Figure 15) and the temperature increases to the bottom. This enables the operation of the reformer at low steam to carbon ratio at high outlet temperature, and an average higher heat flux, with improved process performance.

In time catalyst deactivates losing its activity. The reduction of the catalyst activity results in a significant temperature increase in the top of the tube (right side of Figure 15). In case of a top-fired reformer; therefore, due to these effects, the reformer must be designed with a considerable margin above the maximum temperature at the start of the run. Moreover, the high temperature at the top also makes the carbon formation riskier. Indeed, carbon might form preferentially in the inlet of the steam reformer tubes at T above 650 ºC. It is worth mentioning that the addition of CO_2 to the feed gas reduces the risk of carbon formation.

As opposed to the top fire, also in the side-fired reformer the catalyst deactivation brings about an increasing temperature in the upper part; however, the temperature will still be highest in the lower end. Therefore, in this case, the reformer does not need to be designed for much higher temperatures than at the start of the run. Moreover, the short residence time of the flames in the side fired reformer ensures very low emissions of NO_x.

Top-fired reformers can have several parallel rows of tubes - while side-fired reformers only can have one row - and the heat is exchanged through both radiation and convection mechanism.

On the top, the tubes are supported by spring systems designed to keep them in traction in order to avoid the temperature induced creeping of the tubes material. On the bottom, the catalytic tubes connect with a refractory lined header by means of pigtail designed to absorb thermal expansion.

One furnace can contain 500÷600 tubes, made of exotic material, with inner diameters of 70÷130 mm and lengths from 7 to 12 m. The wall thickness of the tubes ranges from 10 to 20 mm. The reason why the catalytic tubes have small diameters is to enable the highest possible heat flux, and hence to achieve the highest possible capacity for a given amount of catalyst.

In the convection section air, natural gas and steam are preheated against the hot flue gas coming from the radiant section. Approximately 50 % of the heat released by the burners is transferred to the process. Most of the remaining part is recovered pre-heating the reactants, and superheating MP/HP steam. The overall thermal efficiency of the reformer may be as much as 95 %.

The temperature of the process gas exiting the steam reformer ranges from 800 to more than 1000 °C. The heat content of this stream is used to raise HP steam in a waste heat boiler (WHB) system located just downstream the steam reforming. Part of the produced HP steam is used as reactant for the steam reforming reactions and part of it is converted to electric power in the *steam balance section* of the plant.

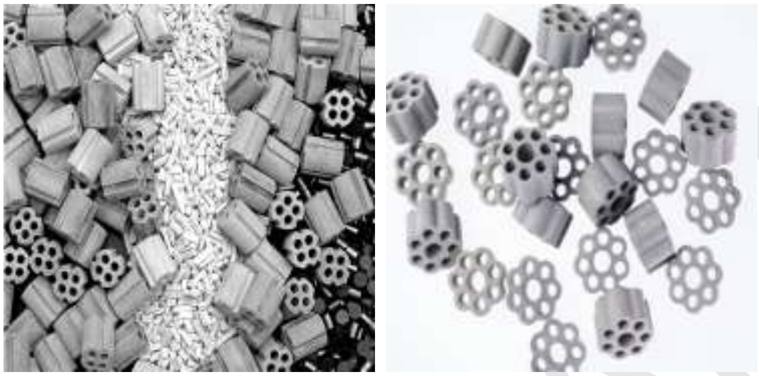


Figure 16 - MSR Catalysts: *Source: Johnson Mattey and Clariant*

The performance of the reforming catalyst is not only determined by its shape (and its resulting geometric surface area) but also by the resulting pressure drop in the reforming tubes. Therefore, the Ni based catalysts should feature high activity, good heat transfer, low carbon formation, high physical strength, and low pressure drop. Typically, they take the form of small shaped "drum" (16/4x8 mm) with 4 to 8 holes. Figure 16 shows two commercial catalysts for SMR (Johnson Mattey and Clariant).

Ni-catalysts for SMR are vulnerable to sulfur, which swiftly deactivates them. In the zones where the catalyst is poisoned, the heat flowing through the tubes wall is not absorbed by the endothermic reactions and dangerous hot spot forms. Therefore, before natural gas is admitted into the tubes, the level of sulfur in the feedstock has be scavenged in a desulfurization unit so that the residual sulfur content in feedstock is less than 0.2 mg/m^3.

Since the piped natural gas contains generally around 4 ppm of S, it is removed from the gas by means of the adsorption onto zinc-oxide absorption beds at 350÷400 ºC. These beds are typically arranged according to the lead-lag plant configuration. Besides hydrogen sulfides, ZnO also absorbs carbonyl sulfide and mercaptans. However, cyclic organic sulfur compounds such as thiophenes require hydrogenation to H_2S over Co-Mo or Ni-Mo catalysts. The formed H_2S is then adsorbed over the zinc-oxide bed. The hydrogenation catalyst is normally hosted in the ZnO pressure vessel.

The S/C ratio is among the process parameters used to counter to carbon deposition. The higher the S/C ratio, the lower the carbon formation, for this reason in industrial practice the steam/carbon ratio ranges from 2.5 to 4.5 depending upon the level of heavy hydrocarbon contained in the feedstock; rich natural gas and naphtha command high S/C.

A S/C ratio higher than stoichiometric, also helps to shift the steam reforming (11.2.1) equilibrium towards the products, and hence to increase the methane conversion.

The steam in excess to the stoichiometric ration parlays into additional operating cost. This cost can be reduced by installing a pre-reformer, which removes the carbon precursors; implementing the advanced catalysts of late; and possibly adding CO_2 to the reactant mix.

Eventually it is worth highlighting that industrial MSR's are cumbersome pieces of equipment.

For a typical production of 40,000÷60,000 Nm^3/h of H_2 in a refinery, a single MSR occupies a volume of more than 10.000 m^3 with 13÷20 tons of costly Ni-based catalyst loaded in 120200 catalytic tubes.

Figure 17 shows the steam reforming of the said 2200 tons/day of the methanol plant installed in Bandar Iman, Iran, in 1999. At that time, this plant was the largest methanol plant ever built in the world. The large volume of syngas to be produced brought the design of a single MSR far beyond its technological boundary; therefore, two paralleled MSR's were installed. The two items were connected to a common syngas refractory lined header. This is why, Figure 17 shows two identical reformers, which all in all costed about €23 million (installation excluded).

Figure 17 - Methane Steam Reforming Assembly. *Source: Haldor Topsoe A/S*

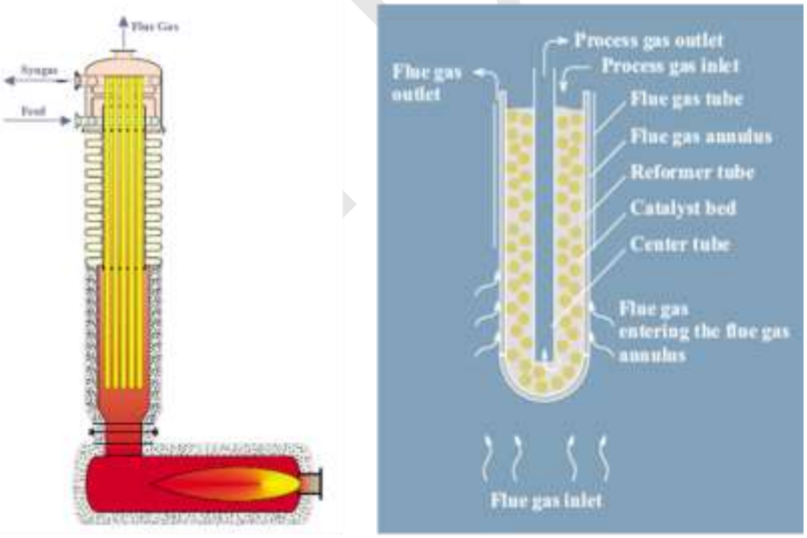
For the level of syngas production an ATR (see below) would have been the best technological solution for the syngas production. However, the choice fell on conventional MSR in the wake of the catastrophic incident occurred in Sasol's FT plant in South Africa, some years prior.

In the MSR described above, almost 50% of natural gas fed to the unit is burned to supply energy to endothermic end of the process, the prevailing heat transfer mechanism being radiation, which involve high temperature.

The thermal efficiency of a reformer could be improved if heat is transferred at lower temperature.

This objective is hit by *convection reformers* – an advanced reforming technology developed by Haldor Topsoe. In this reformer, the catalytic tubes are heated mainly by the flue gas flowing upwards on the outside wall of the tubes and internally by the reformed gas flowing upwards inside the bayonet tube sunk into the catalytic tube (Figure 18 b).

The flue gas is generated with a single burner as shown in Figure 18 (a). As opposed to a MSR, the catalytic tubes are not directly exposed to flames as they are separated from the reaction section of the reformer.



(a) (b)

Figure 18 - Convective Reformer[12]

In this way the share of convective heat transfer mechanism is comparatively higher than that of a conventional MSR. Both the flue gas and the syngas leave the reformer approximately at 600 ºC. With this arrangement as much as 80 % of the fired duty is utilized in the process, against the 50 % of a conventional SR.

By the way, it is worth mentioning that in hydrogen plants based on convection reformer, the fuel demand of the reformer can be supplied by the off-gas of the downstream PSA.

Partial Oxidation Process

Partial oxidation (*aka POX*) is the reaction of coal or hydrocarbons with sub-stoichiometric oxygen–fuel mixture so that the complete combustion of coal and all hydrocarbon species is prevented.

The reactions of partial oxidation, which is exothermic and operated from 800 to 1800 °C, generally yields syngas with H_2/CO ratio between 1.6 to 2. The partial oxidation of natural gas results in a syngas having a H_2/CO ratio of 2, which is ideal for the Fischer-Tropsch or methanol synthesis at temperatures > 900 ºC. The Fischer-Tropsch plant in Malaysia, Bintulu, for example is based on the POX of natural gas.

POX is mainly used for the gasification of coal, heavy oil, and other refinery residues albeit it can accept whatever hydrocarbons as feedstock as biomasses. Since no water is added, the H_2/CO ratio is lower than compared with steam reforming or autothermal reforming.

The general reaction equation taking place in a gasification process can be represented as:

$$C_nH_m + (n+m/2)/2\ O_2 \rightarrow nCO + (m/2)\ H_2O \qquad (11.2.7)$$

$$C_nH_m + n/2\ O_2 \rightarrow nCO + (m/2)\ H_2 \qquad (11.2.8)$$

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)\ H_2 \qquad (11.2.9)$$

Along with the above, also the WGS takes place in a POX plant; the methanation reactions, soot, H_2S, and NH_3 formation take place in a POX reactor as well. Thus the raw syngas contains H_2, CO, CO_2, CH_4, H_2S and NH_3. These latter's have to be removed from the syngas, typically by absorption onto a solvent/water in the downstream gas cleaning section of the gasification plant.

Since the reactions (11.2.7) and (11.2.8) are highly exothermic, steam, generally superheated at 300÷400°C, is added into the POX to keep the temperature controlled. The action of temperature moderator of steam is the result of: i) the sensible heat absorbed for rising its temperature till the gasifier operating condition, ii) the endothermic effect of its reforming reaction with the hydrocarbon stream, reaction (11.2.9). It goes without saying that the use of steam as a temperature moderator results in an increasing of H_2/CO in the syngas mixture.

Despite the efforts aiming at improving the MSR technologies, R&D activities are still in the making for finding less energy-intensive routes, which making the downstream sector less in need of large reactors and large amount of superheating steam, enable significant capital and operating expenditures, and CO_2 footprint reduction.

One of the most promising process to achieve said goal is the *Catalytic Partial Oxidation*[13] (CPOX) of methane. In this process, for few milliseconds the premixed methane and oxygen flow through the hot surface of a thin (< 1 mm) layer of a catalyst so that the chemical reaction

$$CH_4 + {}^{1}/_{2}O_2 \leftrightarrow CO + 2H_2 \quad \Delta H^\circ = -35{,}5\ kJ/mol \qquad (11.2.10)$$

takes place in the solid–gas inter-phase layer surrounding the catalyst particles where the reactants spend 10^{-6} s at temperatures variable between 600÷1200°C.

A key issue for the technological exploitation of this process lays in the possibility of avoiding the propagation of reactions into the gas phase that has to remain at a “relatively low” temperature. This condition favors the formation of primary reaction products (CO and H_2) and inhibits chain reactions. In this way the heterogeneous reaction (11.2.10) can take place at relatively low temperatures without flame formation, without steam input, and without soot or unwanted by-products formation.

It is worth noting that the CPOX produces a synthesis gas with an H_2/CO ratio of 2:1, which enables its direct utilization for methanol or Fischer-Tropsch synthesis without the need of FT feedstock composition adjustment.

Eventually, albeit the CPOX is an alluring technology, it still has a long way ahead to the implementation at industrial scale; one of the most critical hurdles to overcome is the fire hazard due to the flammability and explosiveness of CH_4 and O_2 mixtures.

A CPOX demonstrative plant (capacity of 20 Nm^3/h oh hydrogen) has been constructed and operated in Chieti Scalo, IT in 2011[1].

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[1] In 2011, the CPOX work received a financial support by the European Community throughout the Next GTL project- Contract NMP3-LA-2009-229183

Autothermal reforming and secondary reforming

The autothermal reform is a process that combines in a single pressure vessel the exothermic POX reactions, the endothermic MSR reactions, and possibly CO_2 reforming, in order to have an overall thermodynamically neutral syngas generation. By proper adjustment of oxygen to carbon and steam to carbon ratios, the POX supplies the whole heat required for completing the ensuing endothermic steam and CO_2 reforming reactions. In this process the syngas composition at the exit of the reactor approaches very closely the thermodynamic equilibrium, especially in large scale processes.

The term *autothermal* suggests that all heat required for the steam reforming reaction is supplied directly to the reacting gas by means of the heat released by the partial oxidation of a fraction of the natural gas fed into the reactor; hence no external heating is needed.

Characteristic of the autothermal process is that the oxygen added to generate heat is chemically bound in the product gas; therefore, the H_2/CO ratio in the syngas ranges from 1.6 to 2.65. This range is lower than the MSR. The typical operating conditions of an ATR are: T= 850÷1000 °C and P= 20 ÷100 bar.

An ATR consists of a refractory-lined pressure vessel including a thermal zone, on top of which the oxygen burner is hosted, and a reforming zone, home to a catalytic bed (fixed). Figure 19 shows the rendering of an autothermal reactor and the relevant oxygen burner.

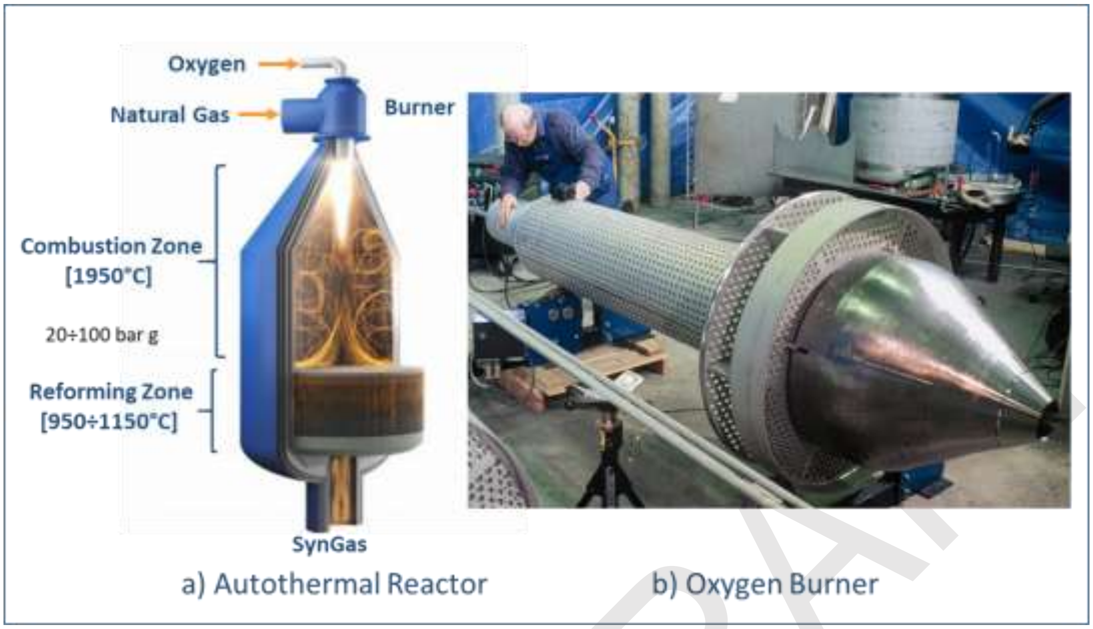


Figure 19 - Autothermal Reformer. *Source: Haldor Topsoe A/S*

The burner provides the effective mixing of the reactants (CH_4, O_2, and steam) in a turbulent diffusion flame. It is designed not only to keep heat from transferring back from the flame to the burner body, but also for avoiding the flame impingement of the catalyst bed. When the burner is designed to operate with pure oxygen, as is the case for methanol and dimethylether synthesis, it is of the uttermost importance that the burner axis is squarely aligned with the reactor longitudinal axis in order to avoid the impingement of the flame to the pressure wall, which might be the source of fatal accidents.

The thermal zone is a turbulent zone that provide the residence time for the hydrocarbon and oxygen to react completely. The overall oxygen to hydrocarbon ratios in the thermal zone vary between 0.55 and 0.6; therefore, in this zone the oxidation takes place under sub-stoichiometric condition, and the oxygen entering the ATR is entirely consumed by the homogeneous gas phase reaction (11.2.7), while the methane conversion to syngas proceeds with the thermal methane reforming (11.2.1) and WGS (11.2.2) in the lower part of the reactor. In the thermal zone the pyrolysis of higher hydrocarbons takes place as well.

The reforming zone hosts a catalytic-bed, in which methane is finally converted in syngas through heterogeneous catalytic reactions. In addition to promoting the reforming reaction, the catalyst loaded in the reforming zone also has the ancillary function of converting soot precursors.

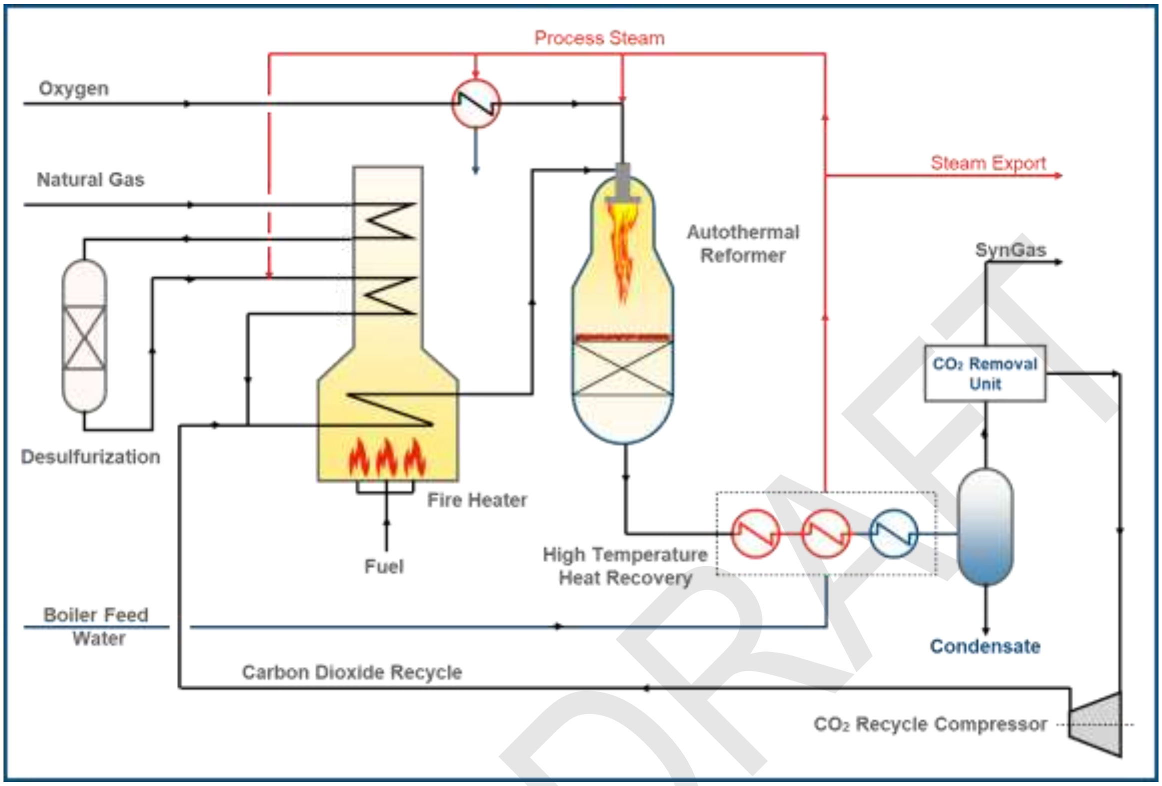


Figure 20 - Autothermal Reformer Process Flow Scheme

At the exit of the catalytic zone, the gas mixture will be in equilibrium with respect to reactions (11.2.1) and (11.2.2) at the exit temperature and pressure. The resultant syngas is completely free of oxygen.

The top layer of the catalyst bed is exposed to high temperatures; thus the Ni-catalyst supported on a magnesia-alumina spinel is required for this part of the ATR.

The overall reaction rate is mainly controlled by the transport rate of the reactants through the gas film surrounding the catalyst pellets. This entails that the process can be carried out at very high space velocities, since the catalytic reaction is not the controlling step of the process.

The thermal efficiency (the ratio of heat content of the produced syngas to that of the feedstock) is higher than that of both MSR (88.5 against 81 %) and of POX (88,5 vs 83.5 %). The maximum temperature at which an ATR can operate finds a limit by the refractoriness of the equipment lining, and by the stability of the catalyst.

By and large the oxidant used in an ATR is pure oxygen; therefore, next to an ATR there must be an air separation unit (ASU). However, in some industrial application the ATR is used as a *Secondary reformer* downstream a primary reformer, typically and MSR, as in ammonia production plants (see Figure 21). In these cases, since the production of NH_3 requires nitrogen as reactant, the oxidant fed to the secondary reformer is air.

ATR shows up also in other reformer arrangements, in particular in the *Heat Exchange Reform* (HER), where the reforming reactions take place inside the tubes filled with reforming catalyst. The heat required for the chemical reactions is supplied by the syngas flowing in the HER shell side and coming from the outlet of the downstream ATR which, in turn, receives as a feedstock the process gas exiting the tubes of the HER; in other word the heat needed in the tubular SR reformer is obtained from the hot product gas exiting the second reformer.

In this configuration the expensive fired reformer (MSR) is eliminated; however only medium pressure steam can be recovered from the syngas plant and electricity for the syngas compressor must be imported.

The main issue in connection with the HER is the risk entailed by the metal dusting – a severe corrosion phenomenon which results in uniform loss of metal that turns into metal powder and/or severe pitting. It is supposed that the corrosion is sparked by the deposition of a layer of soot on the surface of the metal at temperature between 300°C and 850°C. In this temperature window, the syngas will potentially form soot via the Boudouard reaction.

Figure 21 - Primary and Secondary Reformer: *Source: FEPCO.org*

The process characteristics of the syngas generators describe above are summarized in the following Table 9.

Table 9 - Key performance variables of syngas generator[6]

	Steam Reforming	Partial Oxidation	Autothermal Reforming
Feed O_2:C ratio (mol/mol)	0	0,55÷0,65	0,55÷0,6
Feed H_2O:C ration (mol/mol)	2,5÷5	0÷0,15	1,5÷2,5
Outlet temperature (°C)	820÷880	1300÷1400	950÷1050
Outlet pressure (Mpa)	2,0÷2,5	2,5÷4	2,5
Outlet CH_4 content (mol%)	3÷5	0,1	0,5÷1
Product H_2:CO ratio (mol/mol)[1]	4÷7	1,6÷1,9	2,5÷3,5
Product CO_2:CO ratio (mol/mol)[1]	0,5÷1	0,05÷0,1	0,2÷0,3

Alternative Syngas Generation Methods

In addition to steam reforming, dry reforming (DMR) and partial oxidation, many variations and combination of these processes have also been proposed to generate syngas. They include bi-reforming, oxidative bi-reforming, and tri-reforming[11]. The alternative methods have the common advantage, among others, of using CO_2 as a co-feedstock.

The bi-reforming process is the combination of steam reforming, producing a syngas with H_2/CO ratio of 3, with dry reforming, which produces syngas with a H_2/CO ratio of 1. The combination of these two processes, in a single combined operation or in separate steps, allows for the production of syngas with a H_2/CO ratio of 2, suited for FT-synthesis.

Both MSR and DMR are endothermic; thus, energy has to be supplied from external sources. A more direct way to supply heat to the bi-reforming reactions consists in burning one mole of CH_4 to CO_2 and H_2O; thereafter, these combustion products is let to react with 3 moles of CH_4 to form a syngas having a H_2/CO ratio of 2.

The bi-reforming process can also be used for chemical recycling of CO_2 emissions accompanying natural gas and geothermal hot water and steam sources.

The tri-reforming process is a synergetic combination of CO_2 reforming, steam reforming, and partial oxidation of methane in a single reactor for effective production of industrially useful synthesis gas (syngas). The tri-reforming can not only produce synthesis gas with desired H_2/CO ratios (1.5÷2.0), but also could eliminate carbon formation which is usually a serious problem in the CO_2 reforming of methane. These two advantages have been demonstrated by tri-reforming of CH_4 in a fixed-bed flow reactor at 850 °C with supported nickel catalysts.

It should be noted that the technological development of the above alternatives is still at the “infant” stage; therefore, before they can become mature for industrial application, further development efforts are needed.

PART III

SYNCRUDE ECONOMICS AND KEY PERFORMANCE INDICATORS

12. Fischer Tropsch economics

Metrics for plant performance measurements.

The economics of an XTL-FT plant are strongly affected by the cost of carbon-bearing feedstock, the product pricing and the capital cost of the facility.

Carbon-bearing feedstock

The cost of feedstock is a sizable component of operating costs, yet its price cannot be controlled because it depends on its source - for biomass it also depends upon the distance of the production and harvesting site from the syncrude production location.

Therefore, the design of the facility is a key point for reducing the impact of the feed on the economics of a XTL-FT. Indeed, the design defines the two key performance indicators that measure how sensitive the economics will be to the feed cost. These KPIs are the thermal efficiency; that is, the percentage of the energy content of the feed that converts into energy output, and the carbon efficiency; that is, the percentage of carbon in the feed that is incorporated into the products.

The product from a XTL-FT is a synthetic crude that is comparable to conventional crude oil albeit syncrude components are different for different FT technologies and for different catalyst. An HTFT yields a syncrude containing light gases, LPG, naphtha, distillate and aqueous products. Residue/wax, distillate and naphtha are the major components yielded by a LTFT plant. For both cases an upgrading or a syncrude refining is needed to produce more valuable product slate. By and large, the production of upgraded syncrude to be refined elsewhere is not the best choice as a XTL-Methanol is much more profitable than FT-synthesis.

The energy needed for the syngas generation and the energy produced in the FT synthesis are generally recovered as steam and converted into electric power for both internal use and for export. Thus, power is a byproduct of the current XTL-FT that adds to the product slate, which determine the income of the facility.

The metrics used that best represent the economic performance of the plant are thus the feed to electricity conversion, the feed to product conversion and the crude oil price. The electricity conversion is important in that exporting power is regulated, regional and depending on local infrastructures for electricity supply and distribution. This entails that an XTL-FT remains locked into a regional supply agreement and regional supply pricing.

The feed to product conversion impacts on the selection of the location and scale of the plant.

Indeed, as is customary in the petroleum industry, the liquid product prices are netback based; that is, it is set by the market price minus the logistic cost of transporting the liquid fuels to the market. Consequently, the product prices can be eroded if the plant is far from the end-market.

Product Pricing

The object of the GLAMOUR project is the production of Jet fuels and marine bunkering fuels in a sustainable way. Since an aircraft is not restricted to a single Country, the specifications for the civil aviation turbine fuel Jet A-1 as reported in the standard DEF STAN 91-91 is recognized as the international standard for jet fuel. A set of specification for jet fuels is shown in Table 10.

Table 10 - Commercial Jet fuel specification[6]

Property	Jet A-1	Jet A	Jet B
Net heat of combustion [MJ/kg], min	42,8	42,8	42,8
Density at 15°C [kg/m3]	775÷840	775÷840	751÷802
Freezing Point (°C), max	-47	-40	-50
Vapor pressure [kPa], max	-	-	21
Flash point [°C], min	38	38	-
Viscosity at -20°C [cSt], max	8	8	-
Smoke point (mm), min	25	25	-
Existing gums [mg/100 ml], max	7	7	7
Lubricity, BOCLE [mm], max	0,85	-	-
Composition, max			
Aromatic content [v%]	25	25	25
Naphthalene [v%]	3	3	3
Sulfur content [w%]	0,3	0,3	0,3
Thiol content [w%]	0,003	0,003	0,003
Acid content [mg KOH/g]	0,1	0,1	-

In addition to the specification Jet A-1, the jet fuel refined from syncrude have to meet a subset of more stringent requirements, more specifically the flash point has to be in range 38÷50 °C, and the aromatic content is specified to be 8÷25[6] [v%].

Incidentally, the Jet A is a standard for the USA national travel, and Jet B is used only in Arctic regions.

It is worth noting that the synthetic jet fuels from a XTL-FT are rich in alkanes, consequently they have a low density and a high gravimetric energy content, thus its energy weighs is less and the tank capacity is less constrained. However, as fuel are sold volumetrically, these jet fuels costs more for the same energy content as a jet fuel with high volumetric energy (high density).

As shown above, the standardized international specification Jet A-1 of aviation fuel for use in aircraft powered by gas turbine engines, requires that the density of Jet fuel (aviation turbine fuel, ATF) be in the range 775÷840 g/l and that the maximum freezing point be minus 47°C.

The FT-Jet fuel features a density of 740÷747 g/l against the minimum requirement of 775 g/l of the international standard, and a freezing point of minus 48°C, which is too close to the maximum freezing point of said specification. The reason for the lower density of FT-ATF in comparison with crude oil products is that the refinery's kerosene contains naphthenic and aromatic hydrocarbons whose density is higher than that of paraffin's produced from FT plant.

Therefore, the FT-Jet fuel cannot be directly used as aviation fuel unless it is further processed in a conventional refinery after mixing with fossil crude oil. Alternatively, FT-kerosene type jet fuel can be blended with aviation fuel produced from crude oil refining, provided that the refined product is sufficiently within the standard specification to allow for volumetric mixing, or it can be used as an additive for blending winter grades of diesel fuel.

Qatar Airways planes (A380 and A340), for instance, used FT-jet fuel blended (in proportion of 35÷50%) with refinery kerosene on the Doha-London-Doha route as the FT-products are in all respect crude oil products-analogues.

The marine industry is facing several challenges related to emission regulations. Marine fuel is actually one of the most significant contributors to air emissions of SO_x, NO_x, and PM. On 1 January 2020, a new global cap by the IMO on sulfur content in marine fuels will come into effect. The new regulations, known as IMO 2020, mandates a maximum sulfur content of 0.5% (the 'Sulphur Cap'), unless the relevant vessel is trading within an Emission Control Area ('ECA'), in which case the maximum sulfur content is limited to 0.10% w. The driver of this change is the need to reduce the air pollution created in the shipping industry by reducing the Sulphur content of the fuels that vessels use.

There are several different types of fuel with a sulfur content not exceeding 0.50% w ('Compliant Fuel'). This includes new hybrid or blended fuels generally referred to as very low sulfur fuel oil ('VLSFO') and distillate fuels such as marine gas oil ('LSMGO'). These bunker fuels are much more expensive compared to the heavy bunkering fuels.

Among the fuel of fossil origin, LNG is increasingly making inroads into the transportation sector notwithstanding its lower volumetric heat content and its logistic is significantly more complex than the other liquid fuels. The drivers for LNG use as bunkering fuels are the substantial zero

SO_x and particulate emissions along with 20% CO_2 less emissions.

Currently, the average cost of an LNG plant is in the range of 400÷600 \$/t, which tantamount to **15,000÷22,400 €/bbl** (cost adjusted for the density difference between LNG and Diesel of which is a substitute), and the operating costs are around 0.53 €/MW_{LHV}

Since the syncrude and crude oil are refined to the same products, are subject to the same performance criteria, and are sold to same markets, the FT-products are subject to the same market dynamics[14]. Thus the crude oil price is an important factor in determining the XTL-FT economics. The most used metric for evaluating the economic viability of a liquid synfuel production facility is the breakeven point expressed as crude oil equivalent or barrel of oil equivalent, or, more specifically for transportation fuels in gasoline gallon equivalent[15],[16]

The price dynamics of crude oil derivatives generally follow that of a crude benchmark (Brent) with a spread of few \$/bbl, whose value depends on the specific product. Since neither FT-products nor FT-syncrude are quoted on traded markets, it is customary to set these prices to marker or reference price benchmarks (Brent Dated, WTI) in the same token of other crude oil and its derivatives.

The formula used in pricing a specific crude oil can be written as $P_x = P_R*(1\pm \%D)$[17], where P_x is the price of crude x (Arab Light, Urals, Maya blend etc.), P_R is the benchmark crude price (Brent Dated, for example); and %D is the price differential (discount or premium) over the benchmark. %D depends on the quality of the crude, most notably the density and sulfur content: light/sweet crude grades usually command a premium over heavy/sour crude grades.

The scaling price factor for the Oryx Plant (Qatar)'s syncrude, for example, is 1,09[18], which means it commands a premium of 9% over the Brent Dated quotation (see Table 11).

Table 11 Oryx Plant syncrude minimum premium price

SynFuel	t/d	%w	kg/l	w*kg/l	bbl/t	\$/t (2)	Scaling F
LPG	143	3,76	0,54	0,020	11,6	264	0,83
Nafta	693	18,2	0,68	0,124	9,25	381	1,20
Jet-Kerosene	1493	39,3	0,75	0,294	8,42	325	1,02
Diesel	1470	38,7	0,77	0,296	8,21	363	1,14
SynCrude	3799	100,0	0,73	0,73	8,56	347	1,09
Brent	-	100	0,83	0,83	7,57	319	1,09

Moreover, additional premium might be charged to FT-products depending upon the end users. The FT-naphtha, for example, might ask for an additional \$1/bbl of FT-syncrude when FT-naphtha is cracked to produce ethylene because the yield of ethylene is higher than that derived from petroleum. Thus this added value can be shared with the FT-syncrude producer through an additional premium.

The Russian refineries are used to blend diesel with an additive in order to adjust the cetane number. As the FT-diesel has a cetane number of 73 units, compared to 51 units in diesel fuel according to EN-590 standard, it can command an extra premium on account of the additive savings it deliver when FT-diesel is blended in the diesel pool.

The pricing of the FT-Syncrude in terms of a marker is of the utmost importance in capital budgeting decisions as it enables the assessment of the break-even (B/E) point relative to the investors expectation of medium to long term crude oil prices: the final investment decision will be taken if the B/E point is lower than the expected Brent/WTI prices.

The B/E is the price of a products, or a basket of products, that makes neutral the investment in a specific production facility. This happens when the total costs (fixed and variables) become equal to the revenues; that is, when the following equation is satisfied:

$$(P' - C'_v) * Q - C_f = 0$$

Where:
P' = product market price of one barrel
C'_v = variable production cost of one barrel
C_f = fix cost
Q = plant capacity.

It goes without saying that P' must be always greater than C'_v for it to maintain the production running. The above equation suggests that for a given market condition, the window of viability closes quickly as capital costs (C_f) escalate. In conclusion, it is of the utmost importance the development of groundbreaking FT-BTL technology leading to a significant reduction in the capital requirements.

Capital Cost

As to the capital expenditure, it should be said that currently the commercial scale X-TL facilities based on Fischer-Tropsch technologies are capital intensive. Figure 22 shows the capex per thousand barrels produced in a day versus the plant capacity for the GTL facilities currently in operation.

Gas Journal article[19] indicates the range of capital costs lays in between **60,000÷88,000 $/bpd**, in 2012. This range was extrapolated by the investment cost of a demonstration plant.

From Figure 22, it can be seen that the data are pretty much scattered. This is due to the different location of the facilities, which command dramatic different construction costs, different technologies, and different process line-ups.

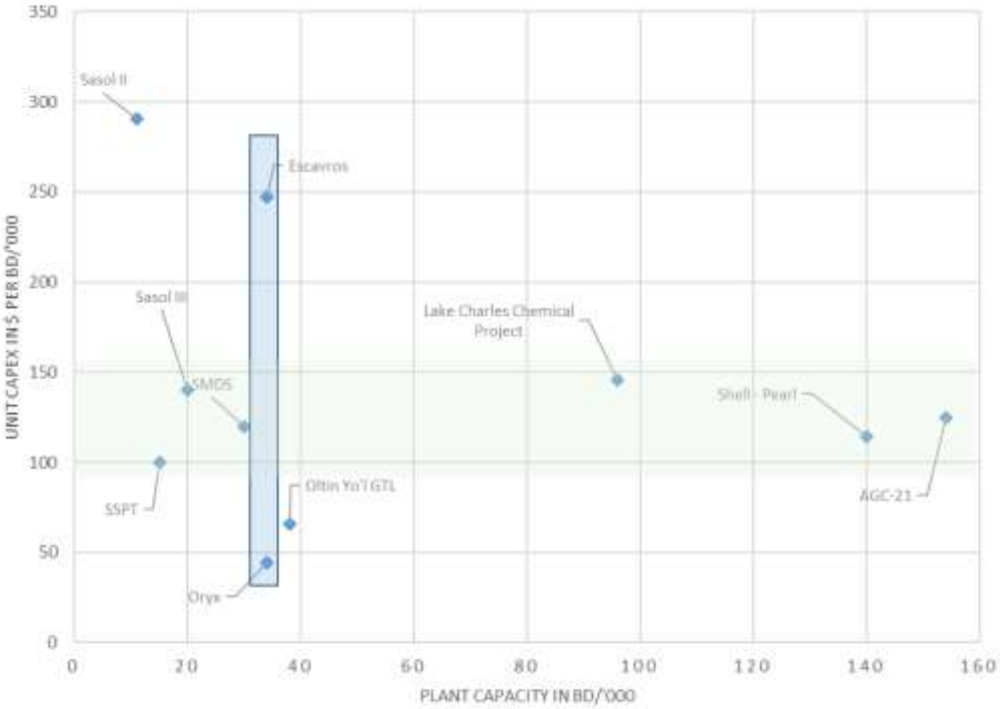


Figure 22. Specific capital cost of the current industrial running plants

In particular, it can be noted that the Oryx (Qatar) and Escavros (Nigeria) plants have the same name plate capacity, however the unit capex's are pretty much different. This is due to:

- The Escavros plant was a "pure" green field that required investment in infrastructure as well. On the contrary the ORYX plant was built in an existing industrial location, and could take advantage from the existing infrastructure
- A higher location factor applied
- The contractor costs have increased in recent years due to scarcity caused by the large number of large projects in the world.

The above observation suggests that a FT-BTL be located in an existing industrial site.

Biomass-to-Liquid plants deviate from GLT plants by the feedstock that is used, i.e. solid biomass instead of natural gas. This has impact on several parts of the line-up of the syngas production and Fischer-Tropsch synthesis system: (i) more extensive feedstock handling and preparation; (ii) application of a slagging entrained flow gasifier, which including all solids handling is typically 50% more expensive than a natural gas reformer, (iii) typically 50% higher oxygen demand, i.e. 50% larger ASU capacity is required; and (iv) requirement of a Rectisol unit to remove higher load of impurities and CO_2.

As to the FT-BTL, it is worth mentioning that the total cost of investment is about 60%[20] higher than for corresponding FT-GTL facility.

The high capital cost makes a GTL, or more broadly the feed-to-liquids, vulnerable to market condition changes throughout the plant lifetime cycle. Therefore, robust R&D's programs are needed[21] - in addition to the selection of the optimal site location - to reduce the investment cost and open the window of economic viability of FT-BTL technology, most notably for supplying bunkering fuels.

13. BENCHMARK

13.1. Gas to Liquid – Fischer Tropsch Case

In 1998, Bechtel[22] and Amoco developed a baseline design for a once-through natural gas Fischer-Tropsch (F-T) plant with 84,1 MW power co-production in the framework of a project contracted by the U.S. Department of Energy for addressing the reduction of the Country dependence of energy and other strategic targets.

The design aimed at examining the economic viability of the conversion of natural gas to FT-syncrude. This design incorporated an enriched air blown autothermal reformer for syngas generation, a slurry catalytic process for F-T synthesis, a FT-products refining unit and the off-sites facilities.

The plant was designed to produce about 8815 barrel per day (bpd) of F-T liquid products from 100 MMSCF/day of natural gas - corresponding to a thermal input of 17800 MMBtu/h. Primary liquid products were butanes, naphtha and 175÷350°C distillate. The naphtha and distillate could be further processed to produce premium gasoline and diesel blending stocks. The plant used all of the byproduct steam and fuel gas production for its captive power demand. In addition, it produced about 84.1 MW of excess electric power for export.

In this once-through natural gas F-T project, an enriched air-blown autothermal reformer is used for syngas generation. Since the objective of the project is to produce stable, shippable products which can be upgraded to liquid transportation fuels elsewhere, such as in a conventional petroleum refinery, the only product upgrading step is the wax hydrocracking plant.

A hydrogen recovery plant supplies the hydrogen needs of the wax hydrocracking plant by recovering hydrogen from a small portion of the syngas generated in the syngas preparation area. The feed to the hydrogen recovery plant is fresh syngas from the autothermal reforming instead of the unconverted syngas leaving the hydrocarbon recovery plant, which have a too low H_2 content for effective, economic hydrogen recovery. The general arrangement of the process area is shown in the following block diagram.

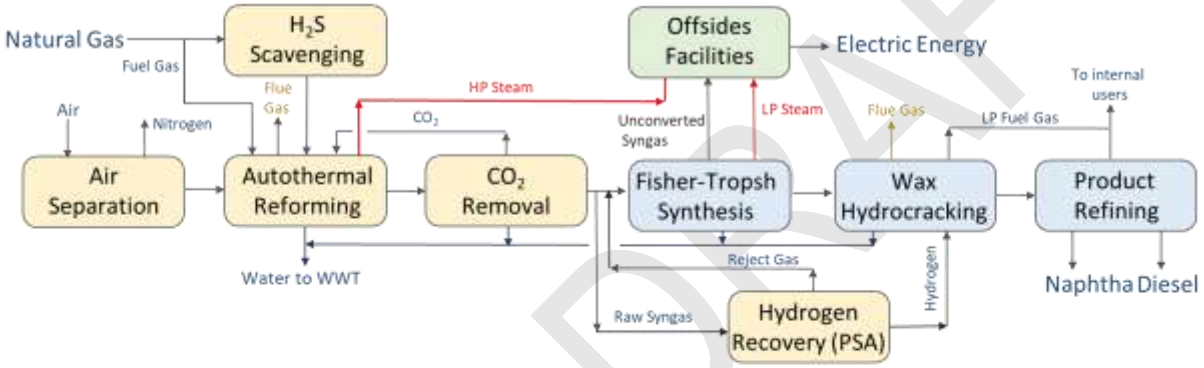


Figure 23 – Gas to Liquid Process Set up

Air Separation Unit (ASU)

The ASU, provides the required enriched air feed to the Autothermal Reforming Plant, for syngas generation. The ASU is a standard cryogenic air separation plant. It produces a stream containing 95 v% oxygen that is then mixed with atmospheric air so that an enriched air stream containing 40 v% oxygen can be fed to the following autothermal reforming. The choice of enriched air versus pure oxygen was driven by the reduction in cost.

The cryogenic air separation plant is a single train with a capacity of about 1,550 tons/day of 95 v% pure oxygen. The design incorporates a backup system including a liquid oxygen storage capacity of 1,550 tons, which is equivalent to one-day production, and a gaseous oxygen storage of 43 tons, which is equivalent to 40 minutes of production. This backup oxygen storage system protects the facility from an unscheduled shutdown of one day or less.

In the air separation section, ambient air is filtered and compressed in a two-stage axial centrifugal compressor with inter-stage cooling. The air from the final stage of compression enters a direct contact aftercooler where it contacts cooling water and chilled cooling water in two separate packed sections.

The cooled air from the top of the aftercooler has lost the majority of its ambient water vapor. Removal of the residual water vapor, carbon dioxide and other atmospheric contaminants occurs in the molecular sieve adsorbers. Two vessels containing the adsorbent are used in a cyclic process. While one vessel is on line purifying the incoming air, the other vessel first is heated with dry waste nitrogen gas to remove the adsorbed contaminants and then cooled to the operating temperature before being placed back in service. The regeneration heater uses high pressure steam to raise the temperature of the regeneration gas to the proper level.

The dry air enters the *cold box* where it is cooled to cryogenic temperature in the main heat exchangers and is separated into oxygen and nitrogen by cryogenic distillation. Final cooling is by expansion. The oxygen stream is further purified in an argon column to 95 v%. The main heat exchangers are brazed aluminum, multi-pass, plate-fin units in which the entering air is cooled against the cold oxygen and nitrogen streams leaving the distillation columns.

The oxygen product stream leaving the cryogenic separation section is warmed in the main heat exchangers and compressed to final delivery pressure in a centrifugal compressor.

Compressed air is mixed with the 95 v% oxygen produced by the air separation section to produce an enriched air stream containing 40 v% oxygen that is sent to the autothermal reforming plant, for syngas generation. The air compressor (63,4 MW) is directly driven by a gas turbine whose exhaust gases are sent to a heat recovery steam generation system to produce steam for power generation.

Autothermal Reforming Plant (ATR)

The objective of the Autothermal Reforming Plant, is to provide a syngas with a H_2/CO ratio of about 2.0 for Fischer-Tropsch synthesis. This objective is accomplished using a 40 v % enriched air-fired autothermal reformer operating with CO_2 recycle.

The ATR reactor was designed to operate at a reasonable O_2/C molar ratio 0.7 to keep the maximum adiabatic flame temperature below 2200 °C, and at a steam/carbon molar ratio of 0.6 to avoid potential soot formation.

The pre-heated natural gas is desulfurized in one of the two H_2S scavengers consisting in mixed CoMo/ZnO fixed-bed reactors arranged according to a lead-lag pattern. The sulfur contained (< 4 ppm v) in the feedstock is removed to the less than 0.1 ppm by volume as required for avoiding catalysts poisoning.

After further preheating in a fire-heater the natural gas is then mixed with heated enriched air, recycle CO_2 from CO_2 Removal unit, and superheated steam (45 barg, 538°C) before going to the ATR reactor. The autothermal reforming reactor effluent is cooled in the heat exchangers train of the ATR's heat recovery steam generation, to produce saturated steam at 45 barg, and preheat the incoming natural gas feed.

Eventually the syngas is cooled down to 65 °C in an air cooler and separated from the condensed water in a flash drum. The syngas produced with the molar H_2/CO ratio of 2.01 is split so that a portion of it goes to the CO_2 Removal Plant and the remaining to the Hydrogen Production Unit.

CO_2 Removal Unit

The CO_2 Removal unit is required to provide the CO_2 needed to control the equilibrium H_2 and CO_2 production in the ATR Plant. In this plant about 66% of CO_2 is recovered, compressed and recycled back to the autothermal reformer reactor.

The syngas is cooled to 43°C and sent to the feed gas knock out drum before going to the amine absorber column for CO_2 removal; Dow's Gas/Spec process, which uses a 50% MDEA solution plus proprietary additives, was the solvent chosen for this project.

To ensure an amine-free vapor product, the absorber overhead vapor is water washed in a scrubber. The scrubber liquid is returned to the rich-amine knock out drum. The washed, lean syngas stream leaving the scrubber is combined with syngas stream coming from Hydrogen Production Unit and sent to the Fischer-Tropsch synthesis.

The rich-amine solution from the bottom of the amine absorber column is flashed in a flash drum. It is then heated by exchange with the lean-amine solution before being sent the amine regenerator. The regenerated lean-amine solution from this regenerator is cooled by heat exchange with rich-amine and sent to a storage tank. The lean-amine then is pumped from this tank, cooled and sent back to the absorber. A portion, approximately 10%, of the cooled lean-amine solution is filtered and returned to the storage tank.

The CO_2 which is removed from the syngas and leaves the amine regenerators is compressed in the compressor and sent back to the ATR Plant to control the CO_2 production during syngas generation.

Fischer Tropsch Synthesis.

In this unit the syngas is converted into hydrocarbon products using cobalt catalyzed, slurry phase Fischer-Tropsch reactors arranged in a single train including two parallel first-stage slurry-bed reactors feeding a single second-stage slurry-bed reactor.

The unconverted syngas leaving the first-stage reactors is cooled to 65,5 °C and flashed to condense and remove water and hydrocarbons before being reheated and fed to the single second- stage reactor. The CO conversion in both first-stage reactors as well as that in the second-stage reactor are both about 61 %.

All three Fischer-Tropsch slurry reactors are about 5,8 m in diameter and about 20 m in height. Each of the two parallel first-stage reactors contain about 2,000 bayonet tubes having a 1.5-inch OD for low pressure (about 10 bar g) steam generation. The second-stage reactor contains 1470 of the same size steam tubes. Design superficial gas velocity in each of the two first-stage reactors is 11.8 cm/sec, and in the second-stage reactor, it is 14.5 cm/sec.

Catalyst replacement is estimated at 0.01 % per hour of total catalyst inventory, which corresponds to an average catalyst life of about 1.2 years.

The syngas is heated with steam to 176,5° before entering the two parallel first-stage, F-T synthesis reactors through a cylindrical gas distributor. In the first-stage F-T reactors, the syngas bubbles upward through the catalyst/wax slurry, dissolves in the slurry phase, and is converted into hydrocarbon products at the catalyst interface. The slurry consists of solid catalyst particles suspended in the non-vaporizable portion of the liquid product (i.e. the wax). The heat of reaction is removed by rising saturated steam at 10,3 barg and 189°C within the steam tubes.

The overhead vapor stream leaving the first-stage reactors goes through cyclone separators to disengage any liquid carryover before being cooled to 65,5°C. This cooled three-phase mixture is separated into an unconverted syngas stream, a liquid hydro-carbons stream, and a water stream. The liquid hydrocarbons stream is sent directly to the hydrocarbon recovery plant, and the water condensate goes to water treatment.

The vapor stream is heat-exchanged to 176,5°C before entering the single second-stage, F-T synthesis reactor through a cylindrical gas distributor. Also, in this F-T reactor, the syngas bubbles upward through the catalyst/wax slurry, dissolves in the slurry phase, and is converted into hydrocarbon products at the catalyst interface. The slurry consists of solid catalyst particles suspended in the non-vaporizable portion of the liquid product (i.e. the wax). The heat of reaction also is removed by rising saturated team at 10,3 barg and 189°C within the steam tubes.

Liquid wax streams are withdrawn from all three F-T reactors at reactor conditions through a slurry valve which produces a catalyst free hydrocarbon stream. Hydrocyclones also are included to aid with producing a catalyst free product. Thus, upon leaving the reactors, the liquid wax passes through hydrocyclones to produce a catalyst free overflow stream and a catalyst rich underflow stream.

The overflow from the top of the hydrocyclones is passed through a valve to reduce its pressure to 6 bara and sent to a product separator. The pressure reduction causes dissolved gases to separate from the liquid product stream. The vapors are cooled to 38°C to recover additional liquid and sent to the fuel system.

The liquids from the product separators are sent to a F-T liquid wax intermediate hold tank, which serves as the feed drum for the wax clarifying and catalyst recovery filters. These are enclosed washing type cake filters. The clear wax stream is sent to the Hydrocarbon Recovery Plant. The underflow catalyst-wax slurry stream from the filters is mixed with make-up wax and recycled back to the F-T reactors.

A portion of the catalyst is removed from the system as spent catalyst. About 270 kg per day of catalyst are removed for disposal to counteract the catalyst makeup and maintain a constant catalyst inventory in the reactors. Naphtha from downstream processing is used for mixing and recovery of wax left in the catalyst cake.

The overhead vapor stream from the second-stage F-T reactor is passed through a cyclone separator to disengage any liquid carryover. The vapor stream then is cooled to 38°C and sent to a three phase separator wherein the aqueous water stream, the liquid hydrocarbon stream, and the vapor stream are separated.

All the liquid hydrocarbons in the FT Synthesis plant is headed to the Hydrocarbon Recovery Section, the unconverted syngas is used as fuel for the gas turbine of the Combined Cycle Power plant and the process waters separated from the separators are sent to the waste water treatment plant.

Hydrogen Recovery Plant

The Hydrogen Recovery Plant, provides the high purity hydrogen required by the Wax Hydrocracking Plant for upgrading F-T wax product to a shippable product. The feedstock of this plant is a slipstream of the syngas produced in the ATR plant.

High purity hydrogen (99 v% H_2) is produced by a standard polybed pressure swing adsorption (PSA) process from the syngas feed containing 47 v% hydrogen. The plant contains ten PSA adsorber vessels, packed with molecular sieves, which are cycled in sequence from 26 barg to 7 barg.

About 1.4% of the fresh syngas from ATR plant is split off and cooled and sent to the Hydrogen Recovery plant. The cooled syngas flows through a knock out drum, enters the feed valve, and flows upward through the adsorber vessel. As the gas flows upward through the adsorber vessel, the impurities present in the gas are selectively adsorbed. To maximize hydrogen recovery, an adsorber is switched from an adsorption position when the impurities front has reached a predetermined level in the adsorber. When a regenerated adsorber has been pressurized to the adsorption pressure, it is switched to the adsorption step and the first adsorber begins its regeneration sequence.

Several concurrent blowdown steps are performed to regenerate a bed. Initially, the pressure in the adsorber is reduced to desorb hydrogen. Pure hydrogen leaving at the top of the adsorber is internally used in the PSA unit to re-pressure and purge other adsorbers. The co-current or upward pressurization step is terminated when the impurities front reaches a second predetermined position in the bed. At this point, little hydrogen is left in the adsorber, and the reduced pressure has started desorption of impurities. The flow in the adsorber is then reversed, and the adsorber is depressured downward to off-gas pressure. In actuality, the regeneration process involves several pressure equalization and depressurization steps which are performed automatically.

The hydrogen product stream from the PSA unit is sent to the Wax Hydrocracking Plant, while the reject stream is compressed and mixed with the syngas mainstream. The combined syngas stream is being directed to the Fischer-Tropsch Synthesis Plant.

Hydrocarbon Recovery Plant (HRP)

This plant section is set to separate the hydrocarbon liquids from the FT-synthesis plant into naphtha, distillate and wax. Some low pressure fuel gas also is produced. The product naphtha and distillate streams are sent to product blending, and the wax stream goes to the Wax Hydrocracking Plant, for upgrading to a shippable product.

The HRP receives all the liquid hydrocarbon streams produced in the Fischer-Tropsch Synthesis Plant, and separates them into a naphtha stream, a distillate stream, a wax stream, and a low pressure fuel gas stream. The cut points for the three liquid streams are listed below:

Naphtha	C5 saturates – 176°C
Distillate	176°C – 350°C
Wax	>343°C

The HRP Plant is basically a single fractionation tower with a steam side-stripper and the associated furnace, heat exchangers and flash drums.

All the liquid hydrocarbon streams from the Fischer-Tropsch Synthesis plant are combined in a product fractionator feed separator drum. The overhead vapor leaving this flash drum goes to the middle of the fractionator to act as a stripping media. The bottoms liquids are heated and sent to tray 9 of the fractionator tower, which separates the liquid hydrocarbons into naphtha, distillate and wax products.

The fractionator tower contains 21 trays. The overhead vapor is cooled from 118 °C to 43 °C through a combination of an air cooler and water cooler before entering a three phase accumulator. The vapor leaving accumulator is a low pressure fuel gas that is admitted to the plant fuel header system. The condensed water stream, produced as a result of utilizing live stripping steam, is sent to the waste water treatment facility. The liquid hydrocarbon stream is refluxed back to the tower. The naphtha product stream is withdrawn from tray 2 and cooled.

A 6 tray side stripper stabilizes the liquid drawn from tray 7 of the fractionator tower to provide a distillate product stream. Saturated steam at 10,3 barg is used as the stripping medium. The distillate product stream is cooled by exchange with the tower feed and with water before going to distillate product blending.

The bottom wax stream from the product fractionator is cooled by exchange with the tower feed from 313 °C to 176°C before being sent to the Wax Hydrocracking Plant.

Wax Hydrocracking Plant (WHP)

In the Wax Hydrocracking Plant, the F-T wax product is catalytically cracked under a hydrogen environment in a single stage fixed-bed hydrocracker with minimum coke formation to yield higher quality naphtha and distillate.

Hydrocracking is led at about 371 °C and between 75.8 barg and 105 barg under a hydrogen atmosphere in a single multi-bed reactor with inter-bed cooling by hydrogen-rich recycle gas. The reactor effluent is cooled and separated into C4- fuel gas, naphtha and distillate. Unconverted material from the bottom of the fractionator is recycled back to the hydrocracking reactor.

In the WHP, the wax stream from the HRP, is mixed with unconverted material from the bottoms of the product fractionator and hydrogen rich gas before being heated. The heated reaction mixture enters the top of the multi-bed, downflow hydrocracking reactor. Interbed cooling is obtained by injection of hydrogen-rich gas. The reactor effluent is cooled to 43.3°C before being flashed. The hydrogen-rich gas leaving the flash drum is compressed, heated and recycled back to the hydrocracking reactor.

The liquid leaving the flash drum is sent to a debutanizer column. The overhead vapor stream is mixed with low pressure fuel gas streams and low pressure gas from the WHP's product fractionator, chilled to maximize liquid hydrocarbon recovery, and flashed in a flash drum. The gas from the top of the flash drum goes to fuel gas, while the liquid from the bottom is mixed with the debutanizer bottoms stream and sent to the WHP's product fractionator after passing through a fired heater. The fractionator overhead product stream is the naphtha product. The distillate is withdrawn from the middle of the product fractionator through a side stream stripping column. The bottoms from the product fractionator is mixed with fresh feed and recycled back to the hydrocracking reactor.

Offsites plants

Combined-Cycle Power Plant (CCPP). It consumes the C4- fuel gas produced in the F-T plant as well as the excess 45 barg steam from the ATR plant and the excess 10,3 barg stream from FTSP to produce electric power, compress the inlet air to the ASU Plant to 45 barg, and produce 3,5 barg steam for use within the process area.

The fuel gas is burned in a General Electric (GE) Frame 7 gas turbine which drives the air compressors and an electric power generator. The hot exhaust gases from the air compressor and the inlet steams from the ISBL go to the CCPP's HRSG section where three levels of superheated steam are generated and sent to the three-stage steam turbine which drives another power generator. 3,50 barg is withdrawn from the low pressure turbine for use in other parts of the plant.

The CCPP supplies the complete electric power needs for the entire complex as well as producing an extra 84 MW for sale against the total power production of 183.3 MW.

Relief and Blowdown – This Plant is set for the collection and flaring of relief and blowdown discharges from all applicable plants. It includes two flare systems; a main flare for all hydrocarbon containing discharges and a small secondary flare for emissions containing H_2S.

Tankage – It provides storage and delivery equipment for products, intermediates and chemicals. Thirty days storage is provided for the naphtha, distillate and butanes products. Two days' intermediate storage is provided for the feed to the Wax Hydrocraking Plant. This two days storage capacity is required to provide feedstock during plant startup and to mitigate the effect on operations due to brief interruptions in the upstream plants which could be the result of scheduled or unscheduled maintenance or due to operating problems. Since byproduct sulfur is not produced, no sulfur facilities are provided.

Interconnecting Piping System – It includes the interconnecting process and utility piping between process plants and offsites. All above ground and underground piping systems are included except i) the cooling water piping which is included in the relevant Cooling Water section, and ii) the fire water piping which is included in the Fire Systems. Relief and blowdown headers are included. In general, water distribution piping is underground and all other piping is located above ground on pipe racks. Storm sewers, sanitary sewer and process wastewater lines are included in the, Sewers and Wastewater Treating system.

Product Shipping provides the pipeline, pumping and metering systems for delivery of the final hydrocarbon products. Separate systems are provided for each of the hydrocarbon products.

Dual meters are provided to assure proper recording and product delivery.

Tank Car/ Tank Truck Loading – This offside provides the tank car and truck loading racks for the hydrocarbon products. Catalyst unloading blowers also are provided to transfer the catalyst from the road receiving point to the storage silo.

Catalyst and Chemical Handling – It provides storage and handling for the catalyst and chemicals used in all the plants. Additionally, it provides a consolidated location for tracking catalyst and chemical start-up and daily consumption requirements. This plant includes an enclosed warehouse for storage and forklifts for transporting pallets into or out of the warehouse.

Electrical Distribution System - Provides the electrical distribution system from the 115 kV high voltage switchyard to the consuming locations.

Raw Cooling and Potable Water – It takes raw water from a nearby lake and provides raw water treatment consisting of water clarification, gravity filtration, potable water chlorination, demineralization.

The clarified water is used for cooling tower makeup, firefighting and utilities. A packaged potable water system is used to treat the water used for drinking, food preparation and sanitary facilities. Clarified and filtered water is the feed to this packaged potable water system. The boiler feed water is clarified, filtered and demineralized.

Fire Protection System - A comprehensive fire water system is provided for general fire protection of the entire plant. Chemical and steam fire suppression systems are provided for specific facilities and equipment. These systems include: fire water to process plants, water and waste treatment, and tankage; fireproofing for vessel supports, pipe racks, etc.; sprinkler systems for buildings, parts of the process equipment such as pumps or heat exchangers, and tank truck and tank car filling racks; smothering steam for compressor buildings and fired heaters; halogen system for computer room and laboratory.

Sewage and Effluent Water Treatment - It provides segregated waste water treatment for the purpose of minimizing both raw water consumption and effluent discharge to public waters during normal plant operation. Waste water streams are segregated on the basis of their compatibility and treated as necessary to make them suitable for reuse, if practical, in lieu of fresh water.

The majority of the water used in the project eventually goes to the atmosphere as water vapor. Some water is disposed of as moisture associated with solid wastes going to landfills. Blowdown streams (cooling tower, boilers and demineralizer) are sent to an intermediate holding pond before being discharged.

This plant contains the following treatment facilities: oily wastewater treatment, process wastewater treatment, solids dewatering, sanitary sewage treatment.

Instrument and Plant Air Facilities – The Instrument and Plant Air Facilities includes all equipment necessary to supply instrument and utility air to the process plants and support facilities. The distribution piping is included in the Interconnecting Piping. Instrument and utility air is dry, oil-free and dirt-free air that is supplied at 7 barg. It has a maximum dew point of -40 °C.

Purge and Flush Oil System - It provides and delivers a light and heavy flush oil for pump seal flushing and instrument purging.

Solid Waste Management – This plant disposes of wastes from Raw, Cooling and Potable Water, and Waste Water Treatment Plants, and miscellaneous sources which include refuse and flotsam.

All the solid waste, excluding the miscellaneous plant refuse, is stored in bins and hoppers, and collected daily to minimize on-site storage. Once collected, it is transported to an approved landfill disposal site outside the battery limits in trucks.

General Site Preparation – The plant is located in Southern Illinois at a green field location with rail and road accessibility. Site preparation involves leveling the land and adding basic improvements such as roads, fencing and drainage needed by the plant as a whole, and the placement of high load-bearing fills, pilings, spread footings and mat foundations for the plant structures in accordance with individual needs.
Drainage of contaminated rain runoff from process and offsite areas is directed to ponds for treatment. Uncontaminated storm runoff from building roofs, parking lots, outdoor storage areas, and uncontaminated process plant areas is routed to the raw water storage pond.

Buildings - Five different types of buildings are provided for different usages. The type of construction selected for each building is dependent on its location with respect to potential hazards, its criticality for plant operation, and its function. The five types of buildings are classified as types A, B, C, D or Administrative according to the major construction features. Type A buildings are blast-proof and house critical equipment and/or instrumentation for the continuous operation of the plant. Type B buildings house the plant laboratory, cafeteria, medical building and change house. Type C buildings are steel-framed structures which serve a number of diverse functions which are generally plant operations or maintenance related. Type D buildings have masonry walls and structural steel-framed roofs and are used for transformer shelters and chemical storage. The administration building (which also contains the computer room) is identical in construction to a Type B building except that the exterior is finished with brick veneer masonry.

Telecommunications System – This plant includes the equipment and wiring for communication throughout the plant, to offsite locations linking plant data processing systems with offsite computing facilities, and for communication with transportation carriers. It provides: interconnecting cables, standby emergency power and grounding; remote computer access; facsimile; fire alarm; public address paging; medical emergency and life-signs telemetry; interplant part paging; land mobile radio paging; security system; telephone.

Distributed Control System and Software – It provides for the distributed control system and operator interface in one central control system except for the shipping and loading facilities which are located at the shipping and loading building.

The main inlet/outlet streams of the described GTL-FT plant and the relevant key performance parameters, as per "[MS1], detailed KPIs identified, defined and calculated for the benchmark technology" issued by UNIMAN, are listed in tables 12 through 15.

Table 12 – Syngas Generation Main Streams

			NG Feed	Enr. Air	W. Water	Fuel Gas	SynGas	HP Steam	Flue Gas
	MW	LHV							
Vapor Phase	kg/kmol	MJ/kmol	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h
N2	28,0	0,0	28,9	4311,0	0,00	1,18	4339,9	0,00	1810,0
O2	32,0	0,0	0,0	2873,8	0,00	0,00	0,00	0,00	62,7
CO2	44,0	0,0	35,4	0,00	0,00	1,45	466,8	0,00	212,9
Ar	39,9	0,0	0,00	0,00	0,00	0,00	0,00	0,00	0,00
H2	2,02	242	0,00	0,00	0,00	0,00	8695,7	0,00	0,00
CO	28,0	283	0,00	0,00	0,00	0,00	4325,3	0,00	0,00
H2S	34,1	518	0,00	0,00	0,00	0,00	0,00	0,00	0,00
COS	60,1	607	0,00	0,00	0,00	0,00	0,00	0,00	0,00
CH4	16,0	801	4717,9	0,00	0,00	192,96	417,7	0,00	0,00
C2H6	30,1	1427	157,4	0,00	0,00	6,44	0,00	0,00	0,00
C3H8	44,1	2043	26,9	0,00	0,00	1,09	0,00	0,00	0,00
iC4	58,1	2658	4,0	0,00	0,00	0,18	0,00	0,00	0,00
nC4	58,1	2658	5,0	0,00	0,00	0,18	0,00	0,00	0,00
C5's	72,2	3292	5,0	0,00	0,00	0,18	0,00	0,00	0,00
C6's	86,2	3889	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Steam	18,0		0,00	0,00	0,00	0,00	82,6	7951,84	455,00
Total kmol/h vapor phase			4980,4	7184,8	0,00	203,7	18328,1	7951,8	2540,6
Liquid Phase									
H2O			0,0	0,00	4141	0,00	0,00	0,00	0,00
Heat Rate [MJ/h]			4.101.220	31.289	12.677	167.635	3.662.222	239.054	24.272,6
Total Stream [kmol/h]			4980,4	7184,8	4141	203,7	18328,1	7951,8	2540,6
Stream Temperature [°C]			29,4	153,5	65,6	29,4	61,1	259	270
Stream Pressure [bar abs]			50,4	45,8	37,2	6,9	36,5	45	1,01
Stream MW [kg/kmol]			17,04	29,61	18,02	17,04	15,77	18,02	27,7
Total Stream kg/h			84866,7	212743,2	74628,3	3470,5	289034	143292	70376

Table 13 – Fischer Tropsch Synthesis Main Streams

Component	LHV	Syngas Feed	Syngas to PSA	Syngas to FT	H_2 to Hydrock.	Unconv. Syngas	HC to Fractionation	H2O to WWT	LP Steam	Distillate	Naphtha	Fuel	Flue Gas
	MJ/kg	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
H2	120,0	17529	241	17355	174	2073	2,27	0,00	0,00	0,00	0,00	3,63	0,000
N2	0,00	121619	1673	121600	24	121347	198,68	10,88	0,00	0,00	2,27	265,81	6709
O2	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	255
CO	10,1	121155	1667	121155	0,00	18388	50,80	2,27	0,00	0,00	0,91	63,50	0,000
CO2	0,00	20541	283	20542	0,00	22320	271,25	17,2	0,00	0,00	27,67	270,35	1721
H2O	0,00	1489	20	1484	0,00	71	155,13	65655	268395	9,98	8,62	6,35	876
CH4	50,0	6701	92	6701	0,00	9052	39,46	0,45	0,00	0,00	2,27	51,26	0,000
C2H4	47,20	0	0	0	0,00	9	0,00	0,00	0,00	0,00	0,00	0,00	0,000
C2H6	47,5	0	0	0	0,00	428	6,35	0,00	0,00	0,00	1,36	14,06	0,000
C3H6	45,8	0	0	0	0,00	583	23,13	0,00	0,00	0,00	6,80	19,05	0,000
C3H8	46,3	0	0	0	0,00	538	24,49	0,00	0,00	0,00	72,6	222,72	0,000
iC4H8	45,1	0	0	0	0,00	30	3,63	0,00	0,00	0,00	2,7	1,81	0,000
nC4H8	45,2	0	0	0	0,00	579	68,04	0,00	0,00	0,00	51,26	31,75	0,000
iC4H10	45,7	0	0	0	0,00	31	3,18	0,00	0,00	0,00	5,44	6,35	0,000
nC4H10	45,7	0	0	0	0,00	572	79,38	0,00	0,00	0,00	69,9	35,38	0,000
C5's	45,6	0	0	0	0,00	1509	576,98	0,00	0,00	0,00	1339	53,98	0,000
C6-C10	44,9	0	0	0	0,00	1269	10119,36	0,00	0,00	2250	8919	9,98	0,000
C11-C19	43,4	0	0	0	0,00	0	16497,43	0,00	0,00	24110	3216	0,00	0,000
Wax		0	0	0	0,00	0	16096,45	0,00	0,00	2933	0,0	0	0,000
Oxygenates	29,7	0	0	0	0,00	8	16,33	157	0,00	0,00	16,3	7,26	0,000
Total Flow Rate [kg/h]		289034	3976	288837	197,8	178809	44232	65843	268395	29303	13742	1063	9561
Heat Rate [MJ/h]		3662222				45.852			537.139			22.048	3233
Total Stream [kg/h]		289034	3976	288837	197,8	178.809	44232	65843	268395	29303	13742	1063,2	9561
Stream Temperature [°C]		61,1	61,1	66,1	43,3	21,1	94,7	68,3	232	1,24	37,8	43,3	270
Stream Pressure [bar abs]		36,5	36,5	36,5	34,5	22,1	6,9	1,5	10,3	37,8	1,52	5,2	1,01
Stream MW [kg/kmol]		15,8	15,8	15,8	2,27	24,87	175,1	18,04	18,02	209,7	107,0	33,47	28,52
Total Stream kmol/h		18328	252	18244	87,1	7189,7	252,7	3650	14894	139,7	128,4	31,77	335,2

Table 14 - Gas to Liquid Fischer-Tropsch - Key Performance Indicators

Feedstock Pre-Treatment

Feedstock Yield		Purification			Overal Consumption
$y_{feedstock}$	h_{carbon}	w_{dry}	w_{wet}	$waste_{pur.}$	$e_{I,FP}$
kg_c/kg_{raw}	kmol/kmol	%mass	%mass	kg_i/kg_{clean}	MJ/kg_{H2+CO}
1,00	1,00	100	100	0,000	0,000

Syngas Generation

Syngas				Consumptions									
Yield			Purity	Electric Energy		Fuel		Steam			Oxygen	Overall Energy	
y_{mass}	y_{mol}	CGE	x_{syngas}	L_{el}	l_{el}	GLHV	g	$Q_{H2O,j}$	q_j	q_j	k_{O2}	$h_{I,SG}$	$h_{II,SG}$
kg_i/kg_{feed}	kmol/kmol	-	%	MW_{el}	MJ/kg_{H2+CO}	MW_{LHV}	MJ/kg_{H2+CO}	MW	MJ/kg_{H2+CO}	kg/kg_{H2+CO}	kg/kg_{H2+CO}	MJ/kg_{H2+CO}	MJ/kg_{H2+CO}
1,63	2,61	0,89	71,4	85,6	2,22	47	1,21	-66,4	-1,7	-1,03	0,40	31,3	32,57

Fuel Synthesis

Syncrude yield				Consumptions								
				Electric Energy		Fuel		Steam		Hydrogen	Overall Energy	
$y_{mass, FT}$	h_{carbon}	$y_{gasoline}$	y_{diesel}	L_{el}	l_{el}	GLHV	g	$Q_{H2O,j}$	q_j	kH_2	$h_{I,SG}$	$h_{II,SG}$
kg/kg_{feed}	kmol/kmol	kg/kg_{feed}	kg/kg_{feed}	MW_{el}	MJ/kg_{H2+CO}	MW_{LHV}	MJ/kg_{H2+CO}	MW	MJ/kg_{prod}	kg/kg_{prod}	MJ/kg_{prod}	MJ/kg_{prod}
0,149	0,587	0,048	0,101	3,08	0,26	6,12	0,51	-149,2	-12,5	0,0046	72,3	71,1

Overall System

h_{carbon}	$h_{products\ (*)}$	h_{el}	$y_{naphtha}$	y_{diesel}	c_I	c_{II}	e_{CO2}	e_{CO2tot}
kmol/kmol	$MJ_p/MJ_{f\&f}$	MJ_{el}/MJ_f	kg/kg_{feed}	kg/kg_{feed}	MJ/kg_{prod}	MJ/kg_{prod}	ton_{CO2}/ton_{prod}	ton_{CO2}/ton_{prod}
0,564	0,513	0,071	0,162	0,345	92,1	87,45	0,559	0,559

(*) Electric power to export factored in as product

The capital expenditure break down worked out for this plant is reported in the following table, while the share of the each process unit making up the ISBL is given in Figure 23.

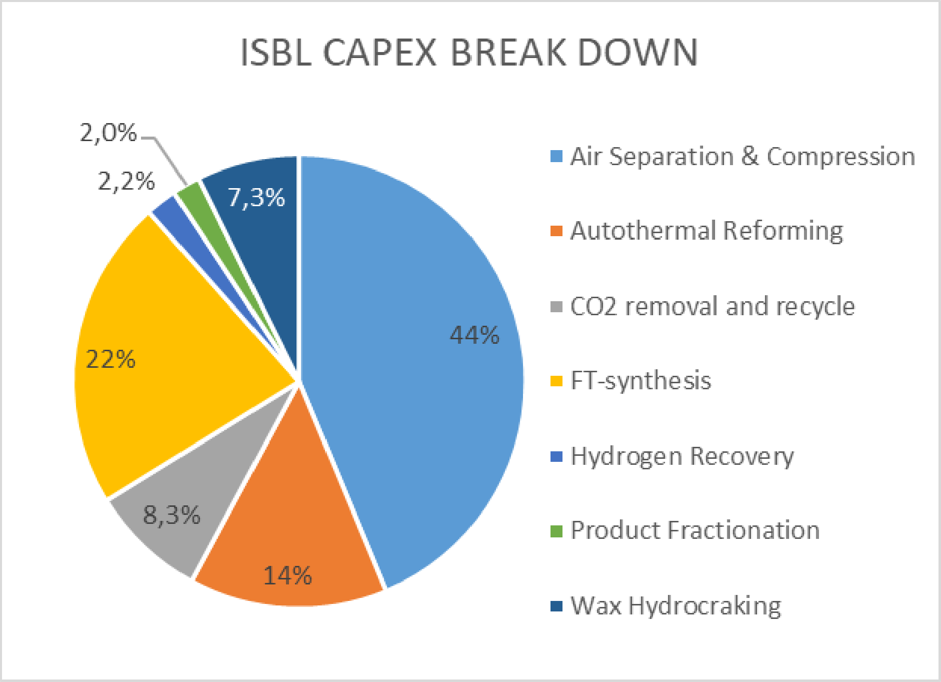


Figure 24 - Once through GTL- FT plant ISBL Cost Break Down

Table 15 – GTL economic performances

Economic Performance			
Capital costs [MM$]		**Operating Costs** [MM$]	
Inside Battery Limits	161	Natural Gas	13,7
Outside Battery Limits	175	Capital Servicing	20,6
Combined Cycle Plant	55	Maintenance & Ins.	4,58
Other offsides	120	Insurance	1,14
EPC contractor fee (8% ISBL+OSBL)	26,9	Labor	3,43
Contingency (10% ISBL+OSBL)	33,6	Overheads	2,40
Owner Costs (15% TFCC)	69,9	General Expenses	11,4
Total Fixed Capital Cost	466	Total Annualized Cost	57,3
Break Even COE [$/barrel]	18,8	**Cost of Production** [$/ton]	1.332

With the 1998 price of natural gas at 0,5 $/MMBtu, and the electrical power priced at 30 $/MWh, the crude oil equivalent (CEO) at the break-even point corresponding to the investment shown in the Table 15 was 18,8 $bbl.

At the time the economic viability was assessed for this once through FT-process, the crude oil had long been in bearish market. Indeed, its price action topped a price hikes at more than 120 $/bbl in 1980. Since then it deeply dived till 17,54 $/bbl after having violated the price support at $26,1 (the red thick line in Figure 10) level and the historical low at $20,8.

Figure 25 – Crude Oil Prices History Charts. *Source: Megatrends.net*[23],

Eventually, the oil trend became finally bullish – orange circle – only in 2002, when the price broke with increasing traded volumes the descending trendline. At the time of the final investment decision, the WTI price was less than plant break-even point and because of the trendless pattern of the oil price action, a rise in the crude oil could not be expected. The project did not pan out.

With today's commodities price levels – 2,7 $/MMBtu for natural gas, 22,3 $/MWh for EE - and adjusting the total plant to take into account the escalation of plant costs up to 2019 as per CEPCI methodology, the COE for the above design would be more than 125 $/bbl.

All in all, it can be concluded that the economics of a Fischer Tropsch plant is strongly correlated to the price dynamics of crude oil, and thus is subject to the typical cyclic nature of the crude oil market. The above spells that the B/E point expressed in terms of CEO or BOE is an important key performance indicator for the economic viability of a FT-process plant.

13.2 Gas-to-Liquid medium scale FT plant

A medium scale plant is also presented as benchmark plant used for the production of gasoline and kerosene through GTL process.

Methodology

The plant has been modelled to represent an industrial benchmark GTL facility for the production of kerosene and gasoline. The size selected for the facility is of **51000 bbl/d of final products, representative of a medium plant.**

The technology for syngas production for a size of this type is the ATR with an adiabatic pre-reformer, both for the affordability and energetic efficiency reached. For kerosene and gasoline production, fixed bed LTFT based on cobalt catalyst is one the best. LTFT cobalt catalyst based leads to a heavy paraffinic syncrude with a very low amount of aromatics and oxygenates, ensuring high activity that allows to reach high conversions.
The process that best fits LTFT for kerosene and gasoline production is the Hydrocracking. Hydrocracking process allows to achieve both cracking of heavier hydrocarbons and hydroisomerization to improve the cold flow properties and cetane number.

In the process modelling, different assumptions have been made on the different parts of the system. Among others, Fischer Tropsch and Hydrocracking are the most complex processes to be modelled on Aspen Plus. In fact, since the amount of reactions and species involved is very high, the kinetics are complex and today still debated.

Plant description
The natural gas input of the overall plant is 117.51 kg/s, this value has been kept constant for all the cases. In particular, it has been investigated the effect of the internal recycle and the effect of the position of the MDEA system, to the internal capture of CO_2, in different parts of the plant. In fact, from the syngas production section, a not negligible quantity of CO_2 is produced. With the internal and the external gas loop, it will built-up in the FT reactor, increasing the inert gases content in the feed.

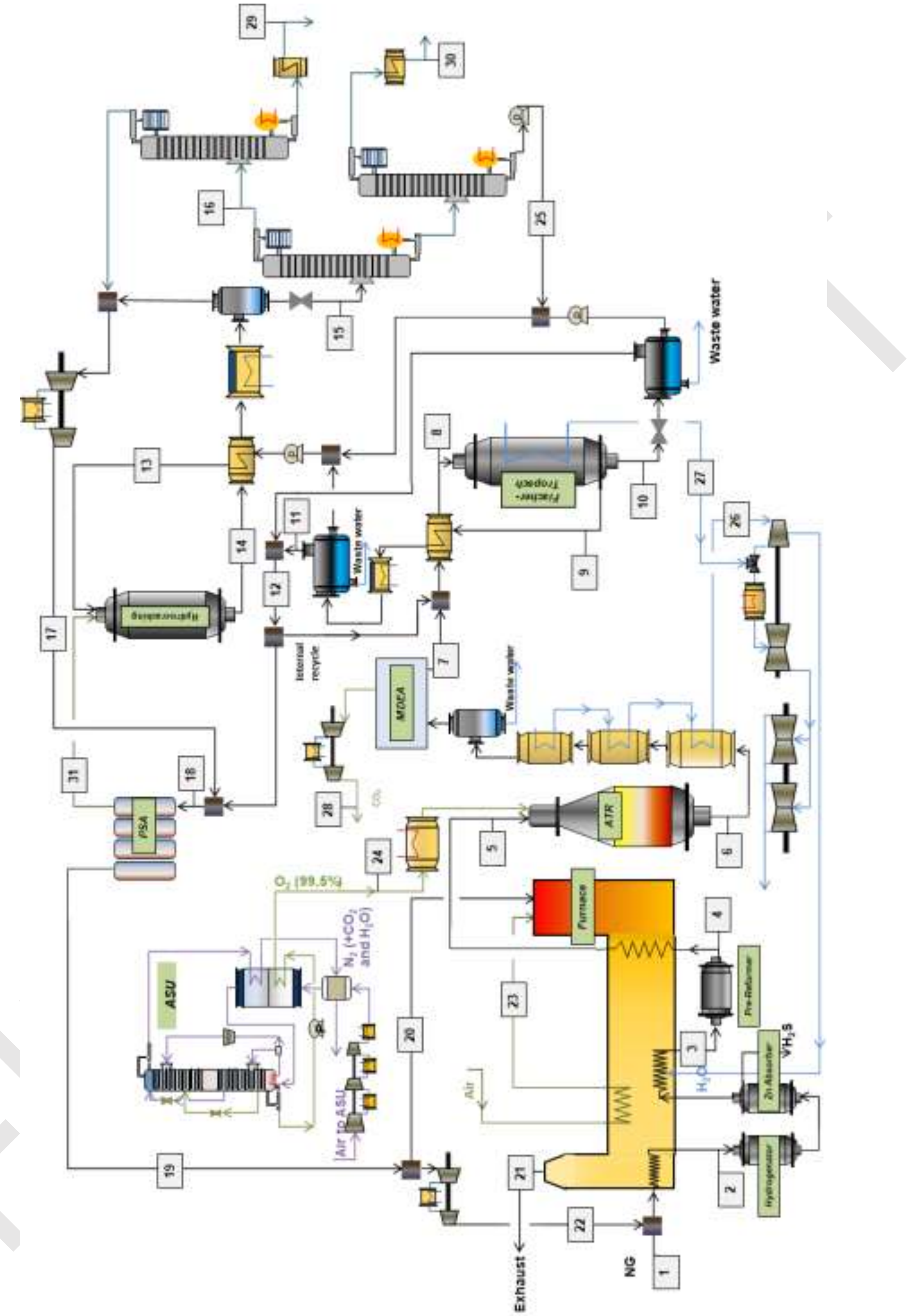


Figure 26 – Scheme of benchmark GTL process FT

Table 16: mass balances and main thermodynamic points referred to figure 26

	P	T	n	m	Composition (vol%)										
#	bar	°C	kmol/s	kg/s	$N_2 + Ar$	O_2	H_2O	H_2	CO	CO_2	CH_4	$C_2{-}C_4$	$C_5{-}C_{10}$	$C_{11}{-}C_{19}$	C_{20+}
1	31	15	6.52	117.51	0.01					0.02	0.89	0.08			
2	30	280	7.55	136.44	0.02			0.06	0.04	0.02	0.78	0.08			
3	30	450	11.85	214.01	0.01		0.36	0.04	0.03	0.01	0.50	0.05			
4	30	483	12.34	212.01	0.01		0.29	0.07		0.05	0.58				
5	30	680	12.34	212.01	0.01		0.29	0.07		0.05	0.58				
6	30	1100	26.32	345.15			0.17	0.53	0.25	0.04	0.01				
7	26	30	21.02	225.18	0.01			0.66	0.32		0.01				
8	25	200	37.28	485.09	0.0			0.59	0.29	0.01	0.04	0.03			
9	22.5	220	24.98	457.88	0.05		0.25	0.36	0.19	0.02	0.07	0.04	0.01	0.01	
10	22.5	220	0.11	27.21			0.11	0.01	0.01		0.01	0.01	0.03	0.26	0.56
11	22	42	18.47	295.28	0.07			0.48	0.27	0.02	0.09	0.05	0.01		
12	26	57	18.53	295.32	0.07			0.48	0.27	0.02	0.09	0.05	0.01		
13	47.5	375	0.89	156.17			0.01		0.01			0.05	0.22	0.62	0.08
14	46	356	9.03	172.56				0.88					0.06	0.06	
15	1.6	163	1.09	153.75			0.01	0.03				0.02	0.47	0.47	
16	1.2	95	0.40	33.56			0.02	0.08				0.06	0.84		
17	36	31	7.97	19.14				0.99				0.01			
18	36	33	10.19	54.47	0.01			0.88	0.06	0.01	0.02	0.01			
19	2.1	33	2.05	38.07	0.08		0.01	0.42	0.28	0.03	0.10	0.07	0.02		
20	2.1	33	1.03	19.03	0.08		0.01	0.42	0.29	0.03	0.10	0.07	0.02		
21	1.1	138	9.07	258.19	0.73	0.07	0.11			0.08					
22	31	101	1.04	19.44	0.08		0.01	0.41	0.29	0.03	0.10	0.07	0.02		
23	1.2	450	8.29	239.16	0.79	0.21									
24	30	30	4.09	131.14	0.005	0.995									
25	48	239	0.39	76.51										0.98	0.02
26	100	478	14.17	255.22			1								
27	19	230	22.93	413.03			1								
28	120	70	0.94	41.40						1					
29	1.01	15	0.25	25.03									1		
30	1.01	15	0.30	43.66									0.58	0.42	
31	34	33	8.13	16.40				1							

The natural gas (stream #1) enters the system with a pressure of 31 bar and it is mixed with the external recycle (stream #22), containing unconverted syngas and light hydrocarbons from the FT synthesis and separation section. The H_2 needed for the purification of gas in the hydrogenator reactor is supplied by the external recycle. Here, the amount of H_2 mixed with the gas flow is in excess (6%), as this will help the purification process. The hydrogen must be added before the gas flow is heated to avoid thermal decomposition of S compounds. The flow is preheated to 280 °C (stream #2) and sent to the purification system in which, through a hydrogenator reactor and a ZnO absorber, all the impurities are removed. The gas flow is now heated and mixed with steam (stream #3) spilled from the HP steam turbine at a pressure of 30 bar.

The flow, at 450 °C, is sent to the adiabatic pre-reformer in which all the heavier hydrocarbons are reformed.

All the higher hydrocarbons have been converted to CH_4, H_2 and CO. In this way, it is possible to increase the temperature of the stream without the risk of thermal cracking and reducing the amount of oxygen required in the ATR process. The flow is now heated to 680 °C and sent to the ATR reactor (stream #5). Before entering, it's gradually mixed with the oxygen (stream #24) to achieve a turbulent diffusion flame in the combustion chamber of the reactor. The oxygen is produced in the ASU by a cryogenic distillation of the air, in a series of nested columns. The inlet S/C ratio is 0.45, this value is much lower than the one typical of conventional reforming process, giving a high economic convenience to the process. In general, this value can be further reduced, but here it needs to have the desired H_2/CO ratio of the produced syngas, that is 2.09. The resulting O_2/CH_4 ratio is 0.57, with a CH_4 conversion of 98%. The produced syngas has, at the outlet of the reactor, a temperature of 1100 °C (stream #6).

The syngas is now cooled down to 30°C into different section of the syngas cooler.
Once that the syngas has been cooled down to 30 °C, the water fraction is removed by means of an adiabatic flash at a pressure of 26 bar. The dried syngas has a CO_2 fraction of 4.5% (mol) that is formed in the reforming process. To avoid high concentrations of CO_2 in the internal gas loop and hence in the FT reactor, which will behave as an inert gas, it is removed through a MDEA system. The amount of CO_2 captured depends by the MDEA removal efficiency, which it has been assumed 94%. The separated CO_2 flow (stream #28) is then compressed to 120 bar and sent to sequestration.

After the removal of CO_2, the syngas (stream #7) can be converted in the FT process.
The syngas is mixed with the internal recycle flow (same composition of stream #12) and heated up to 200 °C (stream #8). The internal recycle is the so called "internal gas loop", in which part of the light gases from the outlet of FT reactor are recycled internally to increase the overall syngas conversion. In fact, the internal recycle is mainly constituted by unconverted syngas. The H_2/CO ratio of the internal recycle is 1.92, this value is lower than the inlet because there is a higher

consumption of hydrogen in the FT process. The resulting H_2/CO ratio at the inlet of the FT reactor is between 2 and 2.05.

The FT process conditions selected are listed below:

- The reactor has been considered isothermal at 220 °C.
- The inlet pressure is 25 bar, with a pressure drop of 2.5 bar (10%).
- A syngas hourly space velocity (GHSV) of 2000 $cm^3(STP)/g_{cat}/h$.

The inert gases fraction at the inlet of the reactor is the 12%. As inert gases, it's considered: N_2, Ar, CH_4, CO_2 and light hydrocarbons.

The syngas per pass conversion achieved is about 55% with a chain growth probability α> 0.9. The result is that the produced syncrude is formed mainly of heavy hydrocarbons with a selectivity to C_{5+} products of about 0.9.

All the heat generated by the exothermic FT reactions is removed by boiling water, at IP (19 bar), that surrounds all the tubes of the reactor (stream #27).

At the outlet of the FT reactor, the products are collected in two different streams: one in liquid phase (stream #10), composed by waxes, and the other in vapor phase (stream #9), composed by lighter products. The first one is laminated to 2 bar and cooled to 30 °C, while the second one is only cooled to 30 °C, and then both are sent in two decanters. In each decanter it's possible to separate the flow in three different phases: pure liquid water, liquid hydrocarbons and gaseous hydrocarbons:

- The water phase is sent to a water treatment process where it's purified from the remaining contaminants;
- The two gaseous flows (one is the stream #11), in which all the unconverted syngas and the lighter hydrocarbon are collected, are compressed to 26 bar and mixed together (stream #12). The resulting flow is mainly (88%) recycled to the FT reactor, in the internal gas loop (the *internal recycle*), while the remaining part is sent to the PSA to recover part of the hydrogen necessary for the plant;
- The two liquid streams, made mainly of waxes and medium hydrocarbons ($C_5 - C_{15}$), are pumped to 48 bar and sent to the refining process.

Since the fraction of the light gas flow, at the outlet of the FT reactor, recycled in the FT internal gas loop is really high (88%), it is possible to reach an overall syngas conversion in FT reactor of 92%.

The refining section consists of a Hydrocracking unit with three downstream distillation columns preceded by a flash.

The liquid hydrocarbons (stream #13) are heated up and sent to the hydrocracking reactor. The working conditions of the process, as reported in Appendix C, are:

- Inlet pressure 47.5 bar
- $H_2/\text{waxes} = 0.105$ wt basis
- Inlet temperature of 375 °C

The great amount of H_2 fed (stream #31) allows to operate with a great excess, which is fundamental to avoid secondary cracking reactions and achieve the desired products. The overall hydrocracking process is slightly endothermic (outlet temperature 356 °C): this is due to the opposite effect of the cracking reactions, that are endothermic, and the isomerization reactions, that are exothermic. After the hydrocracking, in which all the heavy paraffins have been cracked and isomerized (stream #14), the outlet stream is cooled down to 30 °C and sent to an adiabatic flash operating at a pressure of 43.5 bar. The heat released during the cooling is used to heat up the inlet flow at the hydrocracking and the liquid stream that is separated in the flash. In fact, after the flash, the liquid stream, that contains all the hydrocarbons that will constitute the final products, is heated up and laminated to a pressure of 1.3 bar before entering the first distillation column (stream #15).

The distillation columns are operated near atmospheric pressure in order to reduce the energy cost and, most of all, to avoid the thermal cracking of higher hydrocarbons that could take place at temperatures above 280 °C.
In the Table 17, it’s possible to find the main operating conditions of the distillation columns.

Table 17: Main results and operating conditions of distillation columns

Distillation columns	1	2	3
N stages	50	27	50
Reflux ratio [mol basis]	1	2	0.2
Distillate to feed ratio	0.36	0.38	0.43
Condenser			
P [bar]	1.2	1.1	1
T [°C]	95.1	44.7	191.5
Heat duty [MW]	14.5	9.5	3.3
Reboiler			
P [bar]	1.3	1.2	1.1

T [°C]	200.8	95.9	236.8
Heat duty [MW]	27.9	0.8	21.6

The light stream, coming from the flash and the second column (stream #17), is mixed with part of the light stream that is not recycled into the FT (12%) and compressed. This stream (stream #18) has a pressure of 36 bar and, since is mainly constituted by H_2 coming from the hydrocracking and from the not reacted syngas, is sent to a PSA in order to recover all the H_2 that is necessary for the hydrocracking process. The PSA works with an H_2 recovery of 90% .

The H_2 recovered by the PSA (stream #31) is compressed and then sent to the hydrocracking unit at 47.5 bar. The off-gas, from the PSA, (stream #19) is split in two different streams: the first is used as fuel gas (stream #20) while the second is compressed and mixed with the natural gas (stream #22). The fuel gas, having a LHV of 25.3 MJ/kg, is burnt with air in the furnace, providing all the heat necessary to the syngas production.

The main products obtained are paraffinic gasoline and paraffinic kerosene.
The composition and the main characteristics of the final products obtained from this plant are summarized in the Table 18.

Table 18: kerosene and gasoline composition and main properties.

Density @15 °C	kg/m^3	735
Flash point	°C	41.8
LHV	MJ/kg	40.98

Composition	mol	
C8H18		0.100
C9H20		0.264
C10H22		0.214
C11H24		0.154
C12H26		0.088
C13H28		0.021
C14H30		0.007
C15H32		0.001

Density @15 °C	kg/m^3	690
Boiling range	°C	43-166
LHV	MJ/kg	44.90

Composition	mol	
C5H12		0.023
C6H14		0.161
C7H16		0.533
C8H16		0.279

Results and discussion

In table 19 and table 20 are reported the main results of all the different configurations described.

Table 19: Summary of the energy balance and key performance indicators

Plant Configuration		GTL process
Inert gases % FT feed	mol	12.11%
LHV_{NG}	MJ/kg	46.51
NG	kg/s	117.51
Total products	bbl/d	52018.41
Gasoline	kg/s	25.03
Kerosene	kg/s	43.66
Total products	kg/s	68.69
$\dot{m}_{CO_2}$ captured	kg/s	41.39
Gross power	MW_{el}	601.66
ASU	MW_{el}	115.64
Utilities consumption	MW_{el}	59.47
Net power	MW_{el}	426.56
Key Performance Indicators		
η_{carbon}		76.26%
$\eta_{products}$	$\frac{MJ_{products}}{MJ_{fuel\,\&feed}}$	53.3%
η_{el}	$\frac{MJ_{electric}}{MJ_{fuel\,\&feed}}$	7.8%
c_I	$\frac{MJ}{kg_{products}}$	73.34
c_{II}	$\frac{MJ}{kg_{products}}$	68.85
e_{CO_2}	$\frac{ton_{CO_2}}{ton_{products}}$	0.472
$e_{CO_2,tot}$	$\frac{ton_{CO_2,tot}}{ton_{products}}$	-0.137

Assumption for the economic analysis

All the equipment costs were derived from different works[24],[25] as reported in table 20.

Table 20: assumption for the estimation of the total capital cost using the power law methodology

Equipment	Scaling parameter	Unit	$Capacity_{ref}$	TPC_{ref} M$	f	Year
ASU	Oxygen flowrate	kmol/s	6.49	387.7	0.89	2006
ATR including HE and compressors	Syngas flowrate	kmol/s	13.73	434.60	0.6	2007
Pre-reformer+ Furnace	Heat of reaction	MWth	245	76.35	0.67	2007
Syngas coolers	UA	MW/K	1.31	2.67	0.22	2017
ZnO reactor	NG inlet flowrate	kg/s	23.60	0.32	0.82	2007
Pressure drop blower	Flowrate	kg/s	207.51	1.14	0.72	2007
Gas Turbine	Inlet air flow	kg/s	209	40.85	0.85	2007
Steam turbine	Net power	MW	105	85.03	0.72	2007
Cooling plant unit	Heat rejected	MW_{th}	470	38.17	0.67	2017
FT reactor including upgrading section and distillation columns+PSA	Products flow rate	bbl/day	50000	704.669	1	2006
MDEA, CO_2 separation	CO_2 flowrate	kg/s	47.81	147.82	0.8	2007
MEA, CO_2 separation	CO_2 flowrate	kg/s	16.44	104.99	0.8	2007
CO_2 compressor	Power consumptions	MW	23.02	21.77	0.72	2007
Chemical looping reactors (including valves, piping, etc.)	Reactor volume	m^3	159	8.085	0.6	2017
Pumps	Specific for each pump					

Economic results

The economic performance are reported for the case where: CO_2 from syngas is separated and vented to atmosphere (no CCS), the benchmark scenario in which the pure CO_2 is not emitted and the case where the CO_2 in the flue gases from the boilers and furnace is captured using a post combustion MEA plant (Table 21).

Table 21: Economic comparison between different GTL plant integrated with CO2 capture.

		FT-SoA, no CCS	FT-SoA bench	FT-SoA High CCS
Total plant cost, x item	**M$**			
ATR (pre-ref+reforming +HE+ syngas compressor)		878.47	878.47	878.47
ASU		312.54	312.54	312.53
ZnO sulphur polisher		1.38	1.38	1.38
Blowers /fan		1.46	1.46	1.46
FT reactor + upgrading section + product separation+PSA		891.45	891.45	891.45
Gas turbine				
Compressors		31.17	31.17	31.17
Steam turbines		454.70	454.70	439.64
Pumps		1.95	1.95	1.95
Cooling plant unit		96.97	96.97	96.8
MDEA unit		152.30	152.30	152.30
MEA unit				192.52
CO_2 compression			13.12	21.27
BOP (1% Components cost)		28.22	28.36	29.90
TPC	**M$**	2850.61	2863.86	3051.19
O&OFC		570.12	572.77	610.24
TOC		3420.73	3436.63	3661.42
TASC		4036.46	4055.22	4320.48
CCF × TASC	**M$/y**	444.52	446.59	475.80
O&M fixed	**M$/y**			
Labor		57.00	57.00	57.00
Maintenance		28.26	28.39	29.93
Insurance		72.66	73.00	76.97
O&M variable	**M$/y**			
Catalyst		16.94	16.94	16.94
MDEA solvent		0.11	0.11	0.11
MEA solvent				0.22
Natural gas feedstock		295.10	295.10	295.10
Carbon tax		39.86	17.51	1.76
Total O&M cost	**M$/y**	509.91	488.03	478.02
Electricity		-182.03	-175.96	-158
Specific TASC	**k$/bbl**	77.60	77.96	83.05
COP	**$/kg**	0.416	0.409	0.429
	$/bbl	47.516	46.671	48.931

13.3 Biomass to Liquids – Fischer Tropsch Case

In 2008, Kreutz[26] et at. reported the cost estimation and the key performance indicators of a BTL-FT recycle case fed with 3581 tpd of wet, 15%w moisture level, biomass (switchgrass) corresponding to a plant energy input of 548 MW_{LHV}. The project was in the groove of U.S. Department of Energy search of solutions for addressing the Country energy policy.

The biomass characteristics are reported in the below Table 22:

Table 22 - Switchgrass properties

Proximate Analysis (weight %)

Fixed Carbon (w%)	Volatile Matter (w%)	Ash (w%)	Moisture (w%)	LHV (MJ/kg)	HHV (MJ/kg)
18,1	61,6	5,3	15	14,509	15,935
Ultimate Analysis (w%, dry basis)					
Cabon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
46,96	5,72	40,18	0,86	0,09	6,19

The design FTL output capacity of the BTL-FT systems is 4400 bbl/day of gasoline and diesel.

The plant configurations, which include the option of carbon dioxide capture and storage (CCS), is shown in Figure 27. The plant front-end consists in the chopping of herbaceous feedstock followed by feeding via lockhoppers (using CO_2 as the pressurizing gas).

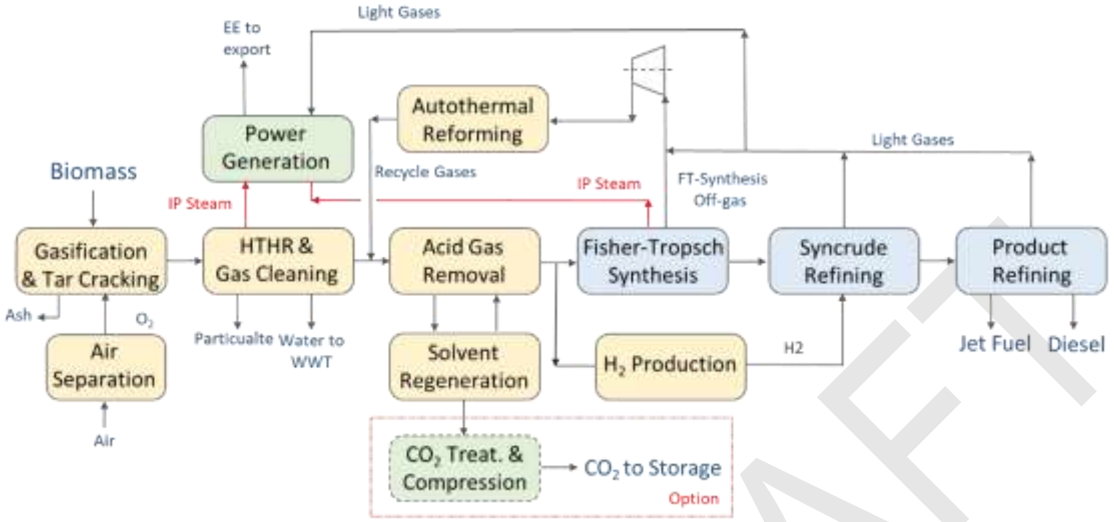


Figure 27 – Biomass to Liquid Process Set up

The gasification section is made of oxygen/steam blown fluidized bed gasifier operating at about 30 bar g including a removal unit of entrained ash and unconverted char in a cyclone, external catalytic tar cracking, and cooling.

Gasification and Tar Cracking

Syngas from biomass is provided by a dry-fed, oxygen/steam-blown fluidized-bed gasifier operating at 30 bar. The O2, 99.5% purity, is provided by an onsite air separation unit (ASU). A small amount of secondary oxygen is injected into the freeboard of the gasifier (above the bubbling fluidized bed) to promote cracking of tars and oils (heavy hydrocarbon molecules) that are produced to greater or lesser degree by all low-temperature (< 1000 °C) biomass gasifiers. Indeed, more than 90% conversion of tars and oils to CO and H2 can be achieved by this oxygen injection.

The heat released in these reactions raises the temperature of the syngas leaving the gasifier to about 1000 °C. A cyclone subsequently separates the syngas from entrained ash and unconverted char. Some ash is also removed from the bottom of the gasifier.

Following the cyclone, an external catalytic tar cracker, adiabatically operated, is used to convert any residual tar in the biomass-derived syngas to light gases. The heat needed by the endothermic cracking reactions is supplied by the gas itself, which cools down to about 800 °C. The tar-free gas is then cooled to 350 °C in a vertical firetubes (hot gas inside the tubes) waste heat boiler designed so that the deposition of small particles still in the gas ant the alkali species that condense during cooling are minimized. Particulates formed during the gasification are removed by a ceramic filter at 350 °C, with subsequent cooling of the syngas to 40°C for the syngas to be processed in the acid gas removal system (AGR).

For this BTL project, the gasification was designed to deliver a syngas with a H2:CO ration of 1.8 with no water gas shift reaction between the gasifier and the synthesis reactor.

Eventually, it is worth mentioning that in addition to the ash production, the water condensed upon cooling of the raw syngas is contaminated by hydrogen cyanide (HCN), ammonia (NH_3) and particulate constituted mostly by the soot formed by incomplete burning of the organic materials. These materials need to be removed from the water in a suitable waste water treatment.

Acid gas removal

The acid gases CO_2, H_2S, and COS contained in the syngas are removed using a Rectisol (operated at 28 bar) acid gas removal unit (using methanol as the working fluid). CO_2 is removed to improve the kinetics and economics of the downstream synthesis process. Moreover, H_2S removal as well in the AGR in order to prevent poisoning of the synthesis catalyst. Since the solubilities of acid gases in methanol increase with decreasing temperature, the Rectisol operating temperatures have to be relatively low, necessitating a refrigeration plan, which is a major electricity consumer.

As the raw syngas contains CO_2 and a low quantity of H_2S, a single column absorber design is adopted for the co-absorption of both acid gases. In this design 0.22% of input H_2, 1.2% of input CO, and 2.55% of input CH_4 are absorbed as well in methanol. These species are recovered during the riche solvent regeneration, compressed and kicked back to the main syngas flow.

CO_2 is recovered from the solvent by flashing at successively lower pressures. The H_2S is removed in a final stripping step (together with residual CO_2). The H_2S is recovered as elemental S by means of a sulfur recovery unit (SRU); alternatively, it could be co-stored underground along with the CO_2.

Fischer Tropsch Synthesis

The Fischer Tropsch designs is based on the slurry-phase F-T synthesis reactor with iron catalyst wherein the syngas is bubbled through an inert oil in which catalyst particles are suspended. The slurry phase reactor technology was chosen because it makes possible a high heat transfer, which turns out in a high extents of reaction, without excessive temperature rise. The desired mixing pattern, intimate gas-catalyst contact, and uniform temperature distribution enable a high conversion of feed gas to liquids in a relatively small reactor volume.

Syncrude Refining

By and large, most FTL systems would produce middle distillates (a mix of jet fuel and heavy diesel) plus naphtha, which would be sold as a feedstock to the chemical process industry. The production of finished gasoline blend-stock is not often considered because of the added cost and energy expenditures associated with upgrading naphtha to gasoline. In this project, however the naphtha upgrading to gasoline has been considered the focus is on understanding FTL prospects under widespread deployment conditions. Thus, the syncrude is refined into finished diesel and gasoline blend-stocks based on Bechtel design.

In the refining section, C_1-C_4 gases (light gases) are generated and separated from the liquid fraction is internally used as fuel gas. These light gases are commingled with the unconverted syngas and the off gas from the PSA; mostly of the resultant gas mixture is and recycled back to the FT synthesis, while a slipstream is directed to power generation isle.

The syncrude is distilled to split naphtha, distillate, and wax. The naphtha stream is first hydrotreated, resulting in the production of hydrogen-saturated liquids (primarily paraffins), a portion of which are converted by isomerization from normal paraffins to isoparaffins to boost their octane value. Another fraction of the hydrotreated naphtha is catalytically reformed to provide some aromatic content to (and further boost the octane value of) the final gasoline blendstock.

The distillate stream is also hydrotreated, resulting directly in a finished diesel blendstock. The wax fraction is hydrocracked into a finished distillate stream and naphtha streams that augment the hydrotreated naphtha streams sent for isomerization and for catalytic cracking.

Electric Power Generation

In this plant isle, purge gases and C_1-C_4 gases from the FTL refinery are used to generate and superheat steam and to superheat the saturated intermediate-pressure (40 bar g) steam raised in the gasification's heat recovery steam generation part and in the FT synthesis. The steam is used to produce, in a steam turbine, 66 MW of electric power. 31.6 MW of this power is used for the on-site needs and 34.4 MW is exported to the electric grid as a byproduct.

Recycle (RC) Process Designs Plants

In this design the syngas unconverted in a single pass through the synthesis reactor is recycled so as to maximize the liquid fuel production. An autothermal reformer downstream of the recycle compressor is included as part of the syngas recycle to convert $C_1 \div C_4$ gases to CO and H_2 and thereby maximize production of the desired FT liquid products (diesel and naphtha that is subsequently refined to gasoline).

Carbon Capture and Storage (CCS)

The project included also the CCS option. In this case the 113,8 t/h of CO_2 released from the Rectisol plant is supposed to be compressed at 150 barg, transported via pipeline to a site 100 km from the conversion facility, and injected for storage 2 km underground in deep saline formations.

The main inlet/outlet streams of the described BTL-FT plant and the relevant key performance parameters, as per "[MS1], detailed KPIs identified, defined and calculated for the benchmark technology" issued by UNIMAN, are listed in tables 23 through 25

.

Table 23 – Biomass to Liquid Main Streams

Component	Treated Feedstock	Oxygen to Gasifier	Char	Raw Syngas	Syngas to FT	H_2 from PSA	HC to Refining	Gasoline	Diesel	Water to WWT	IP Steam to EE Gen	CO_2 to atm
	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
CO		0,00		56064	78486	0,00	891	0,00	0,00	0,00	0,00	0,00
H2		0,00		6078	10221	177	2909	0,00	0,00	0,00	0,00	0,00
CO2		0,00		102028	3818	0,000	33059	0,00	0,00	0,00	0,00	126792
H2O	22381	0,00		26505	0,00	0,00	25947	0,00	0,00	73800	309495	0,00
CH4		0,00		6944	7733	0,00	7476	0,00	0,00	0,00	0,00	0,00
C4H10		0,00		0,00	0,00	0,00	664	0,00	0,00	0,00	0,00	0,00
C9H20		0,00		0,00	0,00	0,00	1529	8820	0,00	0,00	0,00	0,00
C15H32		0,00		0,00	0,00	0,00	844	0,00	13824	0,00	0,00	0,00
C21H44		0,00		0,00	0,00	0,00	5010	0,00	0,00	0,00	0,00	0,00
C4H8		0,00		0,00	0,00	0,00	3624	0,00	0,00	0,00	0,00	0,00
C9H18		0,00		0,00	0,00	0,00	3826	0,00	0,00	0,00	0,00	0,00
C15H30		0,00		0,00	0,00	0,00	199	0,00	0,00	0,00	0,00	0,00
Wax		0,00	0,00	0,00	0,00	0,00	11764	0,00	0,00	0,00	0,00	0,00
MEOH		0,00		0,00	261	0,00	255	0,00	0,00	0,00	0,00	0,00
O2		41551		29,7	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
N2		208,8		1119	17719	0,00	17730	0,00	0,00	0,00	0,00	0,00
H2S		0,00		348	0,00	0,00	254	0,00	0,00	0,00	0,00	0,00
Biomass	126826	0,00		0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C in Char		0,00	21401	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Total Flow Rate [kg/h]	149208	41.760	21.401	199.115	118.237	177	115.980	8.820	13.824	73.800	271.594	126.792
Energy Rate [MJ/h]	2.164.859			1.642.571	2.405.640			388080	612403		463.339	
Stream Temperature [°C]		152,1		800	245	25,00	40,00	58,50	130,0	40,00	252,00	
Stream Pressure [bar abs]		31,4		29	24,4	5,00	28,00	2,60	1,4	4,00	40,00	
Stream MW [kg/kmol]		31,98		21,43	13,09	13,12	23,3	122,5	192,0	18,01	18,01	44,01
Total Stream kmol/h		1306		9288	9036	13,49	4968	72,00	72,0	4098	15080	2880,982

Table 24 - Biomass to Liquid Fischer-Tropsch - Key Performance Indicators

Feedstock Pre-Treatment

Feedstock Yield		Purification			Overal Consumption
$y_{feedstock}$	h_{carbon}	w_{dry}	w_{wet}	$waste_{pur.}$	$e_{I,FP}$
kg_c/kg_{raw}	kmol/kmol	%mass	%mass	kg_i/kg_{clean}	MJ/kg_{H2+CO}
1,00	1,00	79,7	85	0,000	0,000

Syngas Generation

Syngas				Consumptions									
Yield			Purity	Electric Energy		Fuel		Steam			Oxygen	Overall Energy	
y_{mass}	y_{mol}	CGE	x_{syngas}	L_{el}	l_{el}	GLHV	g	$Q_{H2O,j}$	q_j	q_j	k_{O2}	$h_{I,SG}$	$h_{II,SG}$
kg_i/kg_{feed}	kmol/kmol	-	%	MW_{el}	MJ/kg_{H2+CC}	MW_{LHV}	MJ/kg_{H2+CC}	MW	MJ/kg_{H2+CO}	kg/kg_{H2+CO}	kg/kg_{H2+CO}	MJ/kg_{H2+CO}	MJ/kg_{H2+CO}
41,6	-	0,76	64,2	29,5	1,71	-	-	-45,30	-2,62	-1,54	0,67	33,9	34,77

Fuel Synthesis

Syncrude yield				Consumptions								
				Electric Energy		Fuel		Steam		Hydrogen	Overall Energy	
$y_{mass, FT}$	h_{carbon}	$y_{naphtha}$	y_{diesel}	L_{el}	l_{el}	GLHV	g	$Q_{H2O,j}$	q_j	kH_2	$h_{I,SG}$	$h_{II,SG}$
kg/kg_{feed}	kmol/kmol	kg/kg_{feed}	kg/kg_{feed}	MW_{el}	MJ/kg_{H2+CC}	MW_{LHV}	MJ/kg_{H2+CC}	MW	MJ/kg_{prod}	kg/kg_{prod}	MJ/kg_{prod}	MJ/kg_{prod}
0,114	0,511	0,075	0,117	2,50	0,14	-	-	-129	-20,5	0,0078	85,8	83,5

Overall System

h_{carbon}	$h_{products\ (*)}$	h_{el}	$y_{gasoline}$	y_{diesel}	c_{I}	c_{II}	e_{CO2}	e_{CO2tot}
kmol/kmol	$MJ_p/MJ_{f\&f}$	MJ_{el}/MJ_f	kg/kg_{feed}	kg/kg_{feed}	MJ/kg_{prod}	MJ/kg_{prod}	ton_{CO2}/ton_{prod}	ton_{CO2}/ton_{prod}
0,321	0,519	0,057	0,059	0,093	90,2	86,60	5,60	5,60

(*) Electric power to export (34 MW) factored in as product

The capital expenditure breaks down worked out for this plant is reported in the following table, while the share of each process unit making up the ISBL is given in Figure 28.

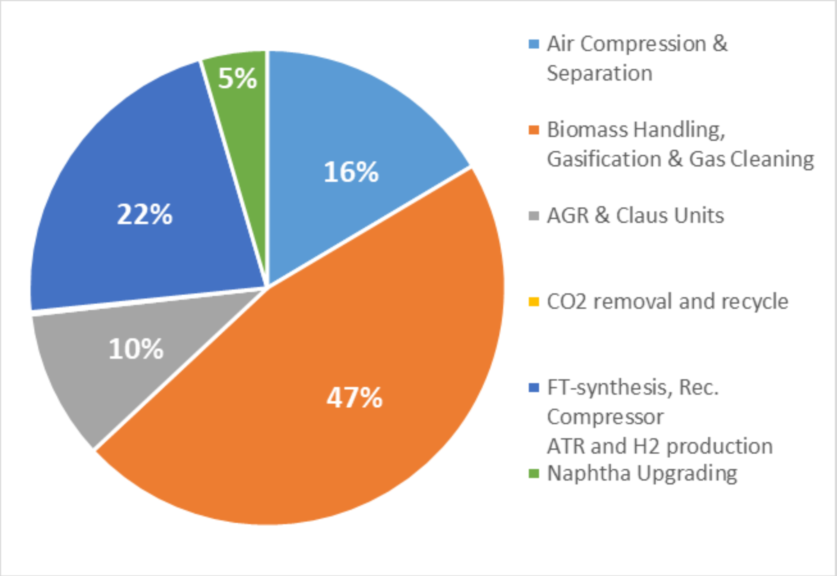


Figure 28 - Once through BTL-FT plant ISBL Cost Break Down

Table 25 – BTL Economic Performance

Economic Performance			
Capital costs [MM$]		**Operating Costs** [MM$]	
Inside Battery Limits	485	Feedstock	50,9
Outside Battery Limits		Capital Annual Charge	69,7
Power Generation	54,4	Maintenance	35,6
Other outsides	102	Insurance	17,8
EPC contractor fee (8% ISBL+OSBL)	51,3	Labor	3,77
Contingency (10% ISBL+OSBL)	64,1	Overheads	2,64
Owner Costs (15% TFCC)	134	General Expenses	12,4
Total Fixed Capital Cost	890	Total Annualized Cost	192,8
Break Even COE [$/barrel]	127,0	**Cost of Production** [$/ton]	1,038

In the scrutinized BTL-FT configuration about 51,7% of C entering the plant is vented; however, since the feedstock is a renewable (switchgrass), the overall CO_2 balance is neutral, thus in Europe said BTL-FT should not be charged with a carbon tax. As can be seen, the breakeven point of this BTL-FT is significantly higher than the current price of the crude, therefore it can be concluded that the implementation of such facilities on an industrial scale can be justified only on base of consideration other than economic.

PART IV

Existing and next to start demonstration plants: BTL & GTL

14 Existing and next to start demonstration plants

The target of benchmarking is the existing and applied processes which may considered alternative or competitive to GLAMOUR, in terms of feedstock, processing and products.
The following plant tracking is restricted to units processing biomass feedstock through gasification, producing syngas suitable for Fischer-Tropsch synthesis to liquid fuel.
Basis of tracking excludes the coal-derived feedstocks, because of the plant complexities pertinent both to feedstock containment and conditioning, and to syngas purification. GLAMOUR, using glycerol or equivalent feedstock will not be charged by the same complexities, making the comparison not practical.
On the other hand, gas (natural or other type) is also a suitable comparative feedstock, due to the similar plant configuration with GLAMOUR.
The environmental impact given by different feedstocks shall be counted in the economics.

Basis of tracking excludes products other than liquid fuels ready to be used for aviation and marine application, in line with GLAMOUR target products.
For this purpose, Fischer-Tropsch synthesis is an essential part of processing.

The basis of SN benchmarking is highlighted in the below picture, within the red box.

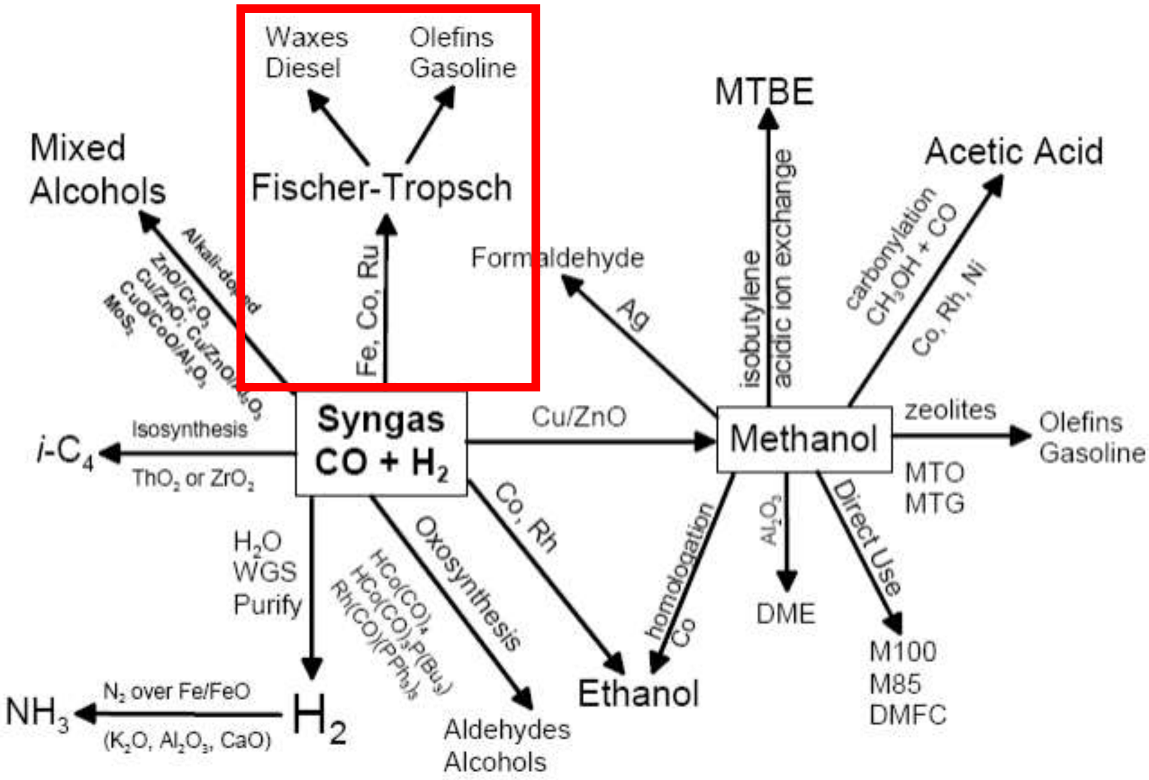


Figure 29. Basis of Benchmarking[27]

In terms of feedstock (biomass and/or waste), processes and products, the benchmark focus is summarized here below.

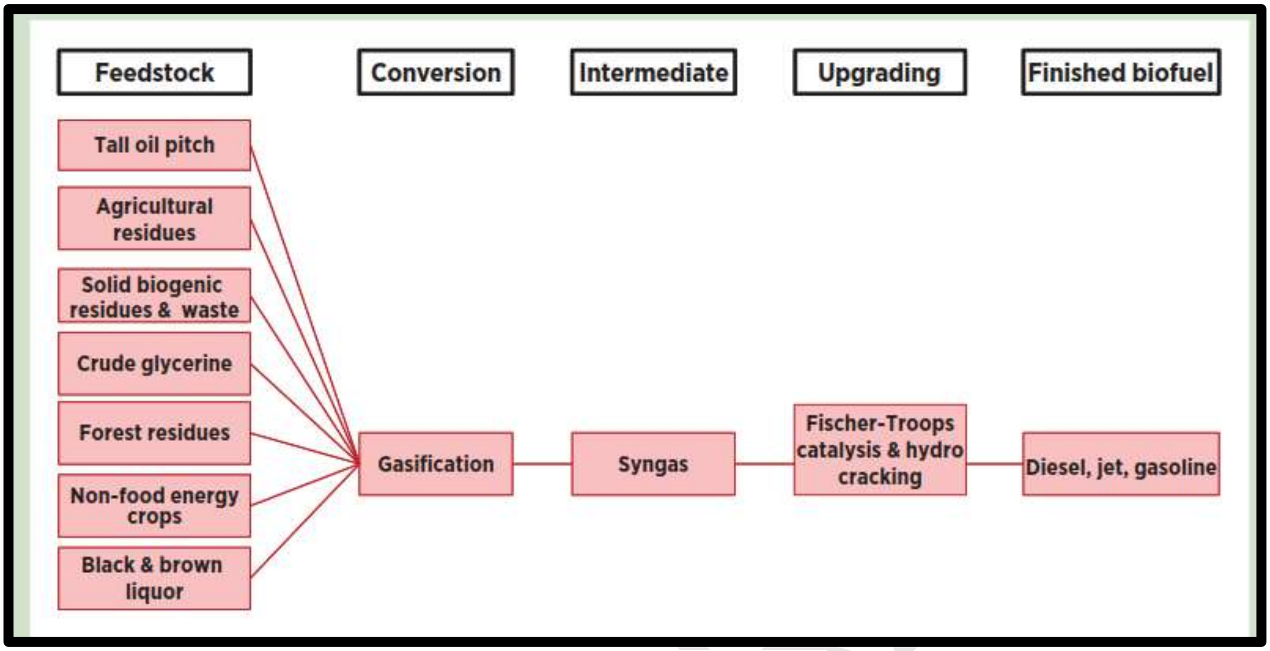


Figure 30. Benchmark focus[28]

Transport biofuels typically refer to liquid and gaseous fuels produced from biomass and are commonly classified as conventional biofuels or advanced biofuels.

There are a number of approaches to making this classification. They are based on feedstock, GHG (Green House Gases) emission savings, technology maturity, and product type and quality:

● Feedstock: biofuels produced from feedstocks that could be used as food or feed are referred to as *conventional biofuels*. Those produced from agricultural and forestry residues, organic waste and in some cases non-food or feed energy crops are defined as *advanced*. This definition aims to differentiate between biofuels produced from feedstocks that potentially compete with food or feed production and those that do not.

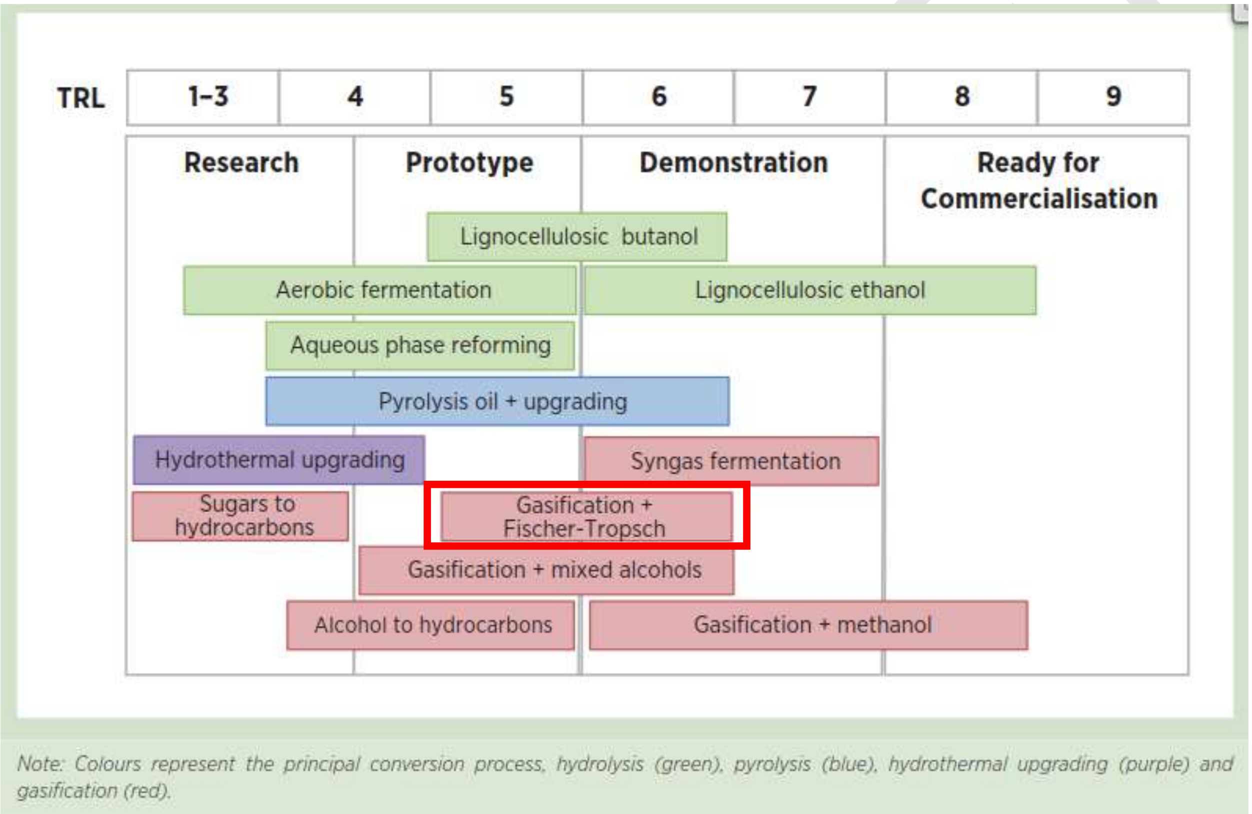
● GHG emissions savings: biofuels which achieve high GHG emissions savings are defined as advanced in comparison to biofuels which achieve GHG emission savings below a certain threshold.

● Technology maturity: conversion technologies which are widely deployed at a commercial scale are referred to as conventional. Technologies at earlier stages of development (including those in first-of-a-kind commercial plants) defined as advanced.

● Product type and quality: advanced (also referred to as ‘drop-in’) biofuels are similar to gasoline, diesel, bunker and jet fuels and can be blended in very high proportions in these fuels or used neat while meeting fuel specifications. This distinguishes them from biofuels whose properties restrict them to relatively low blends in conventional (unmodified) engines and which have limited compatibility with current fuel distribution infrastructure.

This report covers advanced liquid biofuels produced from feedstocks not derived from food or feed sources using pre-commercial conversion technologies.

The advanced biofuels pathways are at various stages of commercial development, which may be defined by Technology Readiness Level (TRL) as summarized below.



Note: Colours represent the principal conversion process, hydrolysis (green), pyrolysis (blue), hydrothermal upgrading (purple) and gasification (red).

Figure 31. Stages of development[28]

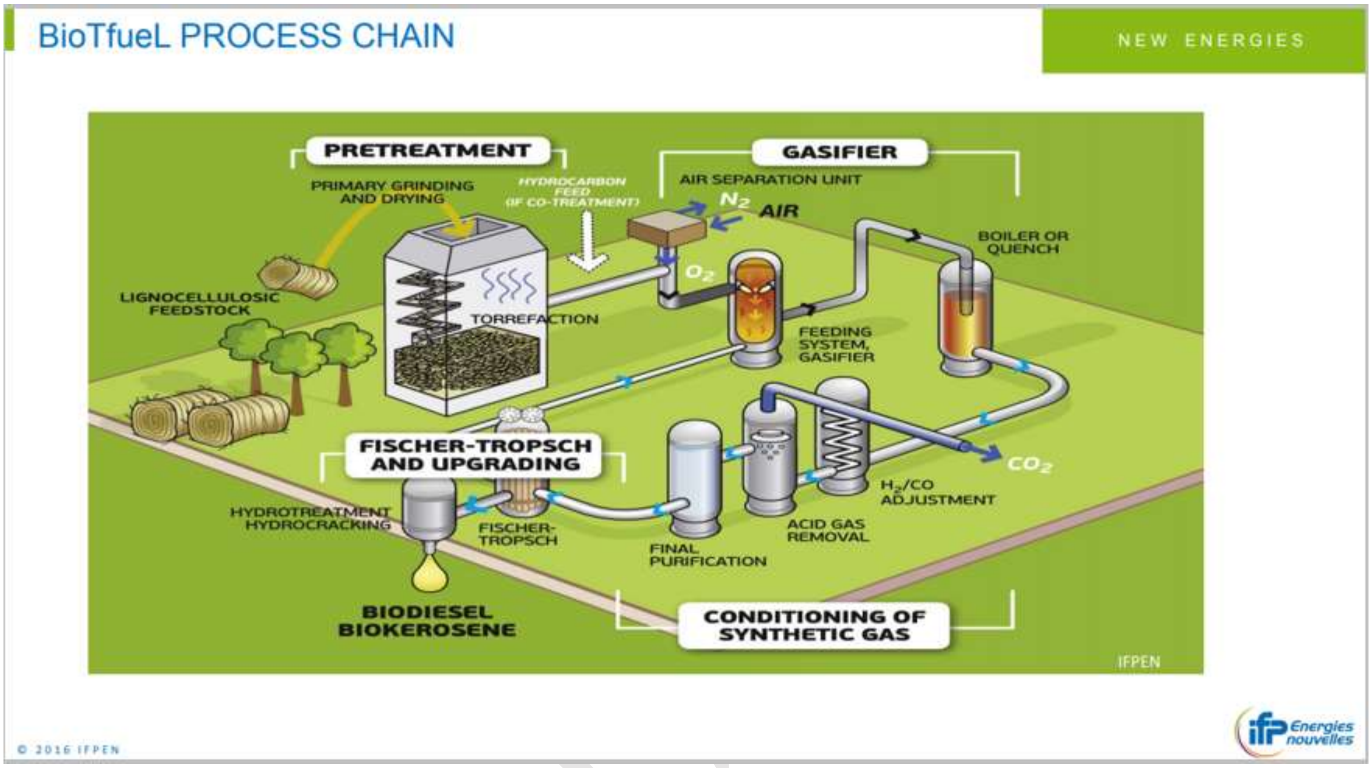
FT technology applied to Gasification, within the above definition of advanced biofuels, is at pilot stage or demonstration stage, working in operational environment at pre-commercial scale.

Demonstration plants have been established to scale down the Fischer-Tropsch process to a size appropriate to a supply chain based on biomass.

Existing Plants at 2019, including FT downstream a working Gasification Unit are the following:

Table 26 – BioTfuel demo[29]

Project name	BioTfuel demo
Project owner	Total
Status	Under commissioning
Start up	HOLD
Country	France
City	Dunkirk
Type	TRL 6-7 demo
Technology	Fuel synthesis
Raw Material	Forest waste, straw, green waste, dedicated crops
Output 1 Name	FT liquids (jet fuel component)
Output 1 Capacity	8000
Output 1Unit	t/y
Partners	Axens, CEA, IFP Energies Nouvelles, Avril, ThyssenKrupp Industrial
Technology Brief	The BioTfueL project is focused on developing an innovative process for converting biomass into high-quality biodiesel and bio-jet fuel. Gasification makes it possible to produce biofuels from lignocellulosic material, such as agricultural by-products, forest waste and energy crops. The process can also convert fossil feedstock mixed with biomass to account for seasonal variations in resource availability. The biomass feedstock is torrefied and then converted into syngas in a gasifier. Once the syngas has been cleaned and conditioned, it is converted into a hydrocarbon mixture that can be used to produce fuel.



BioTfueL PROCESS CHAIN

NEW ENERGIES

© 2016 IFPEN

Figure 32. BioTfuel demo sketch[30]

Table 27 – Synthesis bioliq[29]

Project name	Synthesis bioliq - process Karlsruhe
Project owner	Karlsruhe Institute of Technology (KIT)
Status	operational
Start up	2012
Country	Germany
City	Karlsruhe
Type	TRL 4-5 Pilot
Technology	Fuel synthesis
Raw Material	Lignocellulosic crops
Input 1 Name	Straw
Input 1 Capacity	1
Input 1 Unit	t/h
Output 1 Name	Gasoline type fuels
Output 1 Capacity	608
Output 1 Unit	t/y
Partners	KIT, Lurgi, MUT, MLR
Total Investment	64 mio
Total Investment Currency	Euro
Technology Brief	The bioliq process, developed at the Karlsruhe Institut für Technologie (KIT) aims at the production of synthetic fuels and chemicals from biomass. The bioliq technology is based on a two step process with decentral pyrolysis for the production of transportable slurry from biomass (e.g. straw) and central slurry gasification and BtL production. At KIT Karlsruhe a pilot plant with 2 MW fast pyrolysis and biosyn- crude production and 5 MWth high pressure entrained flow gasifier operated up to 8 MPa (both in cooperation with Lurgi GmbH, Frankfurt), as well as the hot gas clean-ing (MUT Advanced Heating GmbH, Jena), dimethylether and final gasoline synthesis (Chemieanlagenbau Chemnitz GmbH) are in operation.

Table 28 – LLC Thermal Reformer Synthesis West BiofuelsWoodland , CA[29]

Project name	LLC Thermal Reformer Synthesis West BiofuelsWoodland , CA
Project owner	West Biofuels
Status	Operational
Start up	2007
Country	USA, CA
City	Woodland
Type	TRL 6-7 demo
Technology	Fuel synthesis
Raw Material	Forest residues
Input 1 Name	clean wood, waste wood
Input 1 Capacity	5
Input 1 Unit	t/d
Output 1 Name	FT liquids
Output 1 Capacity	-
Output 1 Unit	t/y
Partners	University of California
Technology Brief	West Biofuels uses dual fluidized bed thermal reforming system that breaks down biomass into its molecular components through chemical reactions brought on by high heat, oxygen and steam at low pressure.
Additional Information	Woodland Biomass Research Center, Woodland, CA, USA: The Woodland Research Center is located approximately 20 miles northwest of Sacramento in Woodland, California. The facility was built in cooperation with the University of California.

Table 29– Sierra BioFuels Plant[29]

Project name	Sierra BioFuels Plant
Project owner	Sierra
Status	Operational by 2020 (?)
Start up	2017
Country	Nevada US
City	Storey County
Type	TRL 6-7 demo
Technology	Fuel synthesis
Raw Material	municipal solid waste
Input 1 Name	Prepared municipal solid waste (MSW) feedstock
Input 1 Capacity	82000 - 175000
Input 1 Unit	t/y
Output 1 Name	Heavy Fraction FT Liquids (HFTL) product; a Medium Fraction FT Liquids (MFTL) product; and a Light Fraction FT Liquids (LFTL) product, commonly called Naphtha
Output 1 Capacity	40
Output 1 Unit	Millions of litres
Partners	Fulcrum BioEnergy, Inc., ThermoChem Recovery International
Technology Brief	The feedstock used in Fulcrum's process consists primarily of the organic material recovered from MSW. The prepared MSW is gasified using a ThermoChem Recovery International gasification system. During the gasification process, the prepared MSW feedstock rapidly heats up upon entry into the steam-reforming gasifier and almost immediately converts to syngas. A venturi scrubber captures and removes any entrained particulate, and the syngas is further cooled in a packed gas cooler scrubber. The cleaned syngas is then processed through an amine system to capture and remove sulfur and carbon dioxide. The syngas then enters the secondary gas clean-up section that contains compression to increase syngas to the pressure required by the Fischer-Tropsch (FT) process. The end syngas product is very clean with zero sulfur content.

	The FT portion of Fulcrum's process is an adaptation of the well-established Fischer-Tropsch process. In the FT process, the purified syngas is processed through a fixed-bed tubular reactor where it reacts with a proprietary catalyst to form three intermediate FT products: a Heavy Fraction FT Liquids (HFTL) product; a Medium Fraction FT Liquids (MFTL) product; and a Light Fraction FT Liquids (LFTL) product, commonly called Naphtha. The Naphtha is recycled to the partial oxidation unit with remaining tail gas to be reformed to hydrogen and carbon monoxide. In the last step, hydrotreating, hydrocracking and hydroisomerization upgrading steps are used to upgrade the combined HFTL and MFTL products into jet fuel.
Additional Information	As construction proceeds on Sierra, engineering, siting and permitting activities are underway for the company's next several projects to be sited near large US metropolitan areas where Fulcrum has already secured long-term supplies of feedstock, fuel logistics and fuel offtake agreements. Collectively, these future plants are expected to have the capacity to produce more than 300 million gallons of jet fuel annually.

Choren gasification technology

One of the first commercial BtL Plant was under construction in Frieberg Saxony, utilising the Choren Carbo-V ® Process. Choren Industries filed for insolvency in July 2011. A new investor for Choren Components was announced in October 2011. On 9 February 2012 Choren's biomass gasification technology was sold to Linde Engineering Dresden, who will further develop the Choren Carbo-V® technology used to produce syngas.

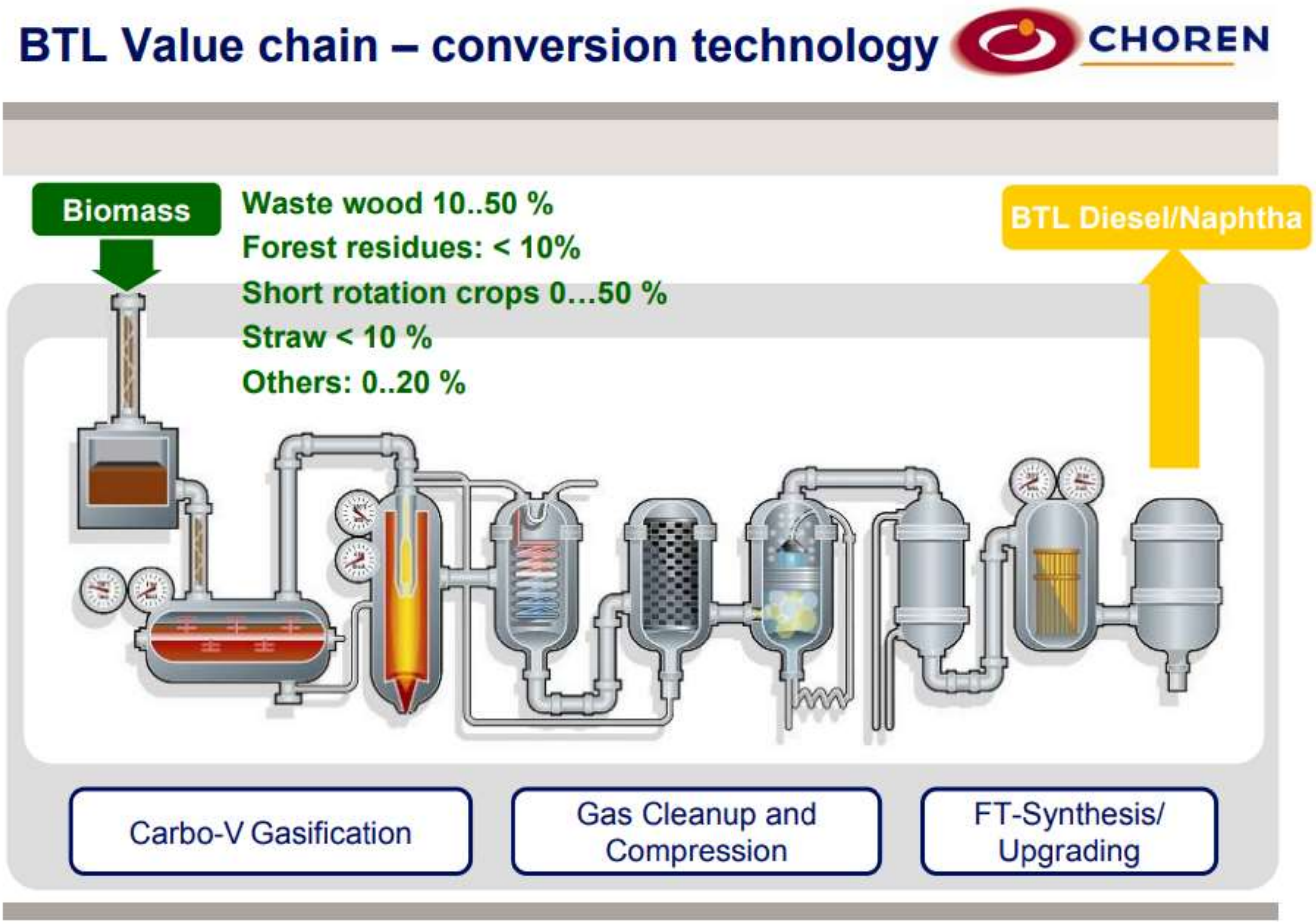


Figure 33. Choren Carbo-V ® Process sketch[31]

The Carbo-V® Process is a three-stage gasification process resulting in the production of syngas:

- low temperature gasification,
- high temperature gasification and
- endothermic entrained bed gasification.

The Fischer-Tropsch (FT) process is then used to convert the synthesis gas into an automotive fuel SunDiesel®.

The Choren plant used the proprietary Shell Middle Distillate Synthesis (SMDS) technology. Syngas production is followed by a modified version of the Fischer-Tropsch process. This favours the production of long chain waxy molecules, which are unsuitable for transport fuels, but substantially reduces the amounts of unwanted smaller hydrocarbons or gaseous byproducts. The hydrocarbon synthesis step is followed by a combined hydro-isomerisation and hydrocracking step to produce the desired, lighter products.

CHOREN Beta Plant Freiberg/D:

- 45 MW thermal
- 68,000 t/a feedstock
- 18.0 million l BTL

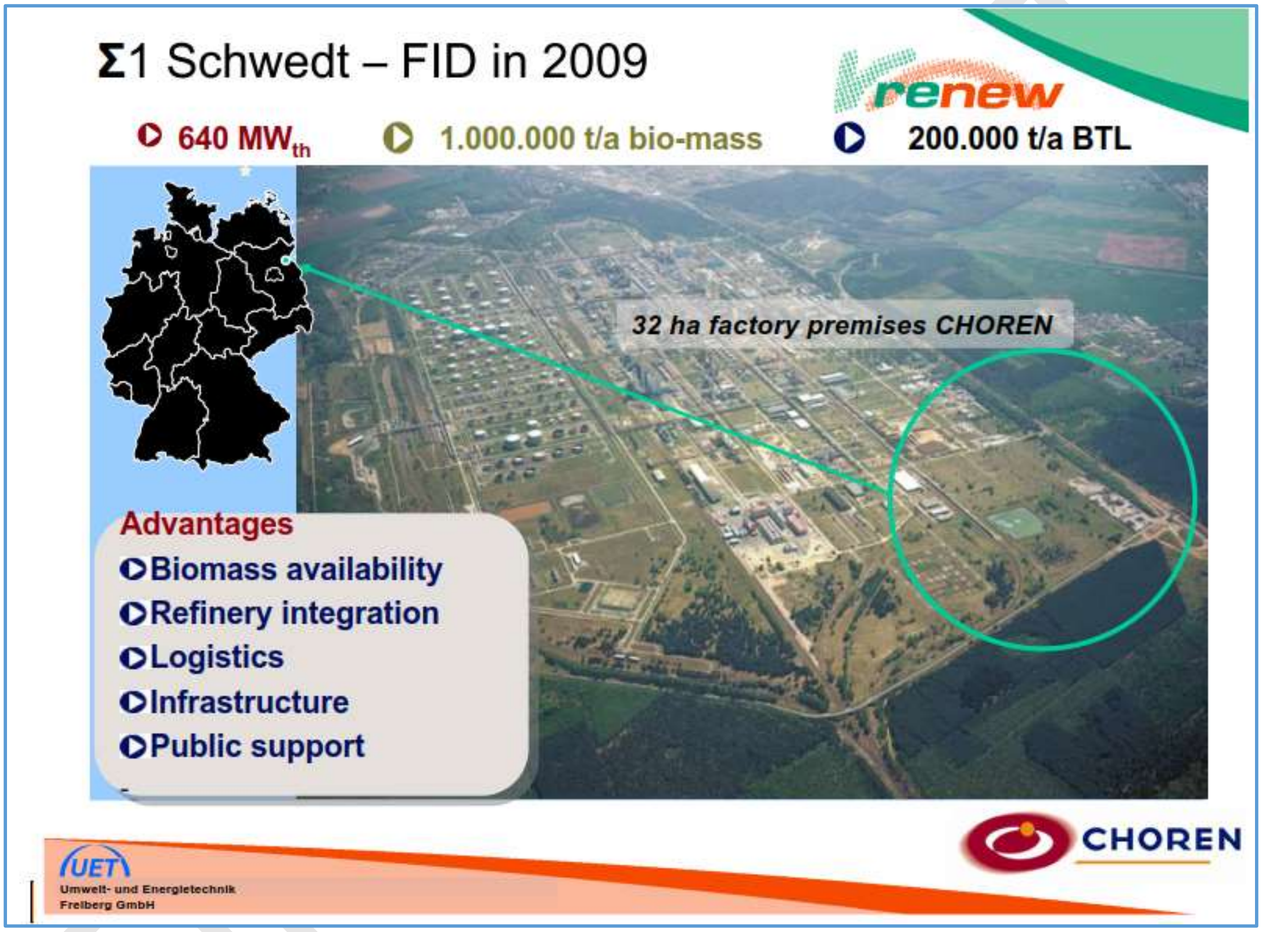
Figure 34. Choren Beta Plant Freiberg[31]

The Choren website listed a number of advantages for SunDiesel®:

- High cetane number and therefore much better ignition performance than conventional diesel fuel,
- No aromatics or sulfur and significantly reduces pollutants from exhaust emissions,
- Can be used without any adjustment to existing infrastructure or engine systems,
- Largely CO_2-neutral.

Key Figures for future scale-up project Σ1 Schwedt

- Fuel production 200.000 t/y BTL = 5.000 BOPD = 270.000.000 Liter BTL
- Gasifier power 4 x 160 MW(th) Parallel = 640 MW(th)
- Biomasse demand ca. 1 Mio. t(TS)/y
- Investment > 800 Mio. €
- Green house gas reduction 650.000 t CO2 / y



Σ1 Schwedt – FID in 2009

renew

- 640 MW_{th}
- 1.000.000 t/a bio-mass
- 200.000 t/a BTL

32 ha factory premises CHOREN

Advantages

- Biomass availability
- Refinery integration
- Logistics
- Infrastructure
- Public support

UET Umwelt- und Energietechnik Freiberg GmbH

CHOREN

Figure 35. Future scale-up Schwedt[31]

Extending the benchmarking to technology using gas as feedstock, GLAMOUR can be compared with GTL plants, in terms of feed conditioning and quality of syngas to fuel.

I this case the feedstock is a fossil fuel and the greenhouse gas footprint depends by the reforming technology.

Reforming of methane is one of the most important industrial processes, which convert natural gas into synthesis gas. Synthesis gas is produced from natural gas via catalytic processes based on dry reforming of methane (DRM), steam reforming of methane (SRM) and partial oxidation of methane (POM). In fact, the available natural gas can be exploited for the production of fuels.

Tri-reforming of methane (TRM) is nowadays of great interest, because it combines the steam and dry reforming and partial oxidation of methane (CH4 + O2 + CO2 + H2O) processes.

The tri-reforming process (TRM) allows to use flue gas and methane to produce syngas, which can be converted to higher hydrocarbons. This new process is a synergic combination of the endothermic CO2 and steam-reforming reactions with the exothermic oxidation of methane, which are carried out in a single reactor.

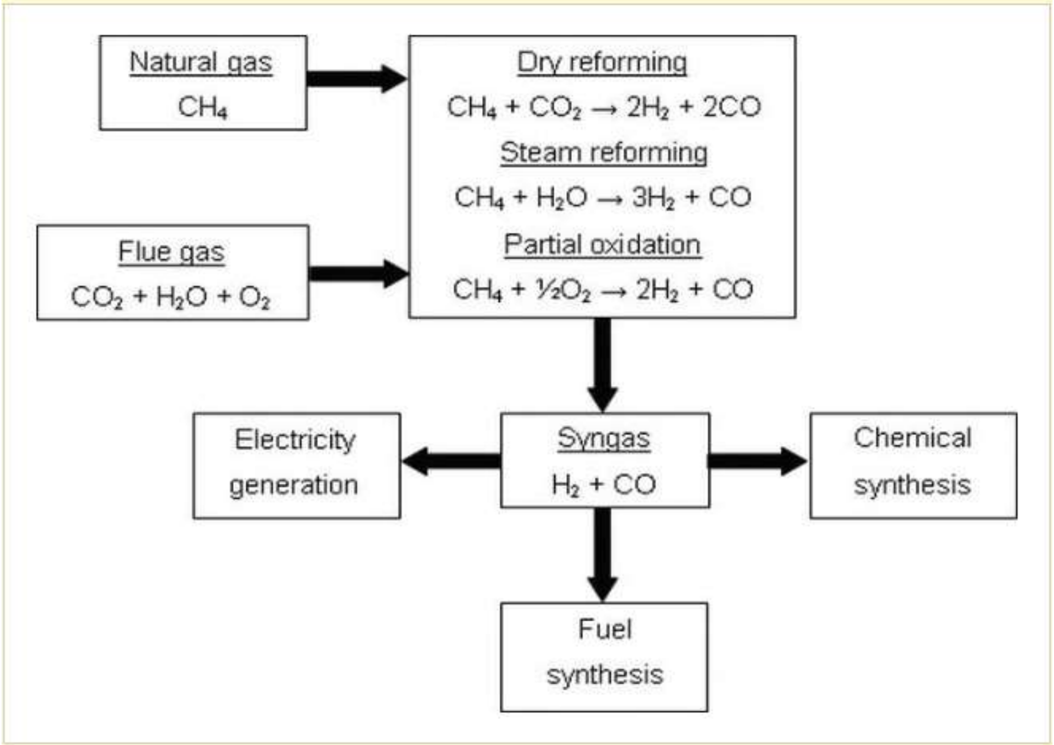
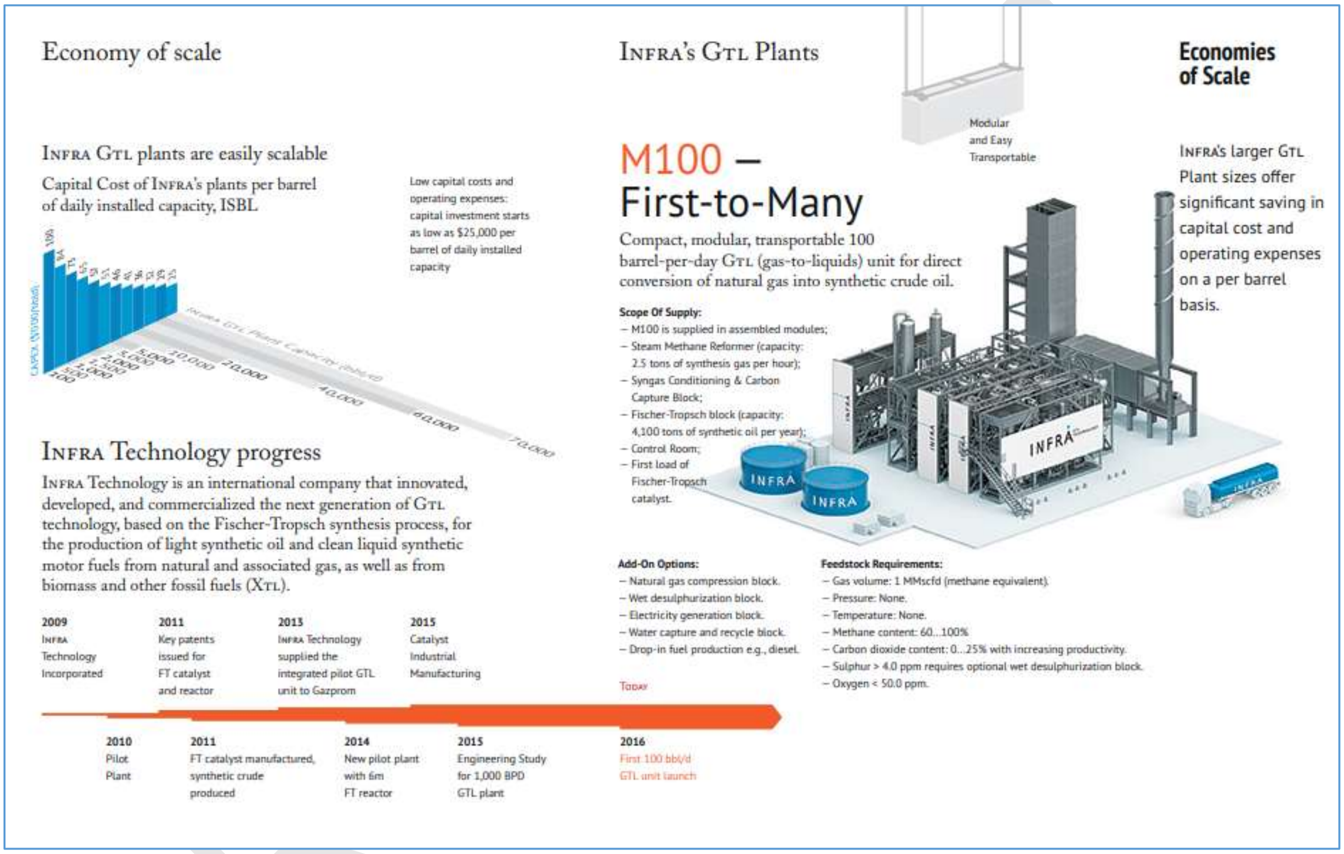


Figure 36. Three reforming flow scheme[32]

Some demonstration plants involve the reforming of gas to produce liquid fuels.

INFRA M100, USA (pilot/demonstration)

INFRA designed and built a modular, transportable GTL (gas-to-liquid) M100 plant for processing natural and associated gas into synthetic crude oil near Houston (Texas, USA).



Economy of scale

INFRA GTL plants are easily scalable

Capital Cost of INFRA's plants per barrel of daily installed capacity, ISBL

Low capital costs and operating expenses: capital investment starts as low as $25,000 per barrel of daily installed capacity

INFRA Technology progress

INFRA Technology is an international company that innovated, developed, and commercialized the next generation of GTL technology, based on the Fischer-Tropsch synthesis process, for the production of light synthetic oil and clean liquid synthetic motor fuels from natural and associated gas, as well as from biomass and other fossil fuels (XTL).

2009 INFRA Technology Incorporated

2010 Pilot Plant

2011 Key patents issued for FT catalyst and reactor

2011 FT catalyst manufactured, synthetic crude produced

2013 INFRA Technology supplied the integrated pilot GTL unit to Gazprom

2014 New pilot plant with 6m FT reactor

2015 Catalyst Industrial Manufacturing

2015 Engineering Study for 1,000 BPD GTL plant

TODAY

2016 First 100 bbl/d GTL unit launch

INFRA's GTL Plants

M100 – First-to-Many

Compact, modular, transportable 100 barrel-per-day GTL (gas-to-liquids) unit for direct conversion of natural gas into synthetic crude oil.

Scope Of Supply:
- M100 is supplied in assembled modules;
- Steam Methane Reformer (capacity: 2.5 tons of synthesis gas per hour);
- Syngas Conditioning & Carbon Capture Block;
- Fischer-Tropsch block (capacity: 4,100 tons of synthetic oil per year);
- Control Room;
- First load of Fischer-Tropsch catalyst.

Add-On Options:
- Natural gas compression block.
- Wet desulphurization block.
- Electricity generation block.
- Water capture and recycle block.
- Drop-in fuel production e.g., diesel.

Feedstock Requirements:
- Gas volume: 1 MMscfd (methane equivalent).
- Pressure: None.
- Temperature: None.
- Methane content: 60...100%
- Carbon dioxide content: 0...25% with increasing productivity.
- Sulphur > 4.0 ppm requires optional wet desulphurization block.
- Oxygen < 50.0 ppm.

Economies of Scale

INFRA's larger GTL Plant sizes offer significant saving in capital cost and operating expenses on a per barrel basis.

Figure 37. Infra M100[33]

M100 has been acquired by a joint venture, including Greenway Technologies, Inc. (OTCQB: GWTI), a company that has developed a proprietary GTL syngas conversion system.
M100 will combine Greenway's patent-pending G-Reformer™ natural gas reforming technology with INFRA's unique proprietary Fischer-Tropsch (FT) system, as well as a number of commercially available technologies integrated into the high-productivity and efficient flowsheet.
The company plans to operate the plant on a commercial basis and sell synthetic crude oil. Synthetic crude oil is a mixture of gasoline and diesel fractions in a 60/40 proportion. Up to 45% of kerosene fraction.

The facility is initially expected to yield in excess of 75 barrels per day of gasoline and diesel fuels from converted natural gas. M100's process equipment footprint is only 4,000 square feet.

M100 will have the capability to test and optimize various configurations of the GTL process, as well as expedite the engineering certifications necessary to license technology to the clients in the oil & gas industry. The successful demonstration of patented and proprietary technologies at this GTL facility will give fresh start to further technology development and allow the stakeholders to participate in a number of other GTL projects worldwide.

Figure 38. Infra M100 sketch[33]

Product

Light synthetic oil with unique quality characteristics:

- More than 95% of liquid light fractions (FBP <360 °C).
- No sulphur and aromatics.
- Large fraction of iso-paraffins and olefins.
- High (up to 70) cetane number for diesel fuel.
- Large (up to 45%) of jet fuel fraction.

Footprint 400 *square meters(ISBL)*

M100 guarantees 100 barrels of synthetic oil (60/40 mixture of gasoline and diesel fractions with high share of jet fuel) from 1 million cubic feet of gas per day (methane equivalent).

Table 30 – Infra M100 - Technical Information[33]

Feedstock requirements	• Gas volume - 1 MMscfd (methane equivalent). • Pressure – None. • Temperature – None. • Methane content - 60-100% • Carbon dioxide content - 0-25% with increasing productivity. • Sulphur > 4.0 ppm requires optional wet desulfurization block. • Oxygen < 50.0 ppm.
Reference Standards	• ASME code for pressure vessels. • API • ASCE 7-10
Scope of supply	• SMR Block. • Syngas Conditioning & Carbon Capture Block. • Fischer-Tropsch block. • Control Room. • M100 is supplied in assembled modules and includes the first load of Fischer-Tropsch catalyst.
Add-on Options	• Natural gas compression block. • Wet desulfurization block. • Electricity generation block. • Water capture and recycle block. • Drop-in fuel production e.g., diesel.
Key Features	• Eliminates flaring in an economically feasible manner. • Converts 1 million standard cubic feet of gas per day into 100 barrels of premium synthetic crude. High value. • No by-products. • Easily relocated. Modular.
Key benefits	• Low CAPEX and OPEX. • Produce high quality single liquid product – synthetic crude (no heavy waxes) which does not require hydrocracking and upgrading, and mixes well with crude oil. • Stable product. No by-products. • Synthetic crude is fully compatible with the existing oil infrastructure and is easily upgradable to diesel. • Processes feed gas with varying density. • Handles CO2 rich gas (up to 25% in feed increases the productivity). • No requirements for NGL & nitrogen removal from feed gas. • High carbon efficiency. • Modular, compact and movable containerized design. • Self-sustained process (no-grid electricity and no fresh water required). No requirement for continuous flaring.

INFRA M450, Russia (FEED in progress)

INFRA Gas plant for processing 45 million cubic meters of natural gas per year into drop-in motor fuels for JSC Nenetsk Oil Company.

The plant will be located in Nenetsk Autonomous Region. It will produce winter diesel fuel and high-octane gasoline from the natural gas of the Vasylkovskoye gas condensate field.
Construction of the gas processing plant using INFRA’s advanced GTL technology will enable Nenetsk Autonomous Region to become self-sufficient in high-quality drop-in fuel — diesel and gasoline — and significantly reduce the current expensive cost of transporting fuel to the Northern areas.
Following project feasibility study in 2017, front-end engineering design (FEED) is to be completed before the end of 2020.

M1000 comparable size as follows:

Figure 39. Infra M450 sketch[33]

Product

Light synthetic oil with unique quality characteristics:
- More than 95% of liquid light fractions (FBP <360 °C).
- No sulphur and aromatics.
- Large fraction of iso-paraffins and olefins.
- High (up to 70) cetane number for diesel fuel.
- Large (up to 45%) of jet fuel fraction.

Footprint 900 *square meters(ISBL)*

M1000 guarantees 1,000 barrels of synthetic oil (60/40 mixture of gasoline and diesel fractions with high share of jet fuel) from 10 million cubic feet of gas per day (methane equivalent).

Table 31 – Infra M450 - Technical Information[33]

Feedstock requirements	• Gas volume — 10 MMscfd (methane equivalent). • Pressure — none • Temperature — none • Methane content — 60—100% • Carbon dioxide content — 0—25% with increasing productivity. • Sulphur > 4.0 ppm requires optional wet desulfurization block. • Oxygen < 50.0 ppm.
Reference Standards	• ASME code for pressure vessels. • API • ASCE 7-10
Scope of supply	• SMR Block. • Syngas Conditioning & Carbon Capture Block. • Fischer-Tropsch block. • Control Room. • M1000 is supplied in assembled modules and includes the first load of Fischer-Tropsch catalyst.
Add-on Options	• Natural gas compression block. • Wet desulfurization block.
Key Features	• Converts 10 million standard cubic feet of gas per day. • Produces 1,000 barrels of premium synthetic crude, or premium synthetic fuel (diesel, kerosene, gasoline). • Modular. Simple technology flowsheet. • Low maintenance requirements.
Key benefits	• Low CAPEX and OPEX. • Produce high quality single liquid product – synthetic crude (no heavy waxes) which does not require hydrocracking and upgrading, and mixes well with crude oil. • Stable product. No by-products. • Synthetic crude is fully compatible with the existing oil infrastructure and is easily upgradable to diesel. • Processes feed gas with varying density. • Handles CO2 rich gas (up to 25% in feed increases the productivity). • No requirements for NGL & nitrogen removal from feed gas. • High carbon efficiency. • Modular, compact and movable containerized design. • Electricity generation block.

Japan Oil, Gas and Metals National Corporation

The JAPAN-GTL Demonstration Test Project has been performed by Japan Oil, Gas and Metals National Corporation (“JOGMEC”) together with the Nippon GTL Technology Research Association (“Nippon GTL Association”) established by six private companies on 25 October 2006. The construction of the JAPAN-GTL demonstration plant in Niigata City, which will produce 500 barrels (about 80 kiloliters) per day, has been completed and the opening ceremony took place on 16 April 2009.

Gas-To-Liquids (GTL) is a technology with which natural gas and coal bed methane (CBM) as a raw material can be converted into petroleum products. The process being developed in the JAPAN-GTL demonstration plant project is a groundbreaking technology that would for the first time ever allow for natural gas containing carbon dioxide to be used directly. The two-year demonstration operation using this plant will work to establish a unique Japanese technology applicable on a commercial scale and advance towards the goal of achieving a stable energy supply for Japan and harmony with the global environment.

Niigata GTL demonstration plant: outline

(1) Location: 2881-45 Tarodai, Kita-ku, Niigata City Research Center, Nippon GTL Technology Research Association

(2) Plant capacity: Production of 500 barrels (about 80 kiloliters) per day

(3) Main process facilities: Syngas Producing Section FT (Fischer-Tropsch) synthesis Section Upgrading (hydrocracking) Section

(4) Future plans: Demonstration operation: FY2009-2010

(5) Photo of plant

Figure 40. Niigata GTL Plant[34]

JAPAN-GTL: outline

GTL is short for Gas-To-Liquids. The technology allows for production of petroleum products such as naphtha, kerosene, and diesel oils from natural gas through chemical reactions. JAPAN-GTL is different from the overseas technologies advanced by Sasol in South Africa and Shell and it features in utilizing carbon dioxide gas as raw material, so that it is a groundbreaking technology that would for the first time ever allow for natural gas containing carbon dioxide to be used directly. This technology focusing on the FT synthetic process can also be applied to produce clean fuels from coal as well as coal seam gas.

Production flow of Japan-GTL process:

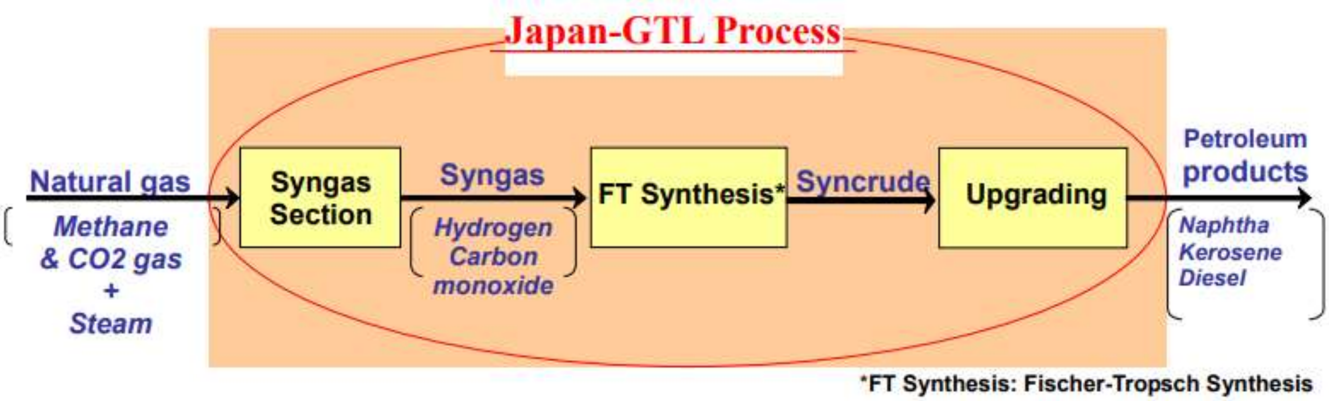


Figure 41. Japan GTL scheme[34]

Demonstration research: outline

(1) Goals The goals are to demonstrate GTL production technology using a demonstration plant at a scale of 500 barrels/day production (stage previous to commercial scale), investigate scaling up towards commercialization, and develop GTL technology which is technically and financially competitive on a commercial scale (daily production of tens of thousands of barrels).

(2) Research organization: Joint research by JOGMEC & Nippon GTL Technology Research Association

(3) Research budget: Total project cost: About 36 billion yen (About 12 billion of this cost to be borne by Nippon GTL Association)

(4) Period: FY2006-2010 (5 years)

CompactGTL's project in Kazakhstan – the world's first fully commercial modular GTL plant

Figure 42. CompactGTL – Kazakhstan[35]

Gas supply:	24 million standard cubic feet per day agreed with the oilfield owner
Production:	c. 2500 barrels per day of synthetic crude, upgrading to diesel blendstock.
Start of production:	2018

Figure 43. CompactGTL – Kazakhstan, 3D model[35]

Fluor – engineering partner

Fluor is responsible for the delivery of pre-FEED and FEED work, plus project management support during the EPC phase.
Fluor is the leader in FEED and EPC execution of GTL projects globally.

CompactGTL's modular solution satisfies a small-scale gas-to-liquid (GTL) vast market opportunity of small and medium sized oilfield assets, where no viable gas monetization option exists so the associated gas is either flared or reinjected.
The Company delivers turn-key modular GTL plants, with capacities ranging from 1,000 to 10,000 barrels per day, producing synthetic crude or diesel, to the resource owners, in return for a royalty stream per barrel produced and a margin on EPC contract

- Associated gas remote from infrastructure
- Flared or re-injected gas of low value
- Often attracting government penalties
- Sometimes constraining oil production
- Environmental concerns
- Resource preservation concerns

- CGTL plant converts gas to oil and/or diesel
- Creates value from an otherwise worthless resource
- Protects the value of oil field resources that might otherwise not be developed
- Avoids the imposition of flaring penalties or caps
- Unlocks shut-in production
- Solution can attract government support / incentives

Figure 44. CompactGTL claims[35]

Petrobras Research Centre (CENPES), Brazil

Following initial start-up at the end of 2010, CGTL received technology approval from Petrobras, at the end of 2011, after a period of testing that covered all conceivable feed gas compositions.

The CompactGTL team was supported by Genesis Oil and Gas Consultants Ltd during the process design stage of the contract. The SMR and FT reactors were manufactured by Sumitomo Precision Products Co, Ltd in Osaka, Japan and due to CompactGTL's modular, small scale approach the complete set of GTL reactors were dispatched to Brazil by air freight. Zeton Inc. was awarded the EPC contract for the balance of plant and the GTL demonstration plant was constructed at Zeton's facility in Burlington, Canada. The Commercial Demonstration Plant was successfully commissioned at Petrobras' Aracaju site in Brazil, at the end of 2010.

The demonstration plant incorporates all the required aspects of a CGTL commercial plant in a fully integrated process:

- Gas pre-treatment
- Pre-reforming
- CGTL SMR process
- Waste heat recovery
- Process steam generation
- Syngas compression
- CGTL 2-stage Fischer Tropsch process
- FT cooling water system
- Tail gas recycling

The demonstration plant has proven CGTL's technology for all aspects of commercial application, as recognised by Petrobras.

Figure 45. CompactGTL Aracaju, Brazil[36]

The CGTL plant, fully integrated with the complete floating facility, will convert all associated gas into synthetic crude for mixing with the produced crude.

The Petrobras owned and operated demonstration plant at Aracaju, Brazil, demonstrates the world's first fully integrated small scale GTL facility, at 200,000scf/d capacity.

The US$45 million contract between Petrobras and CGTL, confirmed in July 2008, included the design, engineering, procurement, construction and testing of the demonstration plant. The plant was delivered on schedule and on budget with costs covered in full by Petrobras. Importantly, CGTL utilized its selected supply chain partners for the manufacture of the SMR and FT reactors, namely Sumitomo Precision Products for reactor supply and Johnson Matthey for the supply of the process catalysts.

The plant is located at a Petrobras Research Centre (CENPES) coastal terminal facility. This facility allows good access to actual associated gas feeds from nearby offshore oilfields as well as the required local utilities. The plant itself occupies an area of about 20m x 15m.

In 2012 Petroleo Brasileiro S.A's CENPES Research and Development Centre successfully concluded its extensive test programme of the CompactGTL modular small scale GTL facility and approved its process conception for use by Petroleo Brasileiro S.A (Petrobras).

ZETON Project: Product Demonstration Unit (PDU) for Rentech, Inc. (Colorado, USA)

Rentech, Inc. possesses a patented and proprietary technology “the Rentech Process” that converts synthesis gas into hydrocarbon liquids that can be processed and upgraded into ultra clear synthetic jet and diesel fuels. When Rentech, Inc. needed vital sections of their demonstration plant in Colorado, they chose Zeton to design and build their Fischer-Tropsch reaction and hydroprocessing product upgrading sections.

Basic engineering on the product upgrading section began in late 2005. Subsequent to approval to proceed into the phases of detailed design, procurement and fabrication the first of the 14 plant modules were completed by Zeton in 2006.

The Product Demonstration Unit was designed to produce approximately 420 gallons per day (10bbl/d) of synthetic jet and diesel fuels, production of which was later achieved and announced by Rentech, Inc. This project incorporates the successful design, construction and operation of a fully integrated synthetic fuels facility utilizing the Rentech Process and includes:

- Conversion of synthesis gas in the Rentech reactor into clean hydrocarbons;
- Processing and upgrading of the hydrocarbons into ultra-clean synthetic fuels using UOP hydrocracking and hydrotreating technologies;
- A complete coal-to-clean liquid fuels process with a coal gasifier (built elsewhere) as the source of the synthesis gas feeds to the Product Demonstration Unit.

Major milestones were achieved following the efforts of Rentech, Inc. and the Zeton project teams: In 2010 a commercial flight flew on a blend of RenJet fuel from the facility and conventional Jet-A, and as of mid-2011 the Rentech, Inc. facility has produced more than 40,000 gallons of bio-based jet fuels.

Syntroleum Corp

HOUSTON, Oct. 7, 2003 -- Tulsa-based Syntroleum Corp. has completed a new gas-to-liquids (GTL) demonstration plant at Port of Catoosa, near Tulsa, that will provide synfuels for a long-term testing and demonstration project using government vehicle fleets such as metropolitan buses in Washington, DC, and National Park Service vehicles.

The US Department of Energy funded $11.5 million of the $52 million plant construction costs, with the balance funded jointly by Syntroleum, which owns a proprietary GTL process for converting natural gas into synthetic liquid hydrocarbons, and Marathon Oil Co.

The plant, which will go on line in early November to produce about 70 b/d of synthetic fuels, consists of three primary components—an autothermal reformer to reform natural gas feed into synthesis gas (hydrogen and carbon monoxide), a Fischer-Tropsch unit that converts the synthesis gas into synthetic crude oil, and a refining unit that upgrades the synthetic crude to finished synthetic diesel.

The plant was designed and constructed under a federal ultraclean fuels program managed by DOE's National Energy Technology Laboratory to pioneer a new generation of clean transportation fuels to reduce tailpipe emissions from cars, trucks, and other heavy vehicles.

The program will produce synthetic diesel for a series of test programs, initially in diesel fleets, but the Departments of Defense and Transportation have indicated interest in producing fuel for military, construction, rail locomotion, and marine applications as well and possible use in jet engines and fuel cells.

Unlike other GTL technologies, the Syntroleum process uses air, rather than pure oxygen. This eliminates the need for an oxygen plant attached to the GTL facility, enabling a more compact facility. Syntroleum has developed a GTL barge that can economically take the processing capability to stranded gas fields. (In the schematic of the process, the shaded area marks where oxygen based equipment would be in other processes.)
Syntroleum’s air-blown process can economically scale down to 10,000 bpd of capacity vs. 35,000 to 50,000 bpd for more expensive oxygen-based processes. The capability cost-effectively to package GTL processing in smaller and even mobile platforms is important to the recovery of an enormous amount of stranded gas—much of which currently is flared off.

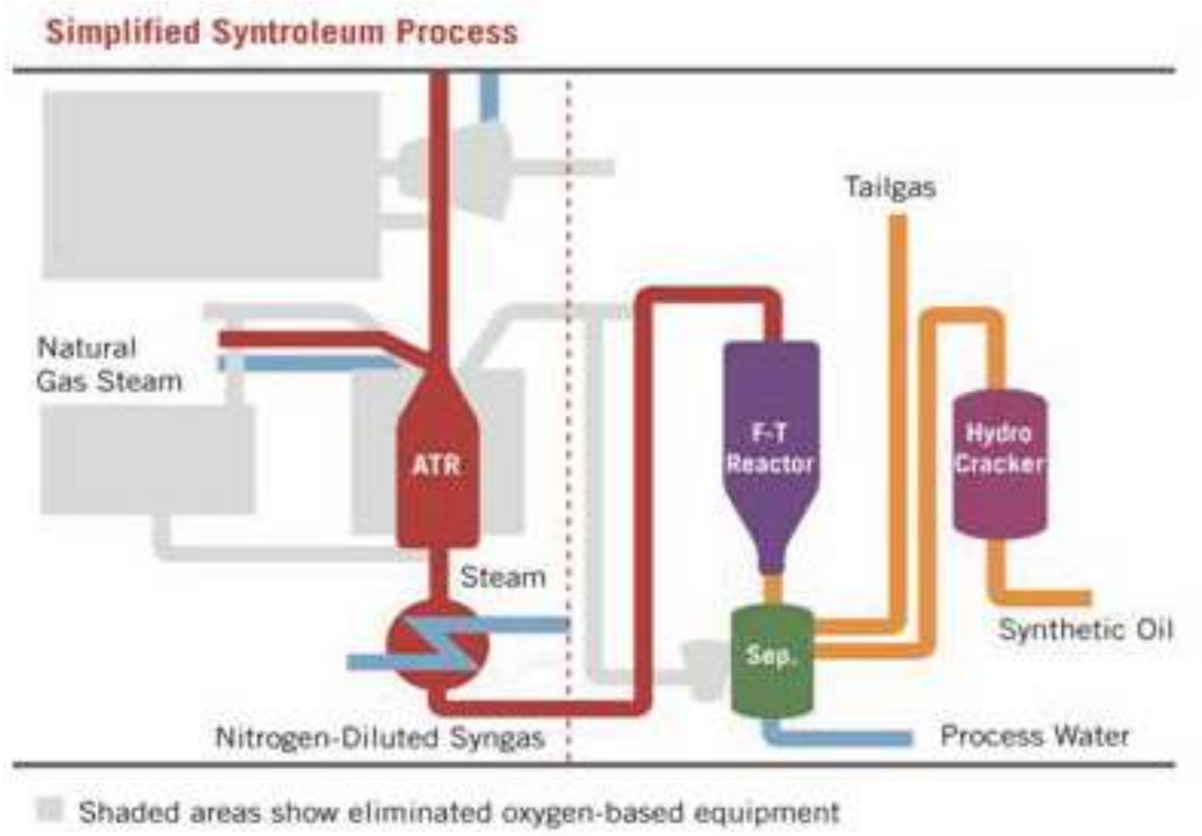
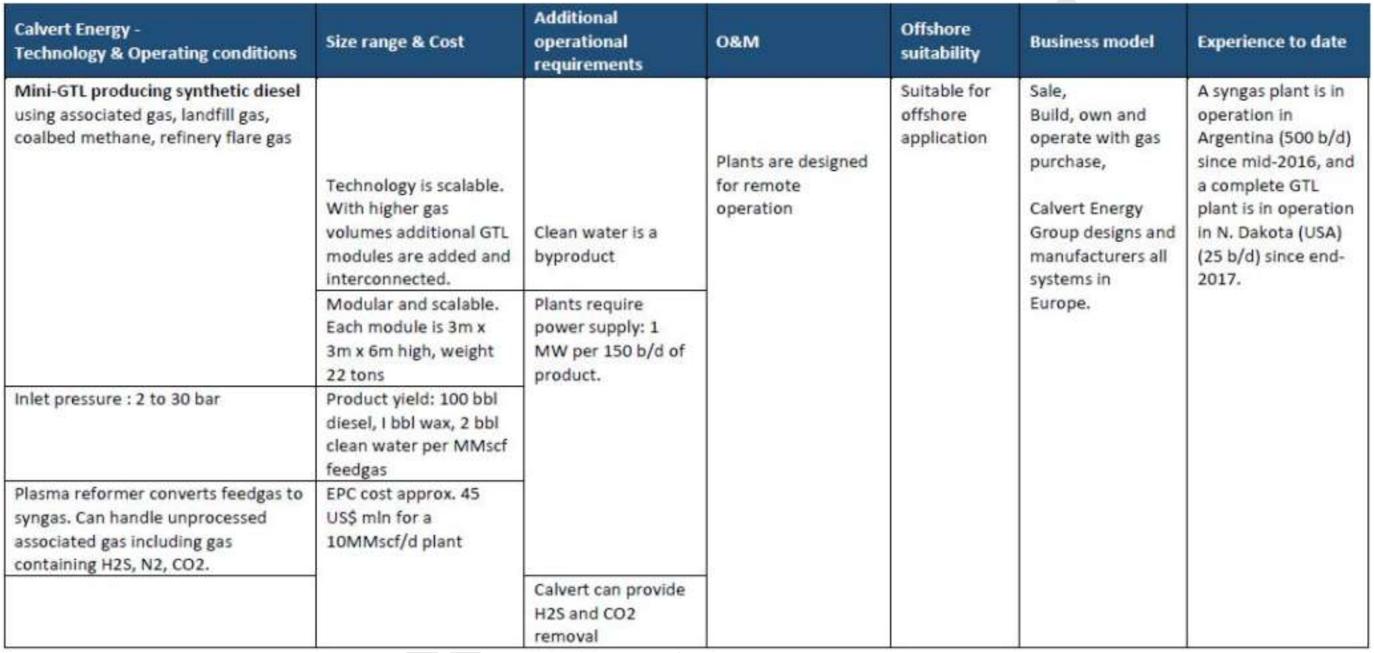


Figure 46. Syntroleum process scheme[37]

Calvert Energy Group GTL plant

The Calvert Energy Group offers modular GTL (Flare & Stranded Gas to Diesel plants ranging in size from 0.2 MMscf/d to 100 MMscf/d. The OEXON technology used is exclusively licensed to Calvert Energy Group by OXEON.

Table 32 – Calvert Energy Group claims[37]

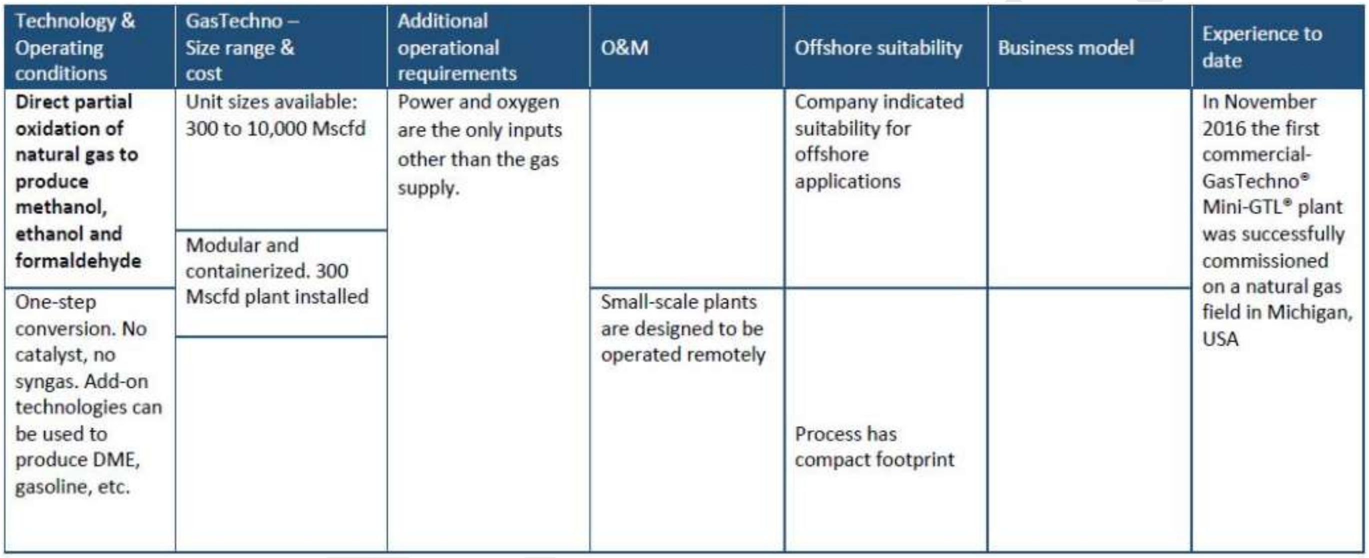


Calvert Energy - Technology & Operating conditions	Size range & Cost	Additional operational requirements	O&M	Offshore suitability	Business model	Experience to date
Mini-GTL producing synthetic diesel using associated gas, landfill gas, coalbed methane, refinery flare gas	Technology is scalable. With higher gas volumes additional GTL modules are added and interconnected.	Clean water is a byproduct	Plants are designed for remote operation	Suitable for offshore application	Sale, Build, own and operate with gas purchase, Calvert Energy Group designs and manufacturers all systems in Europe.	A syngas plant is in operation in Argentina (500 b/d) since mid-2016, and a complete GTL plant is in operation in N. Dakota (USA) (25 b/d) since end-2017.
	Modular and scalable. Each module is 3m x 3m x 6m high, weight 22 tons	Plants require power supply: 1 MW per 150 b/d of product.				
Inlet pressure : 2 to 30 bar	Product yield: 100 bbl diesel, I bbl wax, 2 bbl clean water per MMscf feedgas					
Plasma reformer converts feedgas to syngas. Can handle unprocessed associated gas including gas containing H2S, N2, CO2.	EPC cost approx. 45 US$ mln for a 10MMscf/d plant					
		Calvert can provide H2S and CO2 removal				

GasTechno Energy & Fuels (GEF)

Gas Technologies LLC manufactures, installs and operates modular gas-to-liquids plants that utilize the patented GasTechno® single-step GTL conversion process. GasTechno® Mini-GTL® plants convert associated flare gas and stranded natural gas into high-value fuels and chemicals including methanol, ethanol and gasoline/diesel oxygenated fuel blends while serving to reduce greenhouse gas emissions. The unit capital cost of the plants is approximately 70% lower than traditional methanol production facilities and they require relatively limited operation & maintenance costs.

Table 33 – GasTechno energy & fuels claims[37]

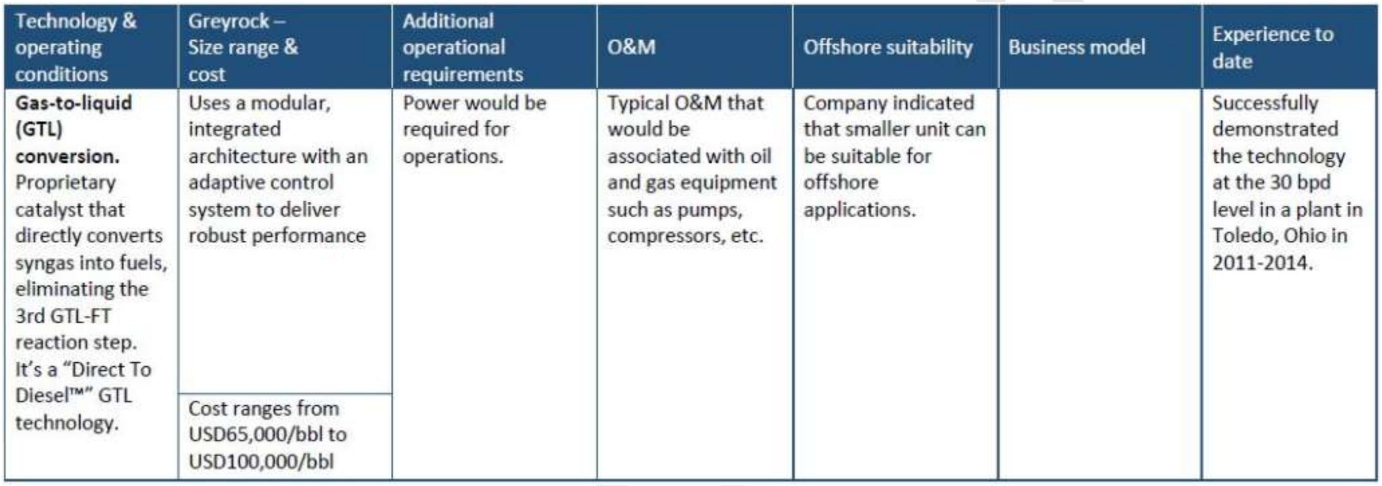


Technology & Operating conditions	GasTechno – Size range & cost	Additional operational requirements	O&M	Offshore suitability	Business model	Experience to date
Direct partial oxidation of natural gas to produce methanol, ethanol and formaldehyde	Unit sizes available: 300 to 10,000 Mscfd	Power and oxygen are the only inputs other than the gas supply.		Company indicated suitability for offshore applications		In November 2016 the first commercial-GasTechno® Mini-GTL® plant was successfully commissioned on a natural gas field in Michigan, USA
	Modular and containerized. 300 Mscfd plant installed					
One-step conversion. No catalyst, no syngas. Add-on technologies can be used to produce DME, gasoline, etc.			Small-scale plants are designed to be operated remotely	Process has compact footprint		

Greyrock

Greyrock Energy was founded in 2006 and is headquartered in Sacramento, California, with offices and a demonstration plant in Toledo, Ohio. Its sole focus is small-scale GTL Fischer-Tropsch plants for Distributed Fuel Production®, and it has a commercial offer of both a fully integrated 2000 bpd plant consuming about 20 MMscfd and smaller "MicroGTL" plants (5 – 50 bpd).

Table 34 – Greyrock claims[37]



Technology & operating conditions	Greyrock – Size range & cost	Additional operational requirements	O&M	Offshore suitability	Business model	Experience to date
Gas-to-liquid (GTL) conversion. Proprietary catalyst that directly converts syngas into fuels, eliminating the 3rd GTL-FT reaction step. It's a "Direct To Diesel™" GTL technology.	Uses a modular, integrated architecture with an adaptive control system to deliver robust performance Cost ranges from USD65,000/bbl to USD100,000/bbl	Power would be required for operations.	Typical O&M that would be associated with oil and gas equipment such as pumps, compressors, etc.	Company indicated that smaller unit can be suitable for offshore applications.		Successfully demonstrated the technology at the 30 bpd level in a plant in Toledo, Ohio in 2011-2014.

Velocys

Velocys is a smaller-scale GTL company that provides a bridge connecting stranded and low-value feedstocks, such as associated gas and landfill gas, with markets for premium products, such as renewable diesel, jet fuel and waxes. The company was formed in 2001, a spin-out of Battelle, an independent science and technology organization. In 2008, it merged with Oxford Catalysts, a product of the University of Oxford. Velocys aims to deliver economically compelling conversion solutions. It is traded on the London Stock Exchange, with offices in Houston, Texas; Columbus, Ohio; and Oxford, UK.

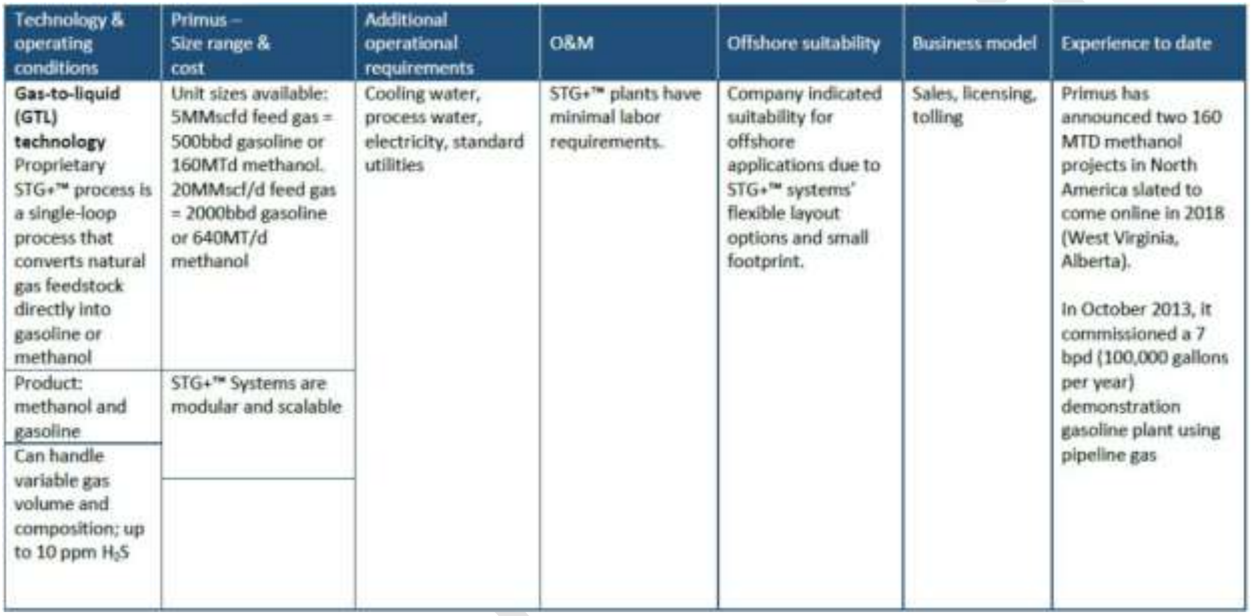
Table 35 – Velocys claims[37]

Velocys – Technology & operating conditions	Size range & cost	Additional operational requirements	O&M	Offshore suitability	Business model	Experience to date
Small-scale single-stage Fischer-Tropsch (FT) converting associated gas to diesel, jet fuel and naphtha. Combines micro channels reactors and super-active catalysts to provide high conversions to desired products	Plant sizes available 1,400 and 5,000 bpd	Power and water supply, wastewater treatment.	Opex ~ 25-35 USD/bbl for a stand-alone plant in the US Gulf Coast.	Currently under evaluatio	License or sale of FT reactors and FT catalyst.	First product produced at commercial reference plant: ENVIA Energy's Oklahoma City GTL plant. 26,000 hours of testing at demonstration scale including one test at Petrobras' facility. 1.3 million hours testing of catalyst in laboratory
Conversion rate efficiency > 91%	FT island is modularized, scalable and containerized					

Primus Green Energy

Primus Green Energy is based in Hillsborough, New Jersey, USA. The company is backed by Kenon Holdings, a NYSE-listed company with offices in the United Kingdom and Singapore that operates dynamic, primarily growth-oriented, businesses. Primus Green Energy™ has developed Gas-to-Liquids technology that produces high-value liquids such as gasoline, diluents and methanol directly from natural gas or other carbon-rich feed gas.

Table 36 – Primus Green Energy claims[37]



Technology & operating conditions	Primus – Size range & cost	Additional operational requirements	O&M	Offshore suitability	Business model	Experience to date
Gas-to-liquid (GTL) technology Proprietary STG+™ process is a single-loop process that converts natural gas feedstock directly into gasoline or methanol	Unit sizes available: 5MMscfd feed gas = 500bbd gasoline or 160MTd methanol. 20MMscf/d feed gas = 2000bbd gasoline or 640MT/d methanol	Cooling water, process water, electricity, standard utilities	STG+™ plants have minimal labor requirements.	Company indicated suitability for offshore applications due to STG+™ systems' flexible layout options and small footprint.	Sales, licensing, tolling	Primus has announced two 160 MTD methanol projects in North America slated to come online in 2018 (West Virginia, Alberta). In October 2013, it commissioned a 7 bpd (100,000 gallons per year) demonstration gasoline plant using pipeline gas
Product: methanol and gasoline	STG+™ Systems are modular and scalable					
Can handle variable gas volume and composition; up to 10 ppm H_2S						

Beyond the demonstration technologies described above, Gas-To-Liquids plants at commercial scale have been already discussed in Part I.

15 Economics

Advanced Biofuels

The reported commercial-scale operation ranges do not differ much between advanced biofuels pathways, especially given the potential for future downscaling and cost reductions in certain technology components. Most biofuel pathways potentially operate at 75-750 MW feedstock input, equivalent to 120,000 and 1.2 million dry tonnes of biomass per year.

Estimated total capital costs ranges are presented in USD2014/kWbiofuel. Commercial-scale Fischer-Tropsch synthesis processes may emerge from 2020. Capital investment will range at USD 3,000-5,000/kW biofuels.

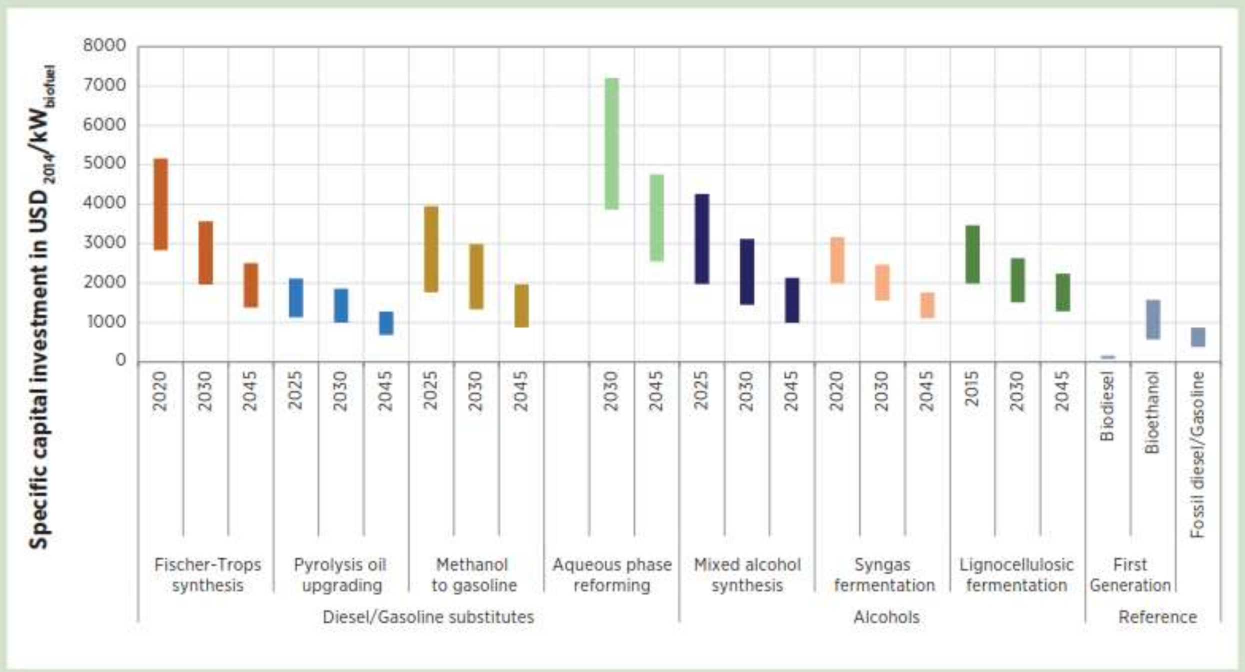


Figure 47. Capital investment for advanced biofuels[28]

Estimated production cost ranges are presented in USD2014/GJfuel and amount to about USD 30-50/GJ for FT synthesis.

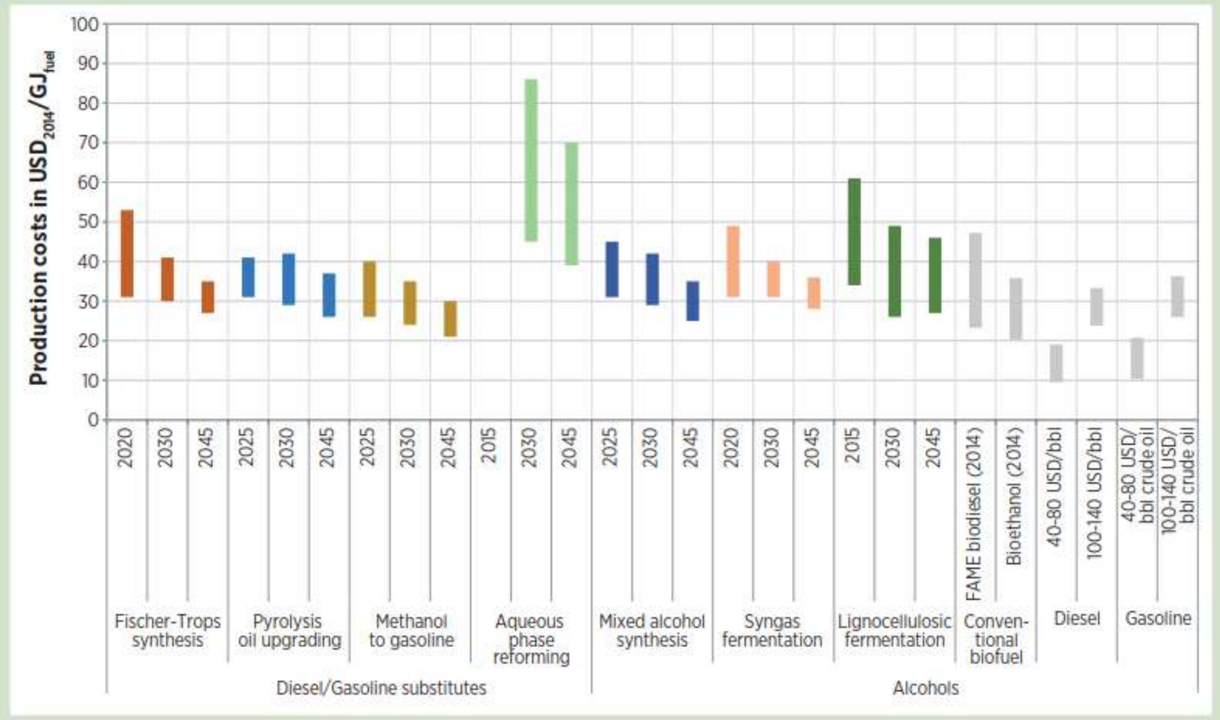


Figure 48. Production cost for advanced biofuels[28]

For all pathways except aqueous phase reforming, feedstock costs account for 40%-70% of production costs and represent the greatest single contribution to costs. The percentage contribution increases over time as learning rates and improved conversion efficiencies reduce the specific capital costs.

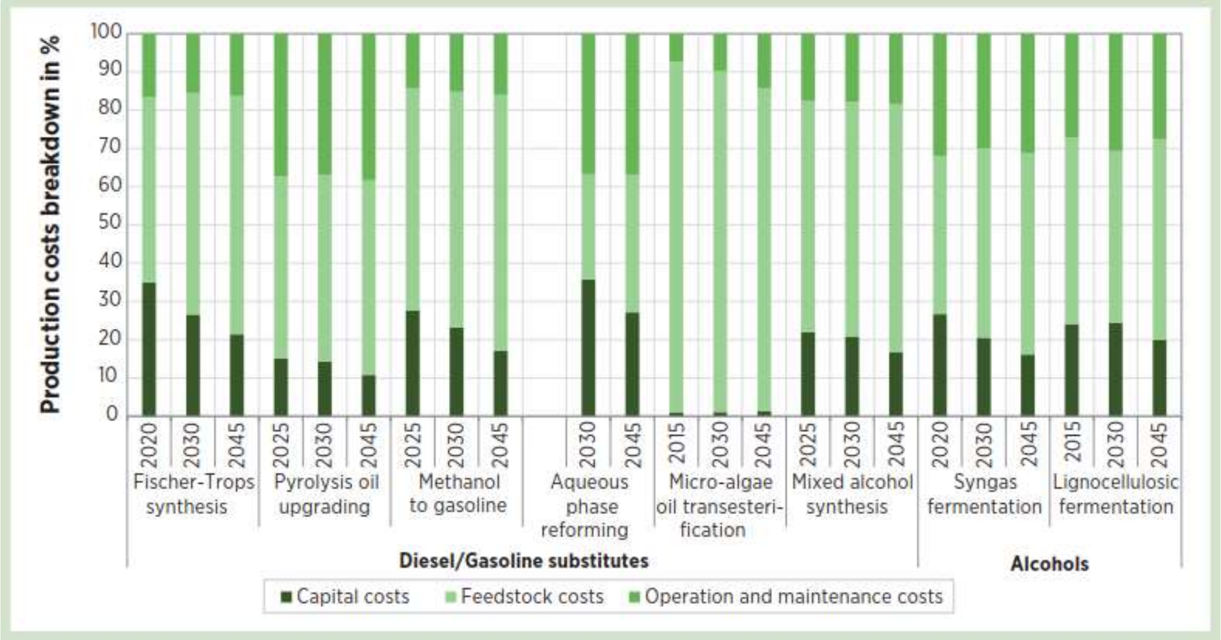


Figure 49. Production cost breakdown[28]

The following parameters for each pathway are based on literature and publicly available data. Assumptions and estimations are explained as follows:

- Based on the current status of technology development or industry plans, it is estimated a start date for first-of-a-kind commercial-scale plants and assumed a tenfold increase in installed capacity every 15 years from this point.

- The medium-term performance is indicative of 2030, and the long-term performance is indicative of 2045.

- Conversion efficiency – a ratio calculated using theoretical efficiency limits. This parameter illustrates the efficiency of converting biomass to different fuels, expressed in MJfuel/MJfeedstock, dry on a lower heating value basis. The conversion efficiency is based on actual or modelled commercial-scale plants (2010-2015 average).
Future improvements are based on a saturation curve model approaching technical limits defined for each specific pathway. The model is fitted to historical data and/or projections from other studies depending on data availability.

- Conversion yields: calculated using the conversion efficiency and lower heating value.

- Life cycle Green House Gas (GHG) emissions: references typical values of the Renewable Energy Directive. Future improvements are correlated to conversion efficiency improvements.

- GHG emissions savings: calculated on the basis of the difference between life cycle GHG emissions and the fossil fuel reference value: 83.8 kg CO2/GJ.

- Scale of operation: the expected range of commercial-scale plants as reported in the existing published literature and evidence base.

- Specific capital investment (reported in 2014 USD): calculated from the capital investment by dividing by the plant capacity. Reported values are mean values based on normalized capital investment for large and small-scale capacities. The specific capital investment is also expressed in USD/kWfuel output based on the conversion efficiency.

- The capital investment (in 2014 USD): capital investment of the first commercial plants is based on existing published literature and evidence. Original data are normalized to small and large-scale capacities applying economies of scale.

Future specific capital investment is projected on the basis of a learning rate model, with average learning rates from literature specific to each pathway. The learning rate represents the cost reduction while doubling installed capacity (e.g. a learning rate of 0.9 is equivalent to 10 % cost reduction when installed capacity is doubled).

- Production costs: a sum of the feedstock costs, specific capital cost, and operational and maintenance costs. A range of production costs is provided, reflecting variations in plant size and feedstock costs and assuming a plant lifetime of 20 years, plant availability of 90% and interest rate of 10%.

- Energy demand: all calculations assume that plants are self-sufficient in terms of heat and power, and that biomass required to provide these utilities is included in the feedstock consumption.

The performance indicators represent the expected performance of a first commercial plant. This is based on recently published literature with data points adjusted to 2015 values where necessary. The indicators presented do not represent realized conversion yields, efficiency, production costs, and life cycle GHG emissions but expected performance at commercial scale.

The pathway assessment is based on the following general assumptions, which are typical of techno-economic analysis available in the literature:

- plant is self-sufficient in energy (feedstock is the only major energy input)
- fuel calculations (feedstock, biofuel) energy are based on lower heating value

Table 37 – Technology parameters[28]

	Fischer-Tropsch synthesis	Pyrolysis oil upgrading	MTG	Mixed alcohol synthesis	Ligno-cellulosic fermentation	Syngas fermentation	Aqueous phase reforming	Micro-algae FAME
Technical conversion efficiency limit [MJ fuel/MJ biomass]	0.61	0.77	0.66	0.66	0.49	0.66	0.61	0.96
Scale exponent (d)	0.74	0.70	0.65	0.67	0.75	0.70	0.70	0.70
Learning rate (LR)	0.92	0.92	0.90	0.93	0.97	0.92	0.92	0.94

Table 38 – Conversion of forest residues to diesel via gasification and FT synthesis[28]

Pathway process description: gasification – syngas conditioning – Fischer-Tropsch catalysis – product upgrading

Parameter	Unit	First commercial plant		Medium term		Long term		Assumptions and sensitivities
Conversion efficiency	MJ$_{fuel}$/ MJ$_{feedstock\ dry}$	0.43		0.47		0.52		Based on the following theoretical limits: 85% gasification, 98% syngas conditioning, 75 % Fischer-Tropsch synthesis, 98 % Fischer-Tropsch product upgrading (own calculations and expert interviews).
Conversion yields	t$_{fuel}$/ t$_{feedstock\ dry}$	0.18		0.19		0.21		Based on conversion efficiency calculated with lower heating value forest residues 18 MJ/kg and Fischer-Tropsch fuel 44 MJ/kg.
Life cycle GHG emissions	kg$_{CO2eq}$/ GJ$_{fuel}$	4.0		3.6		3.2		Renewable Energy Directive typical value for Fischer-Tropsch diesel from wood.
GHG emissions savings	%	95.2		95.7		96.0		Compared to 83.8 kg CO$_2$e/GJ (Renewable Energy Directive).
Assumed installed capacity	Million litres/ year	206		1 305		13 045		Assumes the first commercial plant is operational in 2020.
Scale of operation	**MW$_{th,input}$**	**Small scale 75**	**Large scale 750**	**Small scale 75**	**Large scale 750**	**Small scale 75**	**Large scale 750**	**(Müller-Langer, 2015)**
Specific capital investment	USD/ kW$_{th,input}$	2,089	1,148	1,694	931	1,304	717	Cost data adjusted with CEPCI; learning rate 0.92 economy of scale exponent 0.74 (de Wit, 2010; van Eijk, 2014; Chen, 2012; Knoope, 2013; Chen, 2012; Müller Langer 2015; Müller Langer 2012).
	USD/ kW$_{th,output}$	5,161	2,836	3,569	1,962	2,507	1,378	
O&M costs	USD/ GJ$_{fuel}$	9	5	9	5	8	4	Assumes 6% of capital investment per year (de Wit 2010; Knoope 2013; Müller-Langer 2012; van Eijck 2014).
Feedstock costs	USD/ GJ$_{fuel}$	15-24		18		17		(Panoutsou 2011; Kühner 2013; Gerssen-Gondelach 2014; E4tech 2014; IPCC 2012; Lamers 2013; Brinsmead 2014; de Wit 2010; Panoutsou 2009).
Production costs	USD/ GJ$_{fuel}$	31-53		30-41		27-35		
	USD/litre	1.11-1.87		1.07-1.44		0.93-1.22		
Regional activity & opportunities	Current commercialisation activities in Europe, North America and China. Interest in the opportunity to produce aviation fuels in all regions.							

Gas To Liquid (GTL)

M100, USA (pilot/demonstration)

INFRA's advanced GTL technology

Investment estimation based on present cost of natural gas and oil.

Daily gas flow million ft³: 1

Gas price | NYMEX per thousand ft³: $2.60

$10 million CAPEX

Daily capacity: 100 barrels

Annual gross margin: $0.1 million

Oil price | Brent price per barrel: $45

Figure 50. Investment estimation INFRA M100[33]

M450, Russia (FEED in progress)

INFRA's advanced GTL technology

Investment estimation based on present cost of natural gas and oil.

Daily gas flow million ft³: 10

Gas price | NYMEX per thousand ft³: $2.60

$61 million CAPEX

Daily capacity: 1 000 barrels

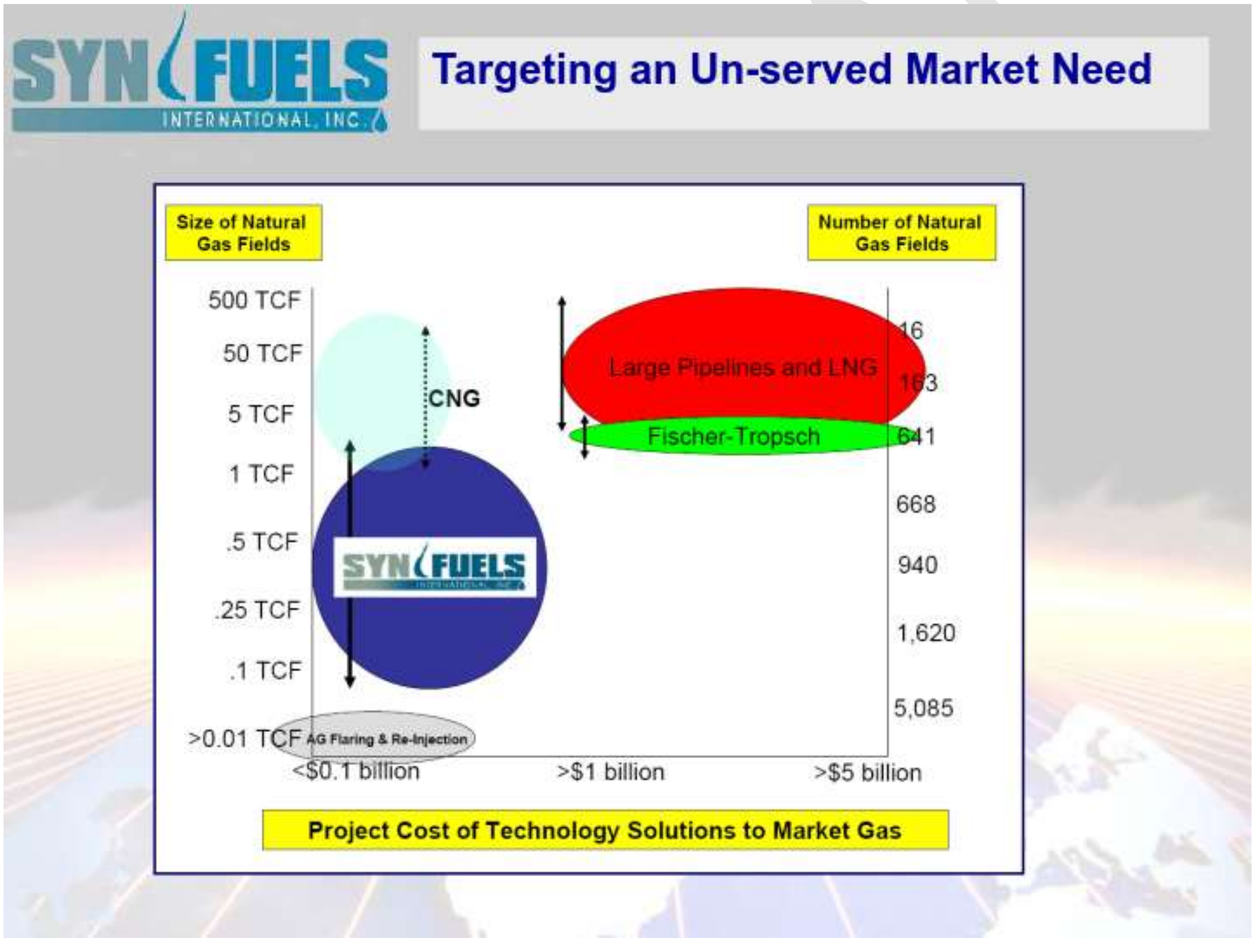
Annual gross margin: $2 million

Oil price | Brent price per barrel: $45

Figure 51. Investment estimation INFRA M450[33]

SYNFUELS INTERNATIONAL INC. - GTL TECHNOLOGY

Synfuels International has developed an alternative to the syngas/Fischer-Tropsch methodology of natural gas conversion with a patented and proven process that significantly reduces capital and process costs. The Synfuels technology is a GTL process that will produce similar or superior end products at a cost below competitive conventional technology. Since its inception in 1998, Synfuels has made significant progress, proving the Synfuels process works with the production of 95 octane fuel from natural gas in a pilot demonstration plant. The success of initial tests have generated worldwide interest resulting in our first fully operational demonstration plant operating for the benefit of gathering data for the construction of an economical and energy efficient commercial GTL plant.



Targeting an Un-served Market Need

Figure 52. Cost area for Synfuels INC. [38]

The New Synfuels GTL Technology

Refinements to existing Fischer-Tropsch processes are not likely to provide the order of magnitude change in economics needed to overcome the obstacles of inefficiency and high capital cost. GTL plants must be economical on a stand-alone basis at a much smaller scale than the mega-plants in order to facilitate a broader and faster commercialization by making it possible for liquid fuel to be marketed from the great multitude of stranded and associated gas fields. Smaller plants need smaller fields and require much less capital, allowing more companies and entities to participate. The new Synfuels GTL technology accomplishes these goals. It is a radically new process that achieves better investment returns than the mega-plants at a fraction of their capacity and capital requirements. There are thousands of gas fields capable of supporting a Synfuels GTL plant.

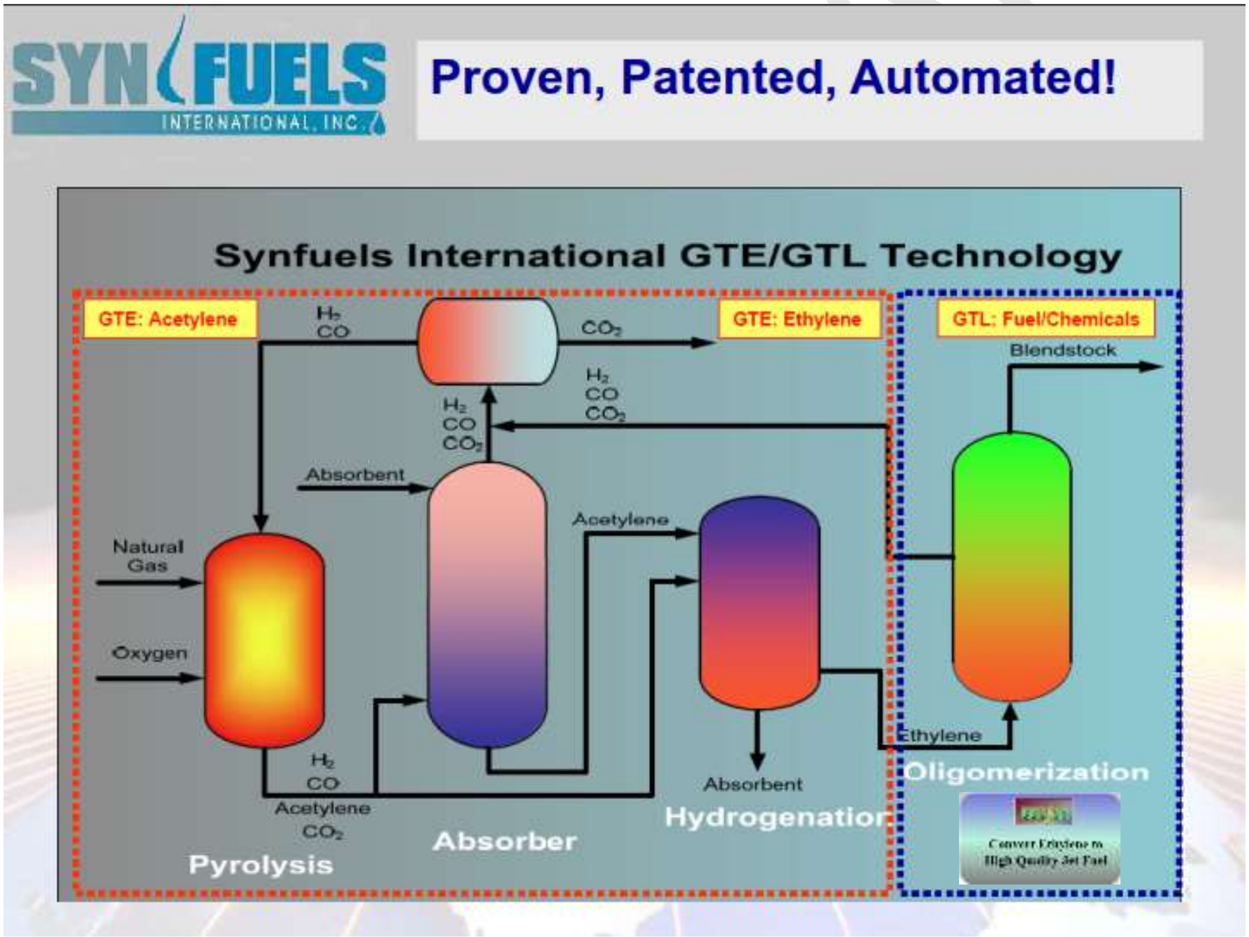


Figure 53. Synfuels INC. technology[38]

The process to produce a gasoline product from a natural gas feed consists of four main steps - conversion, absorption, hydrogenation and oligomerization. The diagram shows the major constituents in the feeds and products of each step. Depending on plant operating conditions and specific equipment utilized, the relative amounts of the intermediate stream constituents will vary, as will the resulting products and by-products.

The key to the new Synfuels technology is the segregation and conversion step where acetylene is separated from other constituents of the cracker effluent and hydrogenated to ethylene using catalysts developed by Synfuels. The second processing step in the Synfuels Process is absorption of the acetylene from the cracked gas using a solvent selective to acetylene. The absorption process has also been used in the acetylene industry for decades.

Variations of the absorption abound within industries with each practitioner having its own solvent, operating conditions, and equipment configuration and design. Temperatures range between approximately 70 degrees F to about 120 degrees F. Column pressures typically range from 100 psig to 250 psig.

The heart of the Synfuels technology lies in the third processing step - acetylene hydrogenation. Gas-phase hydrogenation of acetylene into ethylene is truly commonplace, particularly in ethylene production units. The novel invention used here is conducting the reaction in the liquid-phase. In the liquid-phase process, acetylene-rich solvent from the absorption step is fed into a catalytic reactor along with a hydrogen source the acetylene can be completely converted with 98% selectivity to ethylene. The reactor typically operates between 100 psig and 300 psig at temperatures between 200 degrees F and 350 degrees F. The liquid is easily separated from the product gases, cooled, and recycled to the absorption column. The resultant product gas comprises mostly ethylene.

Advantages Over Fischer-Tropsch Process

1. Majority of stranded gas fields can be utilized.
2. Synfuels GTL process dramatically reduces capital costs.
3. Plants can be configured to produce a variety of products, such as gasoline blendstock, ethylene and acetylene.
4. Keys to the Synfuels process are the innovative and patented steps that isolate and convert the desired intermediates while reducing recycle, compression and system volumes.
5. Synfuels liquid-phase hydrogenation is the technology cornerstone.

Internal Rate of Return (IRR) for GTL via GTE (Gas to Ethylene) – Sensitivity Factors

GAS COST: cost of feed gas for making product

GAS QUALITY: carbon content of the gas on a volume basis

PLANT SIZE: 10 MMSCFD to 500 MMSCFD

PRODUCT VALUE: Sales price of product

EFFECT OF GAS PRICE ON IRR OF GTL AND GTE

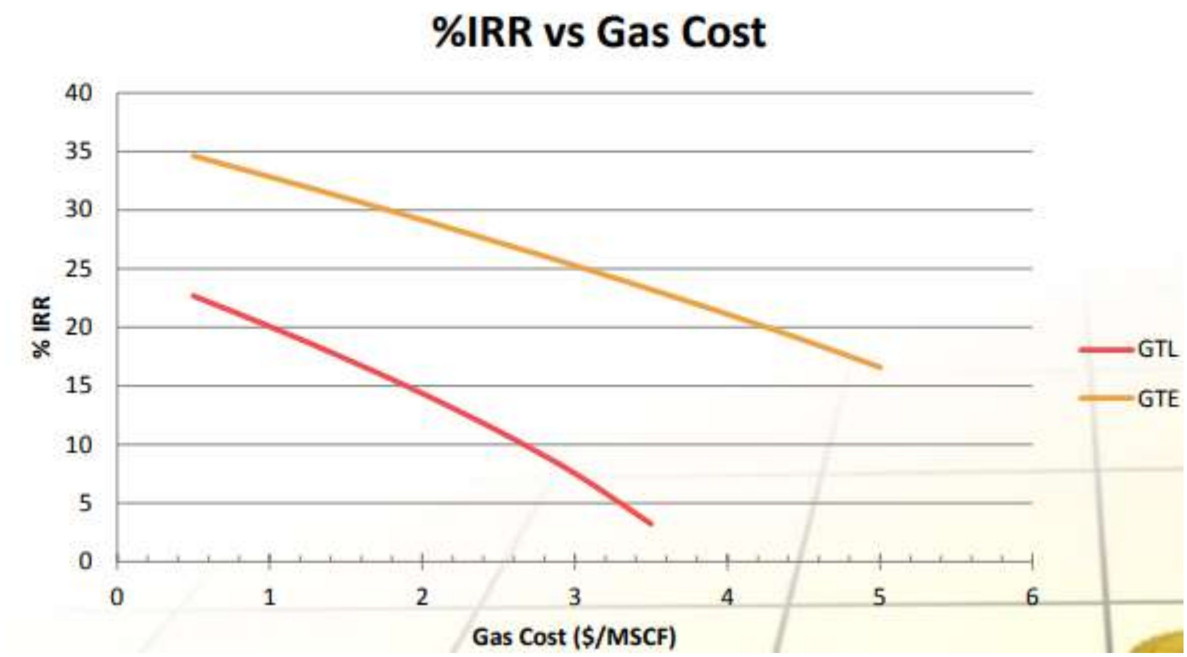


Figure 54. IRR vs gas cost[39]

EFFECT OF GAS QUALITY ON IRR OF GTL AND GTE

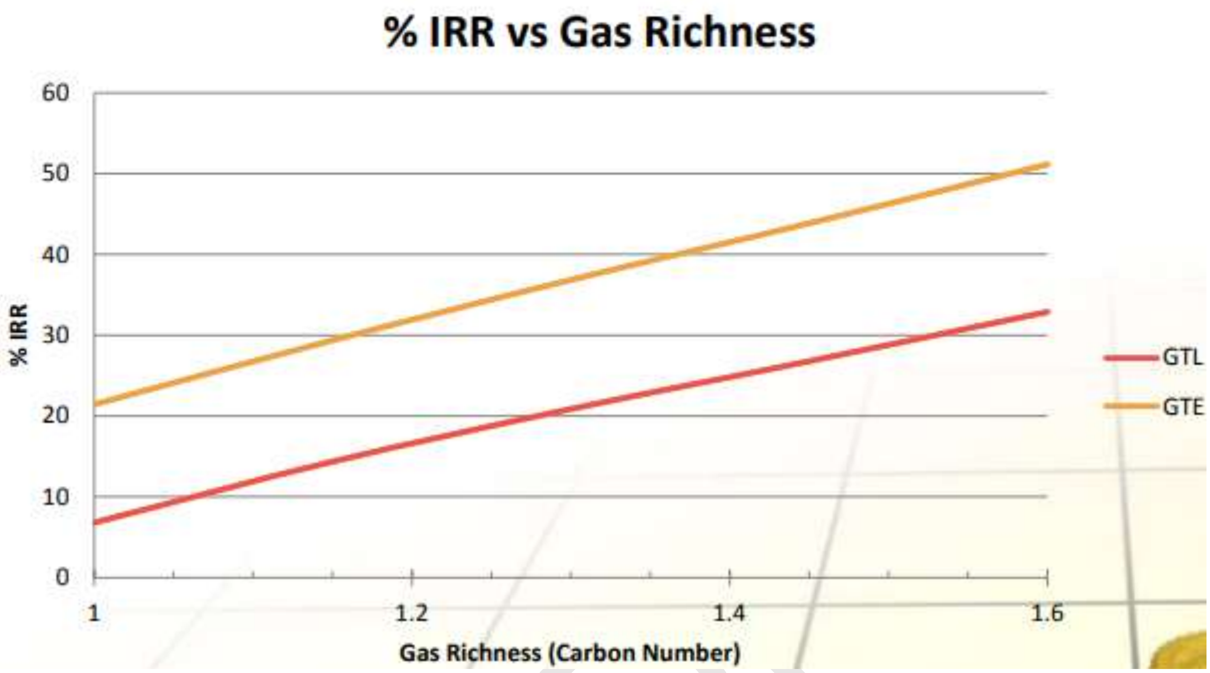


Figure 55. IRR vs gas richness[39]

EFFECT OF PLANT SIZE ON IRR OF GTL AND GTE

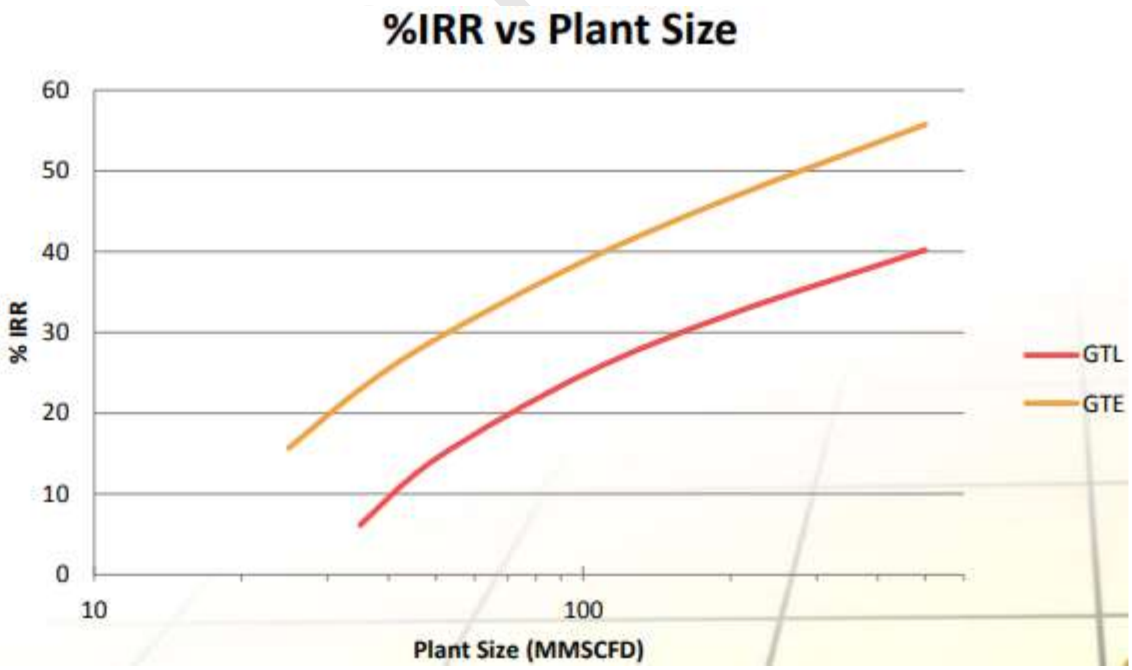


Figure 56. IRR vs plant size[39]

EFFECT OF PRODUCT VALUE ON IRR OF GTL

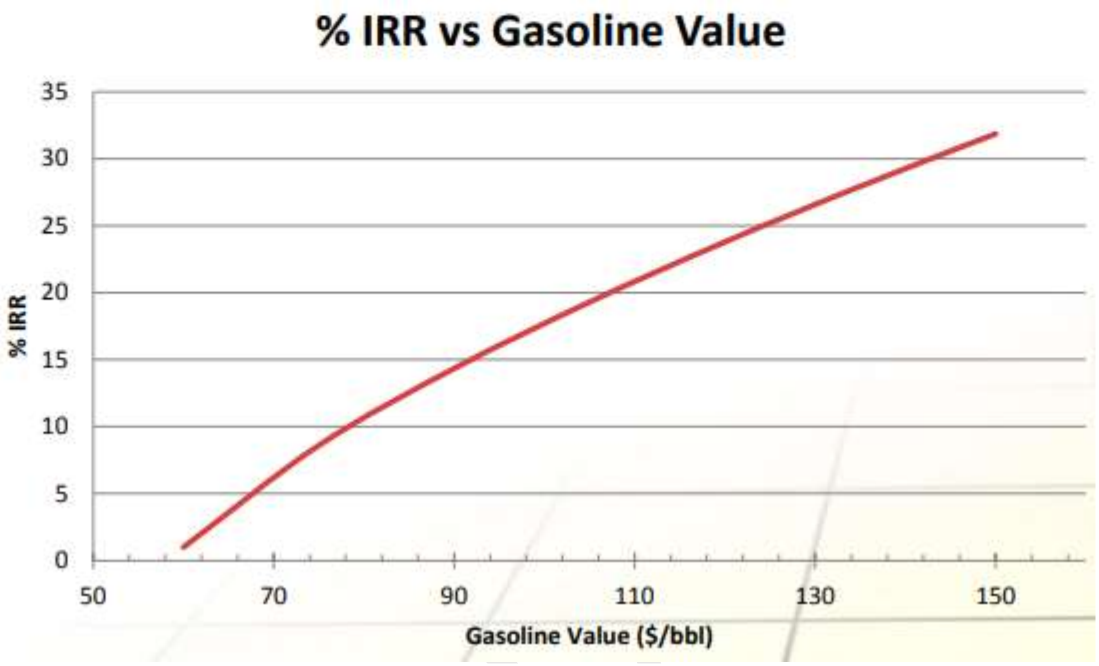
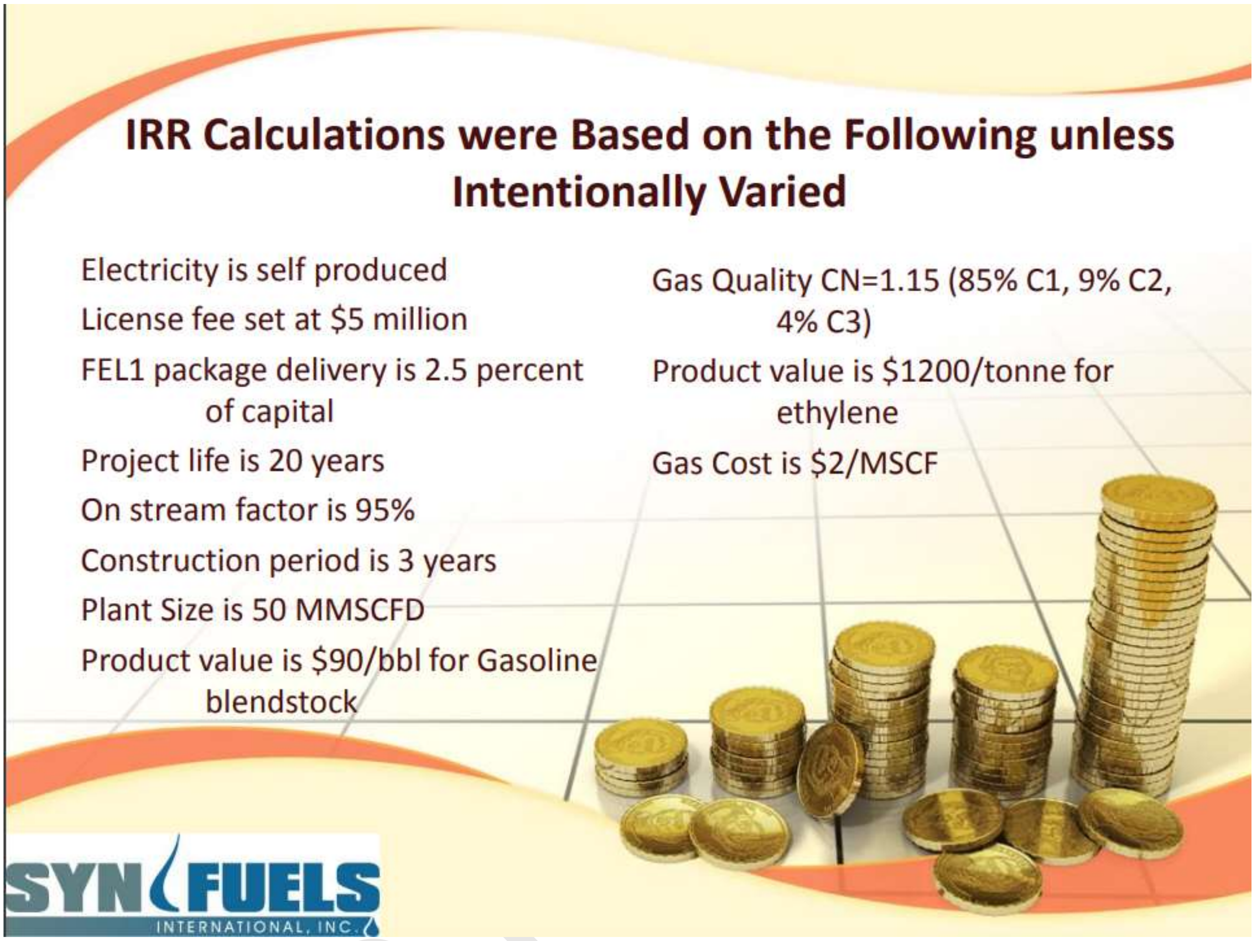


Figure 57. IRR vs gasoline price[39]



IRR Calculations were Based on the Following unless Intentionally Varied

- Electricity is self produced
- License fee set at $5 million
- FEL1 package delivery is 2.5 percent of capital
- Project life is 20 years
- On stream factor is 95%
- Construction period is 3 years
- Plant Size is 50 MMSCFD
- Product value is $90/bbl for Gasoline blendstock
- Gas Quality CN=1.15 (85% C1, 9% C2, 4% C3)
- Product value is $1200/tonne for ethylene
- Gas Cost is $2/MSCF

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Figure 58. IRR base[39]

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