ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.4, pp 494-505, 2017

An Overview of Ferrous and Cobalt Catalysts Used in the Conversion of Synthetic Gas to Fuels

Arul Jayan[1*], Dawn.S.S[2], Kaushik Anand[1], Joel Stephen[1]

*[1]Department of Chemical Engineering, Sathyabama University, Chennai, India

[2]Head, centre for Waste Management, Sathyabama University, Chennai India

Abstract : Syngas or synthetic gas is a gas mixture containing Carbon monoxide, Carbon dioxide and Hydrogen. Synthetic gas can be obtained from coal or biomass gasification process at high temperature conditions. Since syngas is a colorless, odorless and toxic gas which accelerates green house effect so its concentration in the environment must be reduced. This can be effectively done using Fischer tropsch reaction with the help of catalysts like Iron, Cobalt, Ruthenium etc which converts the syngas to fuel. This is effective not only in the reduction in the concentration of syngas but also in the production of renewable synthetic hydrocarbon fuels which can act as a substitution to rapidly declining non renewable fuels. This paper explores the recent status of conversion of synthetic gas to liquid fuel conversion process by catalysis using Iron and Cobalt catalysts in Fischer Tropsch process. It also discusses about the catalysts, its properties and its activity when they are used in Fischer tropsch reaction.

Keywords: Fischer–Tropsch; biomass; synthetic gas; gasification; catalyst.

Introduction:

Synthetic gas can be obtained from a number of sources such as bio-mass, coal, natural gas or any hydrocarbon feedstock by reacting it with steam (steam reforming), with carbon dioxide (dry reforming), and with oxygen (partial oxidation) [1].The composition of synthetic gas highly depends upon the gasifier's input. The raw materials for gasification (creation of syngas) are petroleum based materials, coal or other materials that can be rejected as waste material. Feedstock is prepared from these materials which are further fed into the gasifier in slurry or dry form. In the gasifier, this feedstock reacts with steam in an oxygen deprived atmosphere at elevated pressure and temperature. The compositions of syngas obtained are 85% carbon monoxide, hydrogen and small amounts of methane and carbon dioxide [2]. The composition of synthesis gas is listed below in table 1.

Table 1: Synthesis gas composition

Substance	Composition percentage (%)
Hydrogen	20-40
Carbon Monoxide	35-40
Carbon Dioxide	25-35
Methane	0 - 15
Nitrogen	2-5

Some trace elements of impurities maybe present in the syngas which can be removed by further processing which are either recovered or sent back to the gasifier. For example, sulfur is recovered as sulfuric acid or in the elemental form and both of these can be marketed. If nitrogen content is present in syngas, then it is mandatory to separate it in order to avoid the production of nitric oxides which are pollutants and can contribute to acid rain production. Syngas is generally used as a fuel in an Integrated Gasification Combine Cycle power generation system in order to obtain electricity [3]. A number of commercially available technologies are there to process syngas which can be used to generate chemicals, fuels, industrial gases, fertilizers, and other products. Many useful products from the gasification of biomass can be obtained such as syngas, bio-fuels, heat, fertilizer, power, and bio-char. Syngas can be further processed into dimethyl ether, methanol and other chemical feed stock by means of Fischer Tropsch [4].

Process Analysis:

There are three important steps involved in conversion of synthesis gas to fuels by Fischer Tropsch synthesis [5, 6, 7]. In Step 1, raw syngas is obtained by gasification process and in Step 2, the raw syngas with impurities and trace elements are cleaned by separation equipments to produce clean syngas and in Step 3, the clean syngas is introduced into Fischer Tropsch reactor to convert it into long chain hydrocarbons. The process flow diagram is shown in Figure 1.

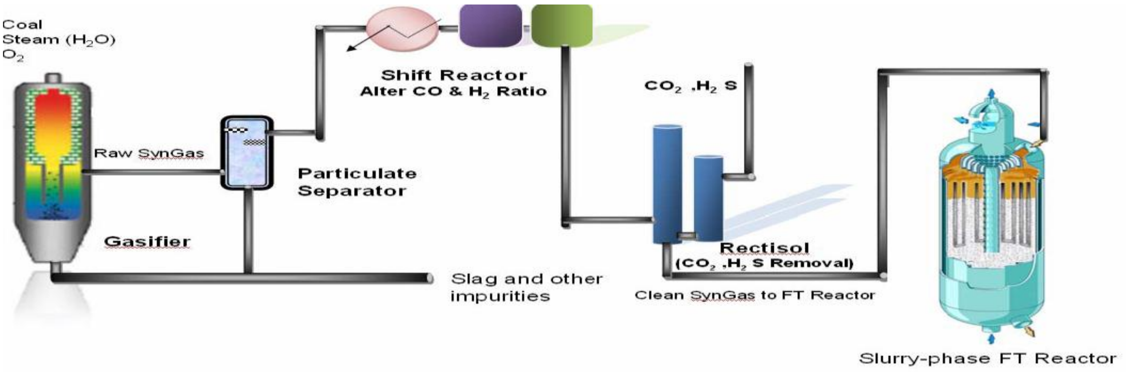


Figure 1: Process flow diagram of biomass to fuel by Fischer Tropsch reaction process

Fisher Tropsh Process:

Fischer Tropsch process is a series of chemical reactions that converts syngas (mixture of carbon monoxide and hydrogen) into liquid hydrocarbons. FT chemistry is a vital technological input for converting syngas to transportation fuels and other liquid products [8].The conversion of syngas from natural gas, coal and biomass to long chain hydrocarbons and alcohols is a matter of great challenge [9,10,11].The Fischer-Tropsch process is a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H_2) mixture are converted into hydrocarbons of various molecular weights according to the following equation:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_n H_{(2n+2)} + n\ H_2O \ ..(Eq.1)$$

Where n is an integer. For n=1, the reaction shows the formation of methane, which is an undesirable byproduct. The Fischer-Tropsch process conditions are specified in order to maximize the formation of higher molecular weight hydrocarbon liquid [12]. Water-gas-shift reaction is predominant compared to the other side reactions which are taking place in the process

$$CO + H_2O \rightarrow H_2 + CO_2 ..(Eq.2)$$

Hydrocarbons ranging from methane to higher molecular paraffins and olefins can be obtained depending on the catalyst, temperature, and type of process employed. Small amounts of low molecular weight oxygenates are formed. The Fischer-Tropsch synthesis reaction is a condensation polymerization reaction of carbon monoxide. Its products is governed by a well-defined molecular weight distribution pattern according to a relationship known as Shultz-Flory distribution [13].

Design of the Fischer-Tropsch Process Reactor

Since reactions are characterized by high exothermicity, the basic need of Fischer–Tropsch reactors is the efficient removal of heat from the reactor. Here four types of reactors are being discussed.

MULTI TUBULAR FIXED BED REACTOR

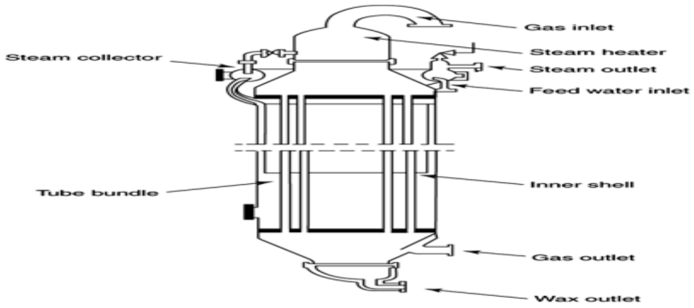
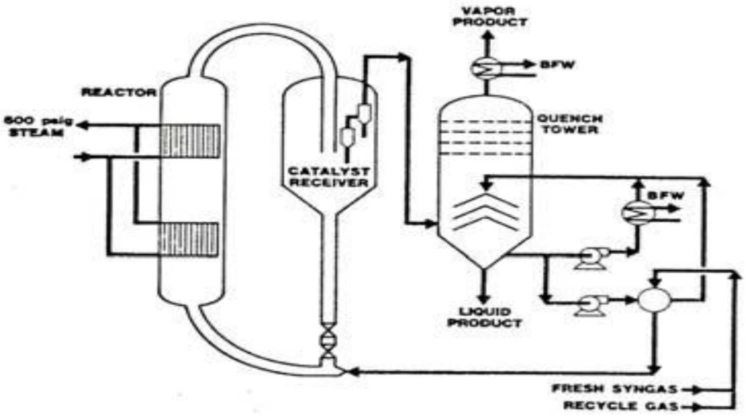


Fig 2: Multi tubular fixed-bed reactor

Multi tubular fixed bed reactor contains a number of tubes with small diameter. The heat of reaction associated with the process is removed by these tubes which incorporate catalyst along with them surrounded by boiling water. In case of low temperature operations, fixed-bed reactor is preferred and has a maximum temperature limit of 530 K. Excess temperature leads to carbon deposition thereby blocking the reactor. This type of reactor can also be called as trickle flow reactor system, since large amounts of the products formed are in liquid state. This reactor has a high wax production.

ENTRAINED BED REACTOR



Entrained bed reactor

Fig 3: Entrained bed reactors

The removal of heat of the reaction is an important requirement for Fischer Tropsch process. The heat is removed mainly by two banks of heat exchangers, rest of heat is removed by the products and recycled back to the system. To avoid fluidization, the formation of heavy waxes should be eliminated, since they condense on the catalyst and form agglomerates. Hence, risers are operated over 570 K.

FLUIDISED BED REACTOR

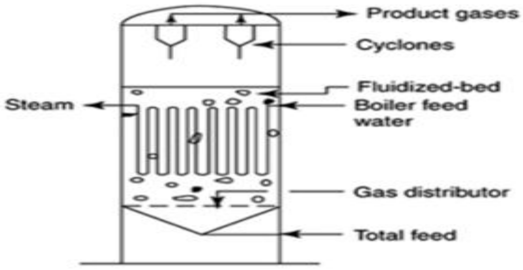


Fig 4: Fluidized bed reactors

In Fixed fluidized bed reactors, the maximum temperature it can withstand is 593 K and the pressure is 2.7 MPa. It has a high gas velocity; LHSV is of the range 2000-3000. Its recycle ratio is 1.5. Advantages of these reactors include high yield, high throughput and good temperature control. In moving fluidized bed, the temperature it can withstand is of the range 593 - 633 K and the pressure is 2.7 MPa. The catalysts which are placed in this reactor lasts about 40 days and are replaced.

SLURRY REACTOR

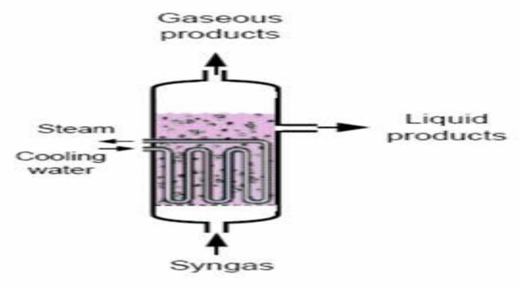


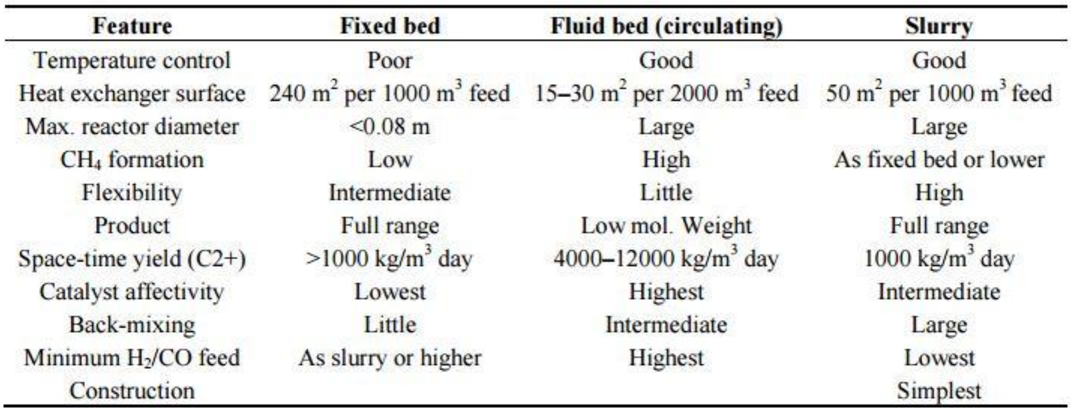
Fig 5: Slurry Reactor

In this reactor, internal cooling coils are provided to remove heat. The waxy products and finely-divided catalyst are suspended in liquid medium through which synthetic gas is bubbled which leads to agitation of the contents of the reactor. The catalyst particle size reduces diffusional heat and mass transfer limitations. By decreasing the temperature, highly viscous product is formed and by increasing to a higher temperature (> 570 K), an undesirable product spectrum is formed. This reactor has a high wax selectivity and has the most flexible design

HTFT and LTFT

There are two temperature ranges Fischer Tropsch reactors which are commercially available. Iron based catalyst is used in high temperature Fischer Tropsch (HTFT) reactor around 340 °C to produce olefins and gasoline. Cobalt based catalyst are used in low temperature Fischer Tropsch (LTFT) reactor around 230 °C to produce diesel and linear waxes [14].Commercially established FT reactors can be divided into three main categories: fixed bed, fluidized bed and slurry FT reactors [15]. The critical features of Fischer Tropsch reactors, such as heat transfer and mass transfer are summarized and compared in Table 2 [16].

Table 2. Comparison of selected FT reactors



Feature	Fixed bed	Fluid bed (circulating)	Slurry
Temperature control	Poor	Good	Good
Heat exchanger surface	240 m^2 per 1000 m^3 feed	15–30 m^2 per 2000 m^3 feed	50 m^2 per 1000 m^3 feed
Max. reactor diameter	<0.08 m	Large	Large
CH_4 formation	Low	High	As fixed bed or lower
Flexibility	Intermediate	Little	High
Product	Full range	Low mol. Weight	Full range
Space-time yield (C2+)	>1000 kg/m^3 day	4000–12000 kg/m^3 day	1000 kg/m^3 day
Catalyst affectivity	Lowest	Highest	Intermediate
Back-mixing	Little	Intermediate	Large
Minimum H_2/CO feed	As slurry or higher	Highest	Lowest
Construction			Simplest

Other theoretical and practical aspects of selecting and designing FT reactors can be found in previous works [17–21].

Process Conditions

Generally, the temperature ranges of Fischer–Tropsch reaction is from 150–300 °C (302–572 °F). At higher temperatures, reaction and conversion rates are higher bus also leads to methane production. Due to this reason, the temperature is usually maintained at the low to middle part of the range. Due to increase in pressure, higher conversion rates occur and also favor formation of long-chained alkanes, which is also desirable. Typical pressures range from one to several tens of atmospheres. Higher pressures would be favorable but the additional costs of high pressure equipment are not justified and higher pressures lead to catalyst deactivation through coke formation.

A variety of synthesis-gas compositions can be used. For cobalt-based catalysts the optimal H_2: CO ratio is around 1.8–2.1. Iron-based catalysts can work on lower ratios due to Water Gas Shift Reaction activity of the Iron catalyst. This reactivity can be useful for syngas which is derived from coal or biomass and tends to have relatively low H_2: CO ratios (less than 1).

The FT reaction is catalyzed by both iron and cobalt at pressures ranging from 10 to 60 bar and temperatures ranging from 200 to 300 °C. Fischer Tropsch reaction is considered to be a surface polymerization reaction. The reactants, CO and H_2, adsorb and dissociate at the surface of the catalyst and react to form a chain initiator [22].

The reaction proceeds by chain propagation, chain termination and product desorption. This product distribution can been explained by addition of CH_2 monomers step wise into the growing chain, as shown in the following equation [23].

$2nH_2 + nCO \longrightarrow -(CH_2)-_n + n\,H_2O;\ \Delta H^o_{250C} = -158{:}5$ KJ/mol (n=1). .. (Eq. 3)
$2nH_2 + nCO \longrightarrow CnH_2n + nH_2O$. ..(Eq. 4)

FT reaction in its simplest form is as described in Eq. (3), towards the formation of alkanes, and Eq. (4), as the formation of alkenes, where water is the prevailing oxygenated product [24].

In Eq. (5), the water-gas-shift reaction (WGS) is a reversible reaction with respect to carbon monoxide and is assumed that CO_2 is essentially formed by this reaction [25]. Iron based catalysts are active WGS catalysts and, therefore, play a major role in Fischer Tropsch chemistry when Fe is used as a catalyst.

$CO + H_2O \leftrightarrow CO_2 + H_{2.\,\ldots}$ (Eq. 5)

The ratio of consumption of H2 and CO, also known as the usage ratio governs the overall stoichiometry of the Fischer Tropsch process. Reactions (2–4) are the simplified versions of several reactions that occur during the Fischer Tropsch process. The usage ratio varies considerably depending on the extent of the other reactions. Water-gas-shift (WGS) also has an impact on the usage ratio [26]. Over Fe catalysts, WGS reaction occurs concurrently with Fischer Tropsch reaction, thereby reducing the usage ratio. This enables to use syngas with H_2: CO ratio less than 2.1 [27]. Cobalt catalysts have very low activity for the Water Gas Shift reaction and hence the extent of Water Gas Shift reaction is almost negligible [28]. For cobalt catalysts, the usage ratio ranges between 2.06 and 2.16 depending on the extent of methane formation, the olefin content in the longer chain hydrocarbons and slight Water Gas Shift activity [29]. Considering the idealized case of biomass as a feed stock that is gasified to generate syngas and subsequently undergoes Fischer Tropsch synthesis, the overall reaction is

$$2C + 1/2\ O_2 + H_2O \longrightarrow -(CH_2)- + CO_2.\ \ldots\ (Eq.6)$$

Fischer Tropsch synthesis yields a wide range of hydrocarbon products. Like conventional crude oil, products of Fischer Tropsch synthesis do not refer to a single product. The composition of the Fischer Tropsch products depends on the Fischer Tropsch catalyst and the reaction conditions. Consequently, the Fischer Tropsch synthesis step directly influences the product quality [30]. The formation of various Fischer Tropsch products is steered by mechanistic and kinetic factors, and the product spectra are very different from the expected thermodynamic considerations.

Fischer Tropsch Reaction Mechanism

Kinetic studies uses empirical power law expressions to describe the overall reactions, but the Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics is used to explain the Fischer Tropsch mechanism. Hydrogen and carbon monoxide adsorbs on Fischer Tropsch catalysts and the extent of their adsorption depends on the catalyst and reaction conditions. Carbon monoxide is adsorbed more strongly than Hydrogen. Hydrogen and Carbon monoxide adsorption forms a product that is capable of combining to form hydrocarbons by polymerization reactions [31]. The various reactions during the polymerization steps are initiation, propagation and termination. Initiation is the formation of the chain-starter monomer runs it from the adsorbed reactants, and propagation is the addition monomers to the growing chains. Finally, termination results in desorption of growing chains from the surface of the catalyst [32].

$$\text{Log}\ (wi/i) = i \log \alpha + \log\left((1-a)^2/\ \alpha\right).\ ..(Eq.7)$$

The above equation is known as Anderson–Schultz–Flory (ASF) chain length statistics.

Where,

wi is the weight fraction of the product,

‘i’ refers to the chain length of hydro carbon,

‘α’ is the chain growth probability.

Fischer Tropsch reaction mechanism is supposed to follow the ASF distribution, although variations may be needed to account for the nature of the catalyst particles [33].

Fisher Tropsh Catalysts:

Fischer Tropsch process is a catalyzed chemical reaction in which carbon monoxide’s hydrogenation takes place to produce liquid hydrocarbons of various forms. The catalyst used is a chemical compound that enhances the chemical reaction rate without altering the final equilibrium. Catalysts reduce the free activation energy in order to speed up the reaction.

Catalysts used for Fischer Tropsch synthesis are generally transition metals of iron, cobalt, nickel and ruthenium. Among these catalysts, it is generally known that:Nickel (Ni) promotes methane formation in methanation process which is generally not desirable.Iron (Fe) is relatively low cost and has a higher water-gas-shift activity, and is therefore more suitable for a lower hydrogen/carbon monoxide ratio (H_2/CO) syngas such as those derived from coal gasification.Cobalt (Co) is more active, and generally preferred over ruthenium (Ru) because of the prohibitively high cost of Ruthenium.In comparison to iron, Co has much less water-gas-shift activity, and is much more costly.

Given these constraints, commercially available Fischer Tropsch catalysts are either cobalt or iron based. In addition to the active metal, the iron catalysts contain a number of promoters, including potassium and copper, as well as high surface area supports like silica or alumina.

Only iron based catalysts are nowadays used for converting coal derived syngas into Fischer Tropsch liquids, given iron catalyst's inherent water gas shift capability to increase the H_2: CO ratio of coal derived syngas, thereby improving hydrocarbon product yields in the Fischer Tropsch synthesis. Iron catalysts are used in high-temperature (300-350°C) as well as low-temperature range (220-270°C), whereas Cobalt catalysts can be only used in the low temperature range. Higher temperatures leads to formation of methane, which is worse for Cobalt compared to iron.

Cobalt catalysts are more costly than iron but are a useful for Fischer Tropsch synthesis because they show activity at lower synthesis pressures, so higher catalyst costs can be offset by lower operating costs. Also, coke deposition rate is higher for iron catalyst than Cobalt catalyst; consequently, Cobalt catalysts have longer lifetimes. Cobalt catalysts have a long lifetime/greater activity.

Both iron and cobalt Fischer Tropsch catalysts are sensitive to the presence of sulfur compounds in the syngas and can be poisoned by them. The reason why cobalt catalysts are preferred for Fischer Tropsch synthesis is due to its sensitivity to sulfur is higher. Iron catalysts are preferred when the syngas is having less sulfur content.

Nickel can also be used as a catalyst for Fischer Tropsch reaction, but at the cost of methane formation which is generally termed as methanation.

Cobalt

If the feed is natural gas, cobalt based catalysts are used. Since natural gas has high H_2 to Carbon ratio, water gas shift reaction is eliminated for cobalt catalysts. For poor quality feed, Iron catalysts are used. For syngas with low amount of hydrogen, water gas shift reaction is used. Fischer–Tropsch catalysts are sensitive to poisoning by sulfur-containing compounds. Cobalt-based catalysts are more sensitive than for their iron counterparts.

Iron

Iron catalysts require alkali promotion to gain high activity and stability. The working catalyst is only captured after reduction with hydrogen in the beginning period of synthesis many iron carbide phases and elemental carbon are formed whereas iron oxides are found in addition to iron. With iron catalysts, there are two such directions of selectivity. One direction has targeted at a low molecular weight olefinic hydrocarbon mixture to be produced in an entrained phase or fluid bed process. Because of comparatively high reaction temperature (~ 330 °C), the average molecular weight of the product is too low to have liquid product phase occurring under reaction conditions. The catalyst particles moving around in the reactor are tiny (particle diameter is approximately 100 µm) and carbon deposition on the catalyst does not affect reactor operation.

Ruthenium

Ruthenium is highly active in the Fischer Tropsch reaction, but its availability is very less and its cost is quite high. Nickel is also highly active, but results in a lot of methane production because of its strong hydrogenating properties. At high pressure nickel tends to form volatile carbonyls and disappears from the reactor gradually. Hence iron and cobalt are widely used catalysts in industries.

Ruthenium is most active even at a low reaction temperature. It results in the highest molecular weight hydrocarbons. It acts as a Fischer Tropsch catalyst as the pure metal, without any promoters, thus providing the simplest catalytic system of Fischer Tropsch synthesis, where mechanistic conclusions should be the easiest e.g., much easier than with iron as the catalyst. Its high price and limited world resources exclude industrial application.

Promoters

Promoters are used to increase the activity and alter the selectivity to desired products [34–40]. In Fischer Tropsch synthesis, promoters are generally not used for Ruthenium based catalysts due to its high catalytic activity. However, iron and cobalt based catalysts require alkali metals, transition metals and noble metals to increase their activities to achieve desired result [41]. For iron based catalysts, alkali metals are used to alter the electronic properties of iron based catalysts, and to increase the carbon monoxide chemisorptions at the time of reaction, and then to promote the activity of the Fe-based catalysts.

Fischer Tropsch Products

The flow sheet shown below depicts the products obtained from a Fischer Tropsch process using a slurry reactor. Initially syngas is passed to slurry reactor where it is separated into various fractions. Alcohols and ketones are the products obtained by oxygenating the water fraction. C_{12} + fraction enter the hydro dewaxing chamber where diesel is obtained as a product. $C_7 - C_{11}$ fraction enters the catalytic reforming chamber where gasoline is obtained. $C_5 - C_8$ fraction enters the isomerization chamber where gasoline is obtained as a product. Carbon dioxide is removed from C_1-C_4 fraction and passes into cryogenic separation tank where methane is separated and sent to auto thermal reformer where syngas is formed and recycled back. The C_3-C_4 is separated by cryogenic separation and sent to oligomerization chamber where LPG and Gasoline are obtained as products. Ethene is also obtained due to cryogenic separation.

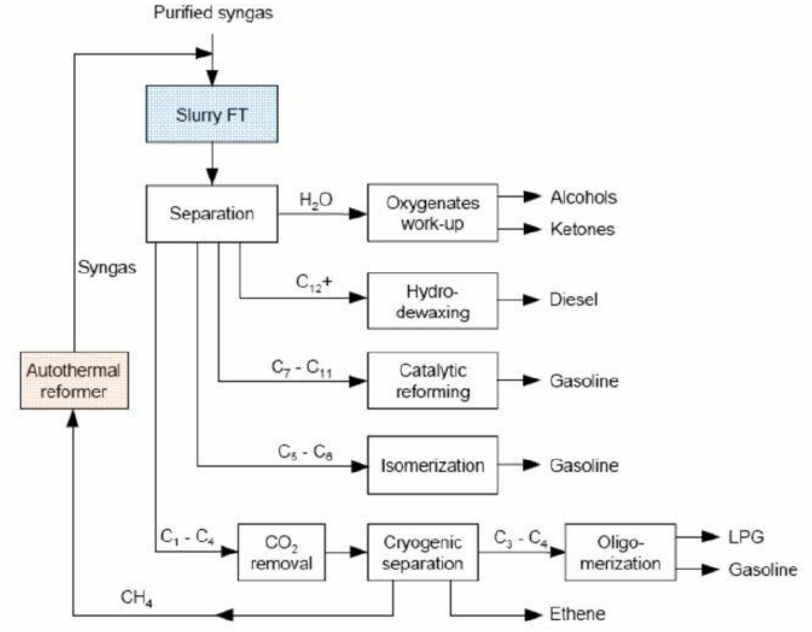
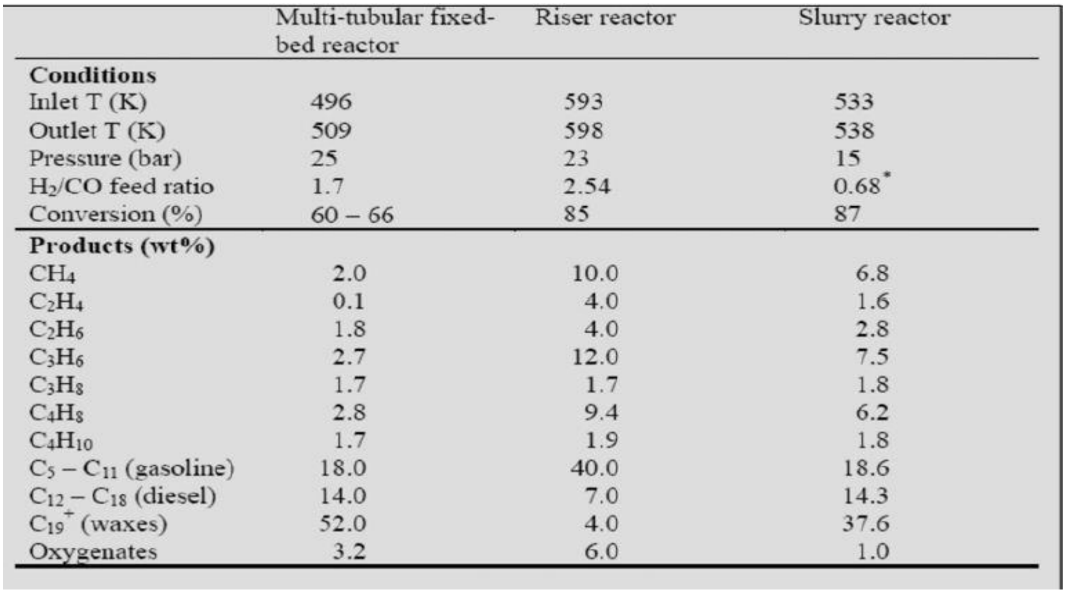


Fig 6: Flow scheme of syn gas and its products

Table 3: Fischer Tropsch Product distribution in several reactors



	Multi-tubular fixed-bed reactor	Riser reactor	Slurry reactor
Conditions			
Inlet T (K)	496	593	533
Outlet T (K)	509	598	538
Pressure (bar)	25	23	15
H_2/CO feed ratio	1.7	2.54	0.68*
Conversion (%)	60 – 66	85	87
Products (wt%)			
CH_4	2.0	10.0	6.8
C_2H_4	0.1	4.0	1.6
C_2H_6	1.8	4.0	2.8
C_3H_6	2.7	12.0	7.5
C_3H_8	1.7	1.7	1.8
C_4H_8	2.8	9.4	6.2
C_4H_{10}	1.7	1.9	1.8
$C_5 - C_{11}$ (gasoline)	18.0	40.0	18.6
$C_{12} - C_{18}$ (diesel)	14.0	7.0	14.3
C_{19}^{+} (waxes)	52.0	4.0	37.6
Oxygenates	3.2	6.0	1.0

Fischer Tropsch Products

A wide variety of hydrocarbon and oxygenated hydrocarbon products are obtained as a result of Fischer tropsch reaction. Selectivity of methane which is an unwanted product, can be of range as low as 1–100%. At the other hand of this product spectrum, the selectivity of long chain linear waxes can range from zero to seventy percent with the intermediate carbon products produced only in small amounts. The carbon number can be changed by varying the operating temperature, the type of catalyst, the amount or type of promoter present, the feed gas composition, the operating pressure, or the type of reactor [42]. Fischer Tropsch synthesis should have high selectivity towards desired products. C_5+ paraffins, low and intermediate-molecular-weight olefins, and C_{20}+ linear hydrocarbons results in the production of fuels and petrochemicals. The selectivity of these products must be maximized. Fischer Tropsch selectivity is determined by the polymerization type kinetics, illustrating the chain growth processes during the catalytic reaction [43]. Fischer Tropsch product distribution obtained from various catalysts indicates specific characteristics on cobalt, iron and ruthenium catalysts. Carbon-number distributions for Fischer Tropsch products show the highest concentration for C_1 and decrease linearly for higher carbon numbers. Around C_3–C_4 often a local maximum is found, as shown in Fig. 7. Monomethyl - substituted hydrocarbons are found in small amounts, and dimethyl products arrive in significantly smaller amounts compared to mono-methyl. None of the branched products has quaternary carbon atoms. A change in chain growth parameter in the distribution is found only for linear paraffins and not for olefins. Alcohol yields maximizes at C_2 and decrease with carbon number [44].

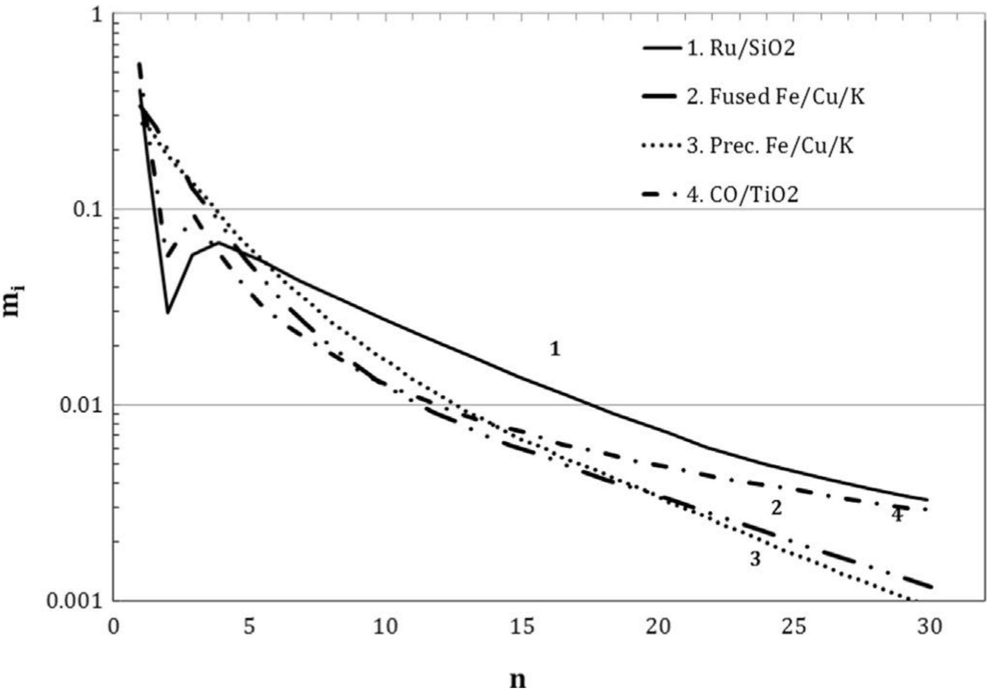


Fig.7.Total hydrocarbon selectivity on Co/TiO_2 (T = 473K, H_2/CO = 2.1, P = 2.0 MPa), Ru/SiO_2 (T = 485 K, H_2/CO = 2, P = 0.51MPa) and fused and precipitated Fe/Cu/K [44].

References:

1) Mehta s, Deshmane V,,Zhao, S,Kuila. D.Comparitive studies of silica encapsulated iron cobalt and ruthenium nano catalyst for fisher tropsh synthesis in silicon – micro channel micro reactors.Ind Eng Chem Res,2014,53(42):16245-16253).
2) Nandan Abhishek, Siddiqui NihalAnwar, Mondal Prasenjit, Chaudhary Kanishak, Pandey Rishi.Hazard s associated to synthesis gas and its mitigation measures. Research journal of engineering and technology, 2014, 5(3):144-146.
3) Samuel .N, *Anyigor, C.M, *Ogah S.P.I Coal gasification A road–map for power generation: A review American journal of scientific and industrial research 2013 ,4 (5),420-428
4) http://biofuel.org.uk/what-is-syngas.html
5) Demirbas, A. Global biodiesel strategies. Energy Educ. Sci. Technol. 2006, 17, 27–63
6) Tijmensen, M.J.A.; Faaij, A.P.C.; Hamelinck, C.N.; van Hardeveld, M.R.M. Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. Biomass Bioenergy 2002, 23, 129–152.
7) Klass, D.L. Biomass for Renewable Energy, Fuels and Chemicals; Academic Press: San Diego, CA, USA, 1998
8) Wilhelm. D, Simbeck. D, Karp A,Dickenson R. Syngas production for gas-to-liquid applications: technologies, issues and outlook. Fuel Process Technol 2001;71(1):139–48.)
9) P.Forzatti, E .Tronconi, I. Pasquon, Catal rev sci eng. 33(1991) 109.
10) J.J. Spivey, A.Egbebi, Chem. Soc, rev.36 (2007)1514.
11) V. Subramani, S.K.Gangwal, Energy fuel 22 (2008) 814
12) Jin Hu, Fei Yu * and Yongwu Lu Application of Fischer–Tropsch Synthesis in Biomass to Liquid Conversion Catalysts 2012, 2, 303-326;
13) Nur Hayati Binti Zulkeflli , Preparation and Characterization of cobalt based and zinc promoted catalyst for fisher tropsch synthesis, march 2011
14) Dry, M.E. Present and future applications of the Fischer–Tropsch process. Appl. Catal. A 2004, 276, 1–3.
15) Sie, S.T.; Krishna, R. Fundamentals and selection of advanced Fischer–Tropsch reactors. Appl. Catal. A 1999, 186, 55–70.

16) Davis, B.H. Fischer–Tropsch synthesis: Overview of reactor development and future potentialities. Top. Catal. 2005, 32, 143–168.
17) Mark, E.D. Practical and theoretical aspects of the catalytic Fischer–Tropsch process. Appl. Catal. A 1996, 138, 319–344
18) Knochen, J.; Güttel, R.; Knobloch, C.; Turek, T. Fischer–Tropsch synthesis in milli-structured fixed-bed reactors: Experimental study and scale-up considerations. Chem. Eng. Process. 2010, 49, 958–964.
19) Guettel, R.; Turek, T. Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study. Chem. Eng. Sci. 2009, 64, 955–964.
20) Jager, B.; Espinoza, R. Advances in low temperature Fischer–Tropsch synthesis. Catal. Today 1995, 23, 17–28
21) Myrstad, R.; Eri, S.; Pfeifer, P.; Rytter, E.; Holmen, A. Fischer–Tropsch synthesis in a micro structured reactor. Catal. Today 2009, 147, S301–S304
22) Hassan kiadeh M N, Khajehfard A, Gol mohammadi M. Kinetic and product distribution modeling of Fischer–Tropsch synthesis in a fluidized bed reactor. Int J Chem En gAppl 2012;3:400–3. http://dx.doi.org/10.7763/IJCEA.2012. V3.227
23) Subiranas A. Combining Fischer–Tropsch Synthesis (FTS and hydrocarbon reactions in one reactor. Karlsruhe: Universitätsverl;2009
24) Adesina A A. Hydrocarbon synthesis via Fischer–Tropsch reaction: travails and triumphs. ApplCatalA: Gen1996; 138(2):345–67.
25) Pour AN, Housain dokht M R, Tayyari S F, Zarkesh J. Kinetics of the water-gas shift reaction in Fischer–Tropsch synthesis over a nano – structured iron catalyst.J Nat Gas Chem2010;19(4):362–8.
26) Dry M.Chemical concepts used for engineering purposes. Stud Surf Sci Catal 2004; 152: 196–257.
27) Lögdberg S. Development of Fischer–Tropsch catalysis for gasified biomass [Ph.D. thesis]; 2007.
28) Tavasoli A, Sadaghiani K, Nakhaeipour A, Ahangari M. Cobalt loading effects on the structure and activity for Fischer–Tropsch and water-gas shift reactions of Co/Al2O3 catalysts. Iran J ChemChemEng 2007; 26(1).
29) De Klerk A. Fischer–Tropsch refining. Wiley-VCH; 2011.p.73–99 [chapter4].
30) Dry, M.E. Present and future applications of the Fischer–Tropsch process. Appl. Catal. A 2004, 276, 1–3.
31) Sie, S.T.; Krishna, R. Fundamentals and selection of advanced Fischer–Tropsch reactors. Appl. Catal. A 1999, 186, 55–70.
32) Davis, B.H. Fischer–Tropsch synthesis: Overview of reactor development and future potentialities. Top. Catal. 2005, 32, 143–168.
33) Mark, E.D. Practical and theoretical aspects of the catalytic Fischer–Tropsch process. Appl. Catal. A 1996, 138, 319–344.
34) Pour, A.N.; Shahri, S.M.K.; Bozorgzadeh, H.R.; Zamani, Y.; Tavasoli, A.; Marvast, M.A. Effect of Mg, La and Ca promoters on the structure and catalytic behavior of iron-based catalysts in Fischer–Tropsch synthesis. Appl. Catal. A 2008, 348, 201–208.
35) Pour, A.N.; Shahri, S.M.K. Promoter effect on the CO2–H2O formation during Fischer–Tropsch synthesis on iron-based catalysts. J. Nat. Gas Chem. 2010, 19, 193–197.
36) Gaube, J.; Klein, H.F. The promoter effect of alkali in Fischer–Tropsch iron and cobalt catalysts. Appl. Catal. A 2008, 350, 126–132.
37) Escalona, N.; Medina, C.; García, R.; Reyes, P. Fischer–Tropsch reaction from a mixture similar to biosyngas. Influence of promoters on surface and catalytic properties of Co/SiO2 catalysts. Catal. Today 2009, 143, 76–79.
38) Zhang, H.; Ma, H.; Zhang, H.; Ying, W.; Fang, D. Effects of Zr and K promoters on precipitated iron-based catalysts for Fischer–Tropsch synthesis. Catal. Lett. 2012, 142, 131–137.
39) Ma, W.; Kugler, E.L.; Dadyburjor, D.B. Promotional Effect of copper on activity and selectivity to Hydrocarbons and Oxygenates for Fischer–Tropsch Synthesis over potassium-promoted iron catalysts supported on activated carbon. Energy Fuels 2011, 25, 1931–1938.
40) Dinse, A.; Aigner, M.; Ulbrich, M.; Johnson, G.R.; Bell, A.T. Effects of Mn promotion on the activity and selectivity of Co/SiO2 for Fischