CHAPTER 2

GTL Process Review

The conversion of natural gas into liquid products (GTL) is a two-step process. The first step involves the conversion of natural gas into Synthesis Gas (syngas), a mixture of Carbon Monoxide (CO) and Hydrogen (H_2). In the second step Synthesis gas is converted into long chain hydrocarbons predominantly paraffins using the Fischer Tropsch (FT) synthesis. Synthesis Gas can be produced by steam reforming, partial oxidation, or autothermal reforming of natural gas. In steam reforming, natural gas and steam are catalytically and endothermically converted to syngas that consists of carbon monoxide and hydrogen. The steam reforming is operated at low temperature. Partial oxidation combines natural gas and oxygen via the exothermic noncatalytic reaction, it is operated at high temperature as opposed to steam reforming. Autothermal reforming combines steam reforming and partial oxidation in one reactor to produce syngas, its temperature is higher than steam reforming and lower than partial oxidation. Autothermal reforming has high thermal efficiency and the desired CO/H_2 ratio for FT synthesis. The FT synthesis is used to convert synthesis gas into higher hydrocarbons, it is conducted in FT reactors, which includes fixed bed, fluidized bed and slurry bed reactors. Fluidized bed is mainly used to produce gasoline, fixed bed or slurry bed is used to produce diesel. The FT synthesis for diesel production produces substantial amount of heavy waxes and lower molecular weight olefins. These products can be upgraded into usable paraffinic fuels that fall in the gasoline and diesel range by upgrading them.

An upgrading step is needed to convert olefins and waxes produced in the FT synthesis into high value products that fall in the boiling range of gasoline and diesel. It is an essential process to improve liquid fuel selectivity and quality of GTL products. The upgrading process includes oligomerization of C_3 to C_6 olefins and hydrocracking of the waxes into valuable paraffins.

In 1992 the first commercial GTL plant using FT technologies was commissioned in South Africa. In 1993, the second commercial natural gas based FT plant was commissioned in Malaysia to convert natural gas into middle distillates. These two commercial GTL plants using FT technologies show the technological viability of FT synthesis process. As the cost of syngas production decreases, the GTL products will be able to compete with the conventional crude oil refined products, and the GTL option via the FT synthesis becomes more and more attractive. The following sections provide a review of syngas production, FT synthesis, and GTL product upgrading processes.

2.1 SYNTHESIS GAS PRODUCTION

The three major methods available to produce synthesis gas from natural gas are as follows:

1) Noncatalytic Partial Oxidation of Natural Gas
2) Steam Reforming
3) Autothermal reforming

2.1.1 Non-Catalytic Partial Oxidation of Natural Gas

Non-Catalytic partial oxidation of natural gas with pure oxygen results in a H_2/CO ratio of synthetic gas close to 2 as shown below.

$$2CH_4 + O_2 \rightarrow 2CO + 4\,H_2$$

The process operates at 1300 to 1500°C and pressures up to 70 bar. The carbon efficiency exceeds 95%(Eilers et al., 1990). The synthetic gas is composed of H_2 and CO (up to 95% by vol), the rest being N_2, CO_2, H_2O and traces of CH_4 and solids. This process needs a little adjustment to become suitable for the production of the middle distillates.

2.1.2 Steam Reforming

Steam reforming is another important technique for producing synthesis gas from lighter Hydrocarbons and free carbon like coke. In this process a steam reformer is used for manufacturing synthesis gas, the CO/H_2 ratio from a steam reformer using Natural gas is 3 as shown below.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

This is a catalytic process operating at 850°C temperature and a pressure of 30 bar over a nickel catalyst. Due to the water gas shift reaction, in which CO reacts with H_2, more H_2 is produced and the actual H_2/CO ratio occurs in the range of 5-7.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The excess hydrogen produced in this process can be used in the hydrocracking process for the conversion of heavier hydrocarbon to usable products and the Synthesis gas can be used in the Fischer Tropsch synthesis of long chain hydrocarbons.Natural gas required for steam reforming should be free from sulphur, in order to achieve this objective the natural gas is compressed to reformer pressure, commingled with CO_2, heated and passed through a zinc oxide drum where all the sulpur compounds are removed. The steam reformer converts the natural gas into synthesis gas that is cooled, compressed and fed to an amine scrubber where CO_2 is removed and recycled. The scrubbed gas is passed through a membrane separation system to adjust the H_2/CO ratio. The adjusted synthesis gas is ready to be fed into the FT reactor for heavy Paraffin synthesis.

2.1.3 Autothermal reforming

Autothermal reforming is an attractive solution to the production of synthesis gas required for FT synthesis. The process combines steam reforming and partial oxidation in one reactor. Reformed methane and ethane are cryogenically fractionated with steam and water over nickel catalysts. The H_2 rich stream that is extracted from the cryogenic unit can be recycled to the FT synthesis unit. This process provides the desired H_2/CO ratio of 2:1 and it has a high thermal efficiency.

Partial oxidation and steam reforming of natural gas are carried out simultaneously in a fluidized bed syngas generator which provides for good temperature control at significantly lower temperature than thermal partial oxidation (Chang et al, 1996). This process provides an inherent thermal efficiency and economy of scale advantages as compared to partial oxidation reactors or the multitude of parallel tubes used in the steam reformers. There is a wide range of operating temperatures to produce a H_2/CO ratio of 2/1.

2.1.4 Process evaluation

The steam reforming of natural gas is strongly endothermic. The steam reformer is larger in size. Because of the water gas shift reaction in the steam reforming, the H_2/CO ratio of syngas is in the range of 5-7. Compared with partial oxidation, the steam reforming requires higher capital cost. Partial oxidation of natural gas is exothermic and generates the H_2/CO ratio that is less than 2. In contrast to steam reformer, the partial oxidation unit is very small, conversion of natural gas to synthesis gas is high. Partial oxidation requires an air separation plant and operates at a very high temperature. Autothermal reforming combines steam reforming and partial oxidation in one reactor, which provides the desired H_2/CO ratio of 2:1 and high thermal efficiency. Compared with the steam reforming and partial oxidation, the Autothermal reforming has a lower capital investment and greater potential for economics of scale. Autothermal reforming operates at a lower temperature than partial oxidation. F-T synthesis requires the H_2/CO ratio of 2:1, the H_2/CO ratio of Autothermal reforming of natural gas satisfy this requirement. Autothermal reforming is an advanced technology. The H_2/CO ratio obtained from steam reforming and partial oxidation needs to be adjusted.

Steam reforming operates at a maximum pressure of 30 bar where as the FT synthesis requires a much higher pressure and thus partial oxidation and Autothermal reforming which operates at pressure close to FT synthesis scores over steam reforming by reducing the costs incurred in compressing the gas. The Synthesis Gas production accounts for one half to two third of the total capital cost incurred in the FT synthesis process plant.

Because of the nature of catalysts used in Fischer Tropsch process the synthesis gas should be free from sulphur and sulphur compounds. Natural gas must be desulpherized prior to synthesis gas production. In practice, zinc oxide beds are used to remove traces of sulphur in the last step. After the synthesis gas is ready and is available at the appropriate ratio of H_2/CO of 2, it is subject to Fischer Tropsch synthesis of long chain Hydrocarbons to form GTL.

2.2 FISCHER TROPSCH SYNTHESIS

Fischer Tropsch synthesis of synthesis gas produced from the above-mentioned processes is the second stage for producing GTL from natural gas or coal. The primary reaction that takes place for the formation of hydrocarbons from synthesis gas is as given below.

$$CO + 2H_2 \rightarrow H_2O + \text{-}(CH_2)\text{-}$$

Synthesis gas reacts over a catalyst in a reactor to form paraffins ranging from light gases to long chain, heavy paraffin. The formation and distribution of FT products is very sensitive to the types of catalysts used and the reactor type. Other factors that govern the product distribution of FT synthesis are pressure, temperature, H_2/CO ratio, recycle ratio and space velocity. The FT synthesis is composed of five plant sections, which are F-T synthesis, CO_2 removal, recycle gas compression, hydrocarbon recovery, and hydrogen recovery.

Fischer Tropsch synthesis can be conducted in fixed bed, fluidized bed, or slurry bed Reactors. Heat removal from the exothermic reaction, effective contact of feed and catalyst, CO conversion per pass, chain growth probability (α), separation of products from catalyst, the desired end products, initial capital cost, and the economics to scale up are the various factors that drives the choice of reactor type, catalyst, and operating conditions to be used

2.2.1 FT Synthesis in Fixed Bed Reactors

The tubular fixed bed reactors (TFBR) are ideally suited for the production of long chain, heavy paraffin, mainly waxes which are upgraded to produce transportable and usable end products that falls in the diesel range and these have the capability of operating with reactants in the liquid phase.

The purified syngas is converted into a broad range of products in the FT reactors. The tubular fixed bed reactors are used to produce high molecular weight hydrocarbons in the diesel range, catalyst used in tubular fixed bed reactor is a precipitated and promoted Fe-catalyst. Cobalt based catalysts are also used in the Multi-Tubular fixed bed reactors, these have a high probability for formation of long chain ($\alpha > 0.90$) hence maximizing wax production and minimizing the formation of undesired light hydrocarbons.

The tubular fixed bed reactor (TFBR) with Fe-based catalyst operates at a pressure of 25 bar and at 220-250°C, hence can be coupled with syngas formed by steam reforming, which is at a lower temperature and pressure close to the tubular fixed bed reactor. Pressure drop across the TFBR is considerable. Since the fixed bed reactors produce higher molecular weight paraffins the carbon build up probability on the catalysts are much higher and this may cause catalyst breakdown and catalyst regeneration becomes difficult, which in turn causes blockage and need the replacement of catalyst. Therefore there is a maximum allowable peak for temperature to avoid carbon formation on the catalyst and hence the range of products produced using TFBR is limited. The fixed bed route diesel fuel is completely free from sulfur, aromatics, naphthenes and nitrogen compounds (Dry, 1983)

2.2.2 Fluidized Bed FT reactors

Fluidized bed FT reactors are ideally suited for production of lower molecular weight long chain Hydrocarbons from synthesis gas. These reactors can operate only when all the reactants are in gaseous phase. Circulating fluidized bed reactor (CFBR) runs at 330-350°C and at 25 bar. Fixed Fluidized bed reactors (FFBR) operate at a pressure of 24 bar and a temperature of 340°C. Two types of reactors are used to produce a light syncrude for production of gasoline. The catalyst used for the CFBR and FFBR is a fused and promoted Fe-Catalyst. The FFBR has the following advantages over CFBR: its simplicity, elimination of catalyst recycling which requires a complex support system to handle the circulating catalysts load, and low operating and maintenance costs. Catalyst consumption of FFBR is about 40% of that of CFBR, the cost of FFBR is about 40% of that of an equivalent CFBR. The FFBR can operate at lower temperature and somewhat higher pressure and flow rate than CFBR. The selectivity of heavier syncrude and higher conversion are higher as obtained in the FFBR than that in CFBR.

In the FFBR increase of the catalyst bed due to increase in the carbon deposition does not cause an increase in conversion considerably. When increasingly fluidized bed height interferes with operations of the cyclones in the CFBR, carbon formation on the iron F-T catalyst reduces the density and the amount of iron catalyst and requires higher catalysts circulating rates to maintain the reaction rates hence a higher space velocity is involved which reduces the conversion per pass. The catalyst activity declines with time in the CFBR due to carbon deposition, which negatively affects normal operations of the CFBR. The FFBR has a larger Capacity than the CFBR. Compared with CFBR, FFBR eliminates recycling of catalyst, it is simpler and has a lower operating and maintenance costs (Jager et al, 1990, Table 2.1).

The chain growth probability (α) in fluidized bed reactors is less than 0.71 for the stable fluidized bed process, which eliminates production of heavy wax. For very high α, removal of hydrocarbon from the catalyst becomes a serious problem. Catalyst regeneration is frequent due to the high proportion of condensable products in the fluidized bed process.

TABLE 2.1

Comparison of capital cost and energy efficiency for Circulating Fluidized bed (CFB) and fixed Fluidized bed reactors (FFB)

Type		CFB (base)	FFB	FFB
Number of reactors		3	2	2
Operating pressure		25 bar	25 bar	High
Relative capital cost	Reactors	1.00	0.46	0.49
	Gasloop	1.00	0.78	0.71
	Total plant	1.00	0.87	0.82
Energy efficiency (%)		61.9	63.6	64.7
Relative power import		1.00	0.44	0.41

Source: Jager et al, 1990

2.2.3 Slurry Bed Reactors

The slurry bed reactors operate in series, with a number of reactors operating together. Fischer Tropsch synthesis involving slurry bed reactors is composed of five stages; FT syntheses, CO_2 removal, recycle gas compression and dehydration, hydrocarbon recovery and hydrogen recovery. Total of 24 slurry bed reactors are arranged in series in eight parallel trains, each train have two first stage slurry bed reactors, which feed a single second stage slurry bed reactor. The synthesis gas is fed in the first-stage slurry bed reactors operating at 220^0C and 21.4 bar over a cobalt based catalyst. The CO conversion in the first stage slurry bed reactor is 56%. Before the unconverted synthesis gas leaving the first-stage slurry bed reactors is reheated and fed to the single second-stage reactor, it is cooled and flashed to recover liquids. The single second stage reactor operates at a temperature of 220^0C and a pressure of 21 bar, over the cobalt based catalyst with the CO conversion of about 56%. An overall CO conversion per pass is about 82% (Choi et al, 1996). The Slurry Bed Reactor (SBR) can operate at higher temperature without carbon formation, higher temperature results in wide product selectivities. Hydrogen is recovered from the unconverted synthesis gas and is used in the downstream hydroprocessing units. The excess hydrogen is recycled to the slurry bed reactors. Excess heat is removed by regenerating 11.4 bar steam from tubes within the slurry bed reactors.

The SBR provides on-line removal and addition of catalyst that is not possible with the TFBR, it is simpler and more easily scaled up then the TFBR. The SBR has higher productivity than TFBR. The capital cost required for a large scale SBR plant is less than 40% of that of an equivalent TFBR plant (Jager et al., 1994). High temperature FT synthesis in the FFBR and CFBR results in carbon deposition as opposed to the SBR, which affects the normal operations. The FFBR and SBR have larger capacities and Potential, are suitable to economy of scale.

Synthesis gas can be converted into higher molecular weight linear paraffin in a bubble column slurry bed reactor over a cobalt-based catalyst. The bubble column slurry bed reactor removes substantial heat, released by the FT synthesis reaction via steam generation and provides significant advantages over conventional fixed bed tubular reactor and fluidized bed reactors, this results in high productivity and selectivity and significant economy of scale advantages. 63% straight run liquid fuel can be obtained from a bubble column slurry bed reactor, with a selectivity of 89% conversion of (H_2 + CO) per pass at 514°C. The product upgrading process provides considerable flexibility of product option that includes high quality diesel and jet fuel, chemicals for manufacturing solvents, alcohols, polymers and specialty such as lube oils and waxes. Table 2.2 compares the product slate of cat-feed option and diesel/jet option in the bubble column slurry reactor. The product produced by the bubble column slurry reactor is free from sulphur, nitrogen, nickel, vanadium, asphaltenes, and multi-ring aromatics.

TABLE 2.2

Typical yield from a slurry bubble column reactor

Product	Cat feed option	Diesel / Jet Option
Naphtha	15	30
Diesel/Jet	50	70
Cat Feed	35	0
Total	100	100

Exxon Research and Engineering Company
Source: Chang et al, 1996

Fixed Bed and Slurry bed reactors yield heavier linear chain paraffins that falls in the diesel range as opposed by the fluidized bed reactors that yields comparatively lighter paraffins falling in the gasoline boiling range. The selectivities from different reactors are given in Table 2.3.

TABLE 2.3

Product selectivity for the FT process

	High temp CFB/FFB	Low temperature Fixed Bed Reactor	Low Temperature Slurry Bed Reactor
CH_4	7.0	2.0	3.3
C_2H_4	4.0	0.2	1.9
C_2H_6	3.0	0.6	1.2
C_3H_6	10.7	0.9	3.2
C_3H_8	1.7	0.9	0.8
C_4H_8	9.4	1.0	3.1
C_4H_{10}	1.1	1.4	1.9
C_5+C_6	16.5	4.8	6.1
C_7-160^{0}C (C7-320^{0}F)	20.0	6.2	7.6
160 - 350^{0}C (320-662^{0}F)	15.5	18.3	17.0
+350^{0}C (+662^{0}F)	6.0	62.3	49.5
Oxygenates	5.1	1.4	4.4

CFB: Circulating Fluidized Bed Reactor
FFB: Fixed Fluidized Bed Reactor
High Temperature. CFB/FFB: 330-350^{0}C, 25 bar, H2/CO: >2.0
Low Temperature Fixed Bed: 220-250^{0}C, 25(or 45 bar), 500 hr^{-1}

Source: Dry, 1990

2.3 RANGE OF PRODUCTS

In order to identify the types of GTL products that could flow through the TAPS, GTL product composition and distribution in different process are identified and compared. The FT product selectivity is very important to economics of FT process. Lower C_{4-} and higher hydrocarbon liquid selectivities are preferred.

The range of products produced by the FT synthesis of natural gas depends on many factors, predominantly,

1) Type of reactors
2) Catalysts Used
3) Operating Condition (Pressure and Temperature)
4) H_2/CO ratio
5) Fresh feed gas composition and recycle ratio

2.3.1 The Fischer Tropsch Process – Reactors, Catalysts and Operating Conditions

All the currently competing GTL processes use the Fischer- Tropsch process to convert synthesis gas to liquid hydrocarbons. Commercial scale Fischer-Tropsch plants were built in Germany during World War II, and during the 1980s and early 1990s in South Africa by the

South African Coal, Oil and Gas Corporation Ltd. (SASOL). In both of these situations the types of feedstock, choice of process operations and products produced were mainly the result of the unique political situations existing in Germany and South Africa.

SASOL has built several plants using the FT process to convert synthesis gas derived from coal with the major focus on gasoline production. Over the years SASOL has explored several reactors, catalysts and types of operating conditions. SASOL initially employed two types of reactors the Avgc, a fixed bed reactor and the Synthol, a circulating fluidized bed (CFR) reactor. In both of these reactors SASOL used an iron-based catalyst. The CFR reactor operated at a higher temperature (315°C versus 225°C for the Avgc) and produced a lighter distribution of products. In 1985, SASOL moved to the fixed fluidized bed (FFP) reactor as an improvement over the CFB reactor. The FFB design that became Synthol 2 was a simpler and hence was less costly to construct and had lower operating and maintenance costs. All of this SASOL FT system used an iron catalyst that produced a light spectrum of products which contain a substantial fraction of olefins along with parafins and a modest fraction of oxygenates as shown in Tables 2.3 and 2.4.

TABLE 2.4

Typical GTL composition from low temperature and high temperature FT synthesis reactors

Product	TFBR		SBR		Fluidized Bed	
	$C_5 - C_{12}$	$C_{13} - C_{18}$	$C_5 - C_{12}$	$C_{13} - C_{18}$	$C_5 - C_{10}$	$C_{11} - C_{14}$
Paraffins	53	65	44	44	13	15
Olefins	40	28	64	50	70	60
Aromatics	0	0	0	0	5	15
Oxygenates	7	7	7	6	12	10
n-paraffins	95	93	96	95	55	60

Source: Jager et al, 1995

While SASOL was building its commercial scale facilities in South Africa a number of companies including GULF Oil, Shell, EXXON and Syntroleum were working on the FT process with a different product focus. These development efforts were focused on producing a high quality distillate product as the primary product. These efforts were to produce a FT product in the very high AFS α range as shown in table 2.6. As discussed in the previous section this would be a product with a large fraction of the product being long chain linear paraffins, which would be wax at ambient temperature. Straight chain paraffins have very high octane number and are excellent as a diesel fuel. The heavier paraffins in the wax range would be hydrocracked to lower molecular weight paraffins and branched paraffins in the diesel boiling range. The heavier α FT products are produced using a cobalt paste catalyst enhanced with a variety of promoting agents based on the development efforts of the companies working on the process.

Shell Oil was the first of those working on a distillate GTL process to build a commercial plant. Shell brought its Shell middle distillate synthesis (SMDS) process on stream at a plant built in Bintulu, Malaysia in 1993. Shell considered 3 reactor types for the plant.

1. A fixed bed reactor
2. An ebulliating (boiling) fluidized bed reactor.
3. A slurry bed reactor

Shell determined that fluidized bed reactor can only be used when the reactants are in the gaseous phase, making it incompatible with producing heavy wax product (Van De Burget-1990). Of these 3 reactors considered, Shell chose the tubular fixed bed reactor for its inherent simplicity. The catalyst is packed in tubes and heat removal is accomplished by contact with the boiling water surrounding the tubes. The SMDS incorporates a hydrocracker to upgrade the heavy waxes. The final product array for the plant for two operating modes is shown in Table 2.5.

TABLE 2.5

Variation in product range and principal properties of SMDS products

Product	Gas oil mode	Kerosene mode
Tops-naphtha (wt%)	15	25
Kerosene (wt%)	25	50
Gas oil (wt%)	60	25
Property	Gas oil (Diesel)	Kerosene
Boiling range (0C)	250-360	150-250
Density (Kgm-3)	780	750
Cetane number	75	-
Smoke point (mm)	-	>50
Freezing point	-	-47
Pour point	-10	

While Shell did not choose the slurry phase reactor, many of the other developers have made that selection. The slurry phase reactor operates with a fine catalyst suspended in an oil medium. EXXON, Syntroleum and SASOL's distillate FT process all use the combination of the slurry reactor and cobalt catalyst. DOE has also participated in the slurry reactor research effort with the construction of the test facility at La Porte, Texas.

All the elements of the GTL process will continue to develop, but it will take the construction and operation of commercial facilities to really determine the best chosen for syn gas generation process, FT reactor types, catalyst and upgrading process. The decline in the estimated capital cost over time and the clear movement on commercial facilities in Nigeria and Qatar should prove the viability of capital cost estimated and provide the commercial operating experience to advance GTL process to full commercial status in the next several years.

TABLE 2.6

Product distribution as a function of chain growth probability (α)

Distribution of Fisher Tropsch Products				Calculated distribution in two stage	
Growth Chance	Product wt%			Product Wt%	
α	<C_{10}	C_{10}-C_{20}	>C_{20}	<C_{10}	C_{10}-C_{20}
0.80	62.4	31.8	5.8	63.6	36.4
0.85	45.6	38.9	15.5	48.7	51.3
0.90	26.4	37.1	36.5	33.7	66.3
0.95	8.6	19.8	71.7	22.9	77.1
0.98	1.6	4.9	93.5	20.9	79.1
0.99	0.4	1.4	98.2	20.0	80.0

Source: Eilers et al, 1990

The FT process yields a wide range pf product from methane to heavy waxes (Table 2.5) with an Fe catalyst you can get a product in the 0.75 to 0.80 range that has lots of naphtha and kerosene with a CO catalyst you could get a product in the 0.90 to 0.95 range with mostly distillate (Kerosene and gas oil) and wax.

2.3.2 Type of Reactors

For Fixed bed and Slurry bed reactors the Selectivity of hydrocarbons (C_5+) is 78 to 80%. These processes can be operated in two modes namely gas oil mode and kerosene mode. Typical product composition as obtained from a tubular fixed bed reactor is given in Table 2.7 (Van Der Burgt et al, 1988).

Gas oil accounts for 60% of the total liquid fraction in the gas oil mode, Kerosene accounts for 50% of the liquid products in the kerosene mode. Fixed Bed and Slurry bed reactors yield heavier linear chain paraffins that falls in the diesel range as opposed by the fluidized bed reactors that yields comparatively lighter paraffins falling in the gasoline boiling range. The selectivities from different reactors are given in Table 2.2.

The Fischer Tropsch technology can be used to produce synthetic crude or syncrude. The syncrude mode consists of production of synthesis gas and syncrude, it does not contain the upgrading of FT products. In the syncrude mode, 25% naphtha, 57% middle distillates and 18% wax are produced. The n-paraffins, i-paraffins and olefins account for 84%, 1% and 15%. The n-paraffins are the predominant products.

TABLE 2.7

Typical composition from a tubular fixed bed reactor

Property	
Sulphur, Nitrogen	None
Pour Point	40
Typical Component Range % wt	
Naphtha	25
Wax	57
Middle distillate	18
n-paraffins	84
i-paraffins	1
Olefins	15
Aromatics	Nil

Source: Van Der Burgt et al, 1988

The fixed bed reactors produces 13.3 % C_{4-}, 18% gasoline (C_5-C_{11}), 14% diesel (C_{12}-C_{18}), 7% C_{19}-C_{23}, 20% medium wax and 25% hard wax. The fluidized bed reactors produce 43% C_{4-}, 40% gasoline (C_5-C_{11}), 7% Diesel, 4% medium wax. Compared to product selectivities of the fixed bed reactor, products of the fluidized bed reactor have more C_1-C_4 paraffins, C_2-C_4 olefins, Gasoline, water-soluble non-acid chemicals and water-soluble acids. They have less diesel, heavy oil and waxes. Lighter hydrocarbons (C_{4-}) from the fluidized bed reactors are more olefinic than that obtained from the commercial fixed bed reactor. In the fixed bed reactors as catalyst ages the selectivities of CH_4 and Diesel increase, selectivities of C_2-C_4 paraffins, C_2-C_4 olefins, heavy oil and waxes decrease, gasoline selectivity remains constant. In the Fluidized bed reactors as catalyst ages the selectivities of CH_4, C_2-C_4 olefins and gasoline decrease, selectivities of diesel, heavy oil and waxes increase. Catalyst aging results in higher diesel selectivity, and lower C_2-C_4 paraffin and C_2-C_4 olefin selectivities in both fluidized bed and Fixed bed reactors. The fixed bed reactor can be used to produce diesel and waxy products that are linear hydrocarbons. The fluidized bed can be used to produce gasoline.

A cobalt-based catalyst has a high probability of chain growth ($\alpha > 0.91$) that maximizes the wax production. Hydrocracking of the Heavy Fractions from the FT process results in minimizing the waxy product associated with the gas to liquids and hence increases the value of products by enriching it with the lower fractions obtained as a result of hydrocracking.

Product distribution is a function of the chain growth probability α. The product distribution as a function of the chain growth chance α is given in Table 2.6.

2.3.3 Catalyst

Cobalt based catalyst has lower water-gas-shift activity, higher cost, lower olefin selectivity, longer life and higher methane selectivity than the iron based catalyst under equivalent operating conditions. It can produce high yields of oils and waxes. The Cobalt based catalyst produces lower yield of oxygenated compounds than the iron based catalyst. Iron based catalyst can be used in low H_2/CO feed ratio due to its high water gas shift activity, but it deactivates faster due to oxidation and coke deposition. Because the iron based catalyst has low water-gas-shift activity, the H_2/CO feed ratios need to be adjusted to 2. Water production reduces per pass conversion with the iron-based catalyst.

Fe based catalyst has been used to produce lower molecular weight mix, mainly by Sasol and Sasol has done it with several types of reactors, starting with average fixed bed, then they have used circulating fluid bed and fixed fluid bed. They have done so for South Africa application and stayed with Fe Catalyst as their focus was gasoline. Typical Gas to liquids (GTL) composition obtained by using different catalyst is given in Table 2.8.

For application outside South Africa (e.g. Nigeria, Qatar), Sasol is planning to use the slurry Phase reactors and Cobalt catalyst, Sasol has experience with slurry reactor and has chosen the combination of cobalt based catalyst & Slurry phase reactor for producing a diesel product in Nigeria and Qatar.

Almost if not all, the GTL process developments are going with some type of cobalt catalyst and a focus on diesel catalyst. Shell is still staying with the multi tubular fixed bed reactor. Table 2.6 shows the typical product composition from different catalysts. Catalyst activity can be increased by increasing pressure, temperature and H_2/CO feed ratio.

TABLE 2.8

Typical product composition from different catalysts

	(Fe Catalyst)		
Final Product Mass %	High Temperature F-T (Fluidized Bed)	High Temperature F-T (Fixed or slurry bed)	(Co Catalyst, Fixed bed)
"Fuel gas"	18	10	20
Gasoline	35	19	21
Diesel Fuel	47	70	58
Diesel/Gasoline Mass Ratio	1.3	3.7	2.8

Source: Dry, 1990

We are still in a technology development phase and reactor and catalyst best choices are not clear. It is partly clear that it will be some form of cobalt catalyst and that it will be primarily diesel fuel product. Paraffinic materials have high Cetane number and low octane number and don't reform easily for gasoline blend stock. The paraffinic naphtha will probably be used as an ethylene cracking stock. It could be used as a fuel cell in automobiles but not likely in the near future.

2.3.4 Pressure

As pressure increases, the (H_2 + CO) conversion, the oxygenate content and the heavier hydrocarbon selectivity increases. When pressure is increased the fresh and recycle feed are increased in proportion, and the percentage conversion remains unchanged, Thus increasing pressure means that the reactor's production capacity increases in proportion. For FT synthesis the operating pressure is dependent upon the pressure at which syngas is produced because gas compression accounts for a significant portion of the overall costs.

2.3.5 Temperature

As temperature increases the product selectivity is oriented toward the lower molecular weight products. At high temperature, secondary reaction occur, aromatics are formed, higher Ketones, acid and ring compounds are produced. The high temperature of the FT synthesis produces more olefins, less paraffins and more gasoline than the low temperature FT synthesis. As temperature increases the degree of branching in FT products and the percentage conversion increase, the low temperature FT synthesis yield the larger fraction of straight-chained products.

High temperature CFBR and FFBR have the same FT product distribution of 36.9% C_{4-}, 16.5% C_5+C_6, 20% C_7- 320^{0}F cut, 15.5% 320-662^{o}F cut, 6% 662^{0}F cut and 5.1% oxygenates. Low temperature slurry bed reactor produces more C_{4-}, C_5+C_6, C_7-320^{0}F cuts and oxygenates, and less 320-662^{0}F and +662^{0}F cuts than the low temperature fixed bed products. C_2-C_4 cuts obtained from low temperature slurry bed process are more olefinic than that from the low temperature fixed bed process. High temperature CFBR/FFBR process produces more C_{4-}, C_5+C_6, C_7-320^{0}F cuts and oxygenates and less 320-662^{0}F and +662^{0}F cuts than that of low temperature fixed bed and slurry bed processes.

Low temperature FT products are free from aromatics. The high temperature FT products contain 5% aromatics in the range of C_5-C_{10} and 15% aromatics in the range of C_{11}-C_{14}. Low temperature fixed bed reactor produces 53% paraffin, 40% olefins, 7% Oxygenates in the range of C_5-C_{12}. Low temperature slurry bed reactors produce 29% paraffins, 64% olefins and 7% oxygenates. Low temperature fixed bed reactors produce more paraffins than the slurry bed reactors in the range of C_5-C_{18}. Typical GTL composition from low temperature FT and high temperature FT synthesis reactors are shown in Table 2.4.

High temperature FT process produces more olefins and oxygenates and less paraffins than the low temperature FT process. At low temperature, the n-paraffins are predominant in paraffins.

2.3.6 H_2/CO Ratio

As H_2/CO ratio decreases, the product selectivity shifts to higher molecular weight products. As H_2/CO ratio increases the syngas conversion increases.

2.3.7 Space Velocity

As space velocity of the fresh feed gas increases, the oxygenate content and the olefinity of the F-T product increase and the (H_2 + CO) conversion decreases.

2.4 FT PRODUCTS REFINING AND UPGRADING

The FT synthesis produces a wide range of products from methane to heavy paraffin waxes. Therefore, product refining is an important process to upgrade the FT products and to increase the quality of the end products that would have high premium in the markets. The FT products are condensed. Water and liquid hydrocarbons are obtained. All water is fed to FT water work-up unit to extract alcohols, ketones, aldehydes and acids. The olefins of C_3 and C_4 products separated from the tail gas are oligomerized to gasoline over a phosphoric acid/Kieshelguhr catalyst at about 190^0C and 38 bar. The C_3 and C_4 paraffinic products are sold as light petroleum gas (LPG). The light oil (C_5 to C_{12}), which contains about 75% olefin, is processed over an acid zeolite catalyst at about 400^0C and 1 bar. The oxygenates are converted into olefins and olefins are isomerized. The process improves the research octane number (RON) of the gasoline from about 65 to 86(Pb free). The liquid hydrocarbons from the FT reactor are treated to extract gasoline (RON 35) and diesel. The gasoline can be improved by catalytic isomerization, which forms a product with RON of about 65. The waxes from the reactor are vacuum distilled and the residue is fed to the hydrocracking unit. The wax cuts are hydrorefined to eliminate all oxygenates and olefins over nickel catalyst at about 270^0C and 70 bar. The tailgas includes methane, ethane, ethylene, CO_2 and the unreacted synthesis gas. A part is blended with methane from the cryogenic unit produce town gas. The H_2 extracted from the tailgas in the cryogenic unit is used to produce NH_3. The remaining tailgas is catalytically reformed over nickel catalyst at about 1000^0C with steam and oxygen to produce synthesis gas, which is water scrubbed to remove CO_2 and recycled to the reactor.

Upgrading of the FT products from the fixed bed and slurry bed reactors becomes necessary for the conversion of heavier waxes into usable and lighter products in the diesel range. Product upgrading is an optional stage added to the FT synthesis of GTL to increase the conversion and premium of the end product, it might not be necessary when a fluidized reactor is used for Paraffin synthesis. The products will be upgraded as a part of the GTL process in the conversion of the heavy wax fraction. This assumes that the GTL plant will be producing a high α product with a significant fraction of the reactor production being high molecular weight (720 carbon number) straight chain paraffins.

The primary reactions that govern the upgrading process is hydrocracking. After obtaining heavy paraffin from the Tubular fixed bed reactor, they are converted into middle distillates to produce kerosene and diesel in the hydrocracking process, which is a mildly selective process using a dual function catalyst. Small amount of oxygenates which exists in the waxy products must be removed. Hydrogenation of the olefins, the hydroisomerisation and the hydrocracking are performed in the trickle flow reactor to produce the desired middle distillates.

Hydrocracking is executed in a conventional column and the product fraction boiling above the diesel range is recycled back to the unit. Desired products are obtained by varying the recycling rate and cut-points as well as the single pass conversion. The process operates at a temperature between 300 and 350°C and at 30-35 bar.

The upgrading process with multi tubular fixed bed reactors for FT synthesis includes hydroisomerization and hydrocracking of heavy paraffins. Straight chain paraffins have excellent cetane number and are great diesel fuel (CI engine) except when in cold temperature they solidify in tank or worse get in the vehicle fuel lines. Thus a desirable fuel is one that has high cetane but also has good cold flow properties. That is we need to sacrifice a little of the cetane so that we don't have a fuel that will form solid at cold temperatures.

Hydroisomerization converts the straight long chain paraffins to branched chain paraffins, which have improved "cold flow" properties. Some process uses oligomerization of the C_3 to C_6 olefins as a part of upgrading the products. C_3/C_5 isomerization, catalytic reforming of the hydrorefined C_7/C_{10} cut and hydrocracking of waxes are also practiced as a part of upgrading the GTL. Table 2.9 shows the GTL production from low-temperature fixed bed and high-temperature fluidized bed Fischer-Tropsch operations. Separation and upgrading of the FT products account for 10-15% of the total investment cost. The syncrude mode using fluidized bed reactors eliminates the upgrading process. No matter what alternate batch or transportation mode is used, there is some mixing between crude oil and liquid fuels or syncrude, which requires facility to separate crude oil and liquid fuel at the receiving end of pipeline. The cost of separation between crude oil and liquid fuels is more expensive than that between crude oil and syncrude.

In order to improve liquid selectivity and reduce the cost of synthesis gas production, the combination of both oligomerization of the C_2 to C_6 olefins and hydrocracking of the waxes are preferable.

TABLE 2.9

GTL production from low-temperature fixed bed and high-temperature fluidized bed Fischer-Tropsch operations

Product selectivity after workup	Fixed bed Scheme (%)	Fluidized bed Scheme (%)
CH_4	3	11
C_2	2	8
$C_3 + C_4$	6	4
Light naphtha	10	14
Diesel Fuel	77	57
Water soluble oxygenates	2	6
Origin of Diesel		
Straight-run	28	38
Olefin oligomerization	7	54
Wax hydrocracking	65	8

Source: Dry, 1983

The upgrading process in a GTL plant will be a hydrocracking process that will crack the heavier wax molecule and will form isomers, i.e. branched chain paraffins as opposed to linear paraffins. A branched chain paraffin of the same molecular weight as a straight chain paraffin stay as a liquid at a cold temperature compared to the straight chain paraffin that will for a waxy solid. So the operating temperature of hydrocracking and its catalyst are chosen to hydroisomerize the heavy wax feed. Sasol has combined with chevron that is providing their isocracking (a hydrocracking technology) for the Nigeria and Qatar projects. Shell and Exxon employs similar upgrading.

2.5 SUMMARY

Amongst the syngas production techniques autothermal reforming seems to be highly attractive because of the excellent thermal efficiency, desired H_2/CO ratio as required for the F-T synthesis. Autothermal reforming operates at a lower temperature and has a lower capital investment as compared to steam reforming and partial oxidation. It has a greater potential for economics of scale.

The slurry bed reactor is best suited for the FT synthesis process because of its higher CO conversion capacity, Normal operation at higher temperatures without carbon deposition on the catalyst surface and it's online removal and addition of catalyst ability. Besides this Slurry Bed Reactor gives higher productivity at a lower cost.

Cobalt based catalyst is more promising for the FT synthesis. It has higher paraffin selectivity as desired for the end GTL products, has lower olefin selectivity and a longer life as opposed by the iron-based catalyst. It can produce higher yields of oils and waxes. Cobalt based catalyst has lower water gas shift activity as compared to iron based catalyst which enables it deliver the desired H_2/CO ratio required for F-T synthesis.

The FT synthesis yields liquid fuels in the diesel and gasoline boiling range. It also yields undesirable high molecular weight paraffinic products and olefins. These undesirable products can be upgraded to useful fuels. The combination of both oligomerization of C_2 to C_6 olefins and hydro cracking of the waxes in the Upgrading process can be used to improve liquid fuel selectivity with higher paraffin productivity. Oligomerization of the C_2 to C_6 olefins into gasoline and diesel can be used to reduce the cost of synthesis gas production.

GTL products obtained from FT synthesis and upgrading of olefins and waxes are free from sulphur and aromatic compounds. These products are paraffinic in nature and have similar liquid density and viscosity as that of diesel and gasoline.

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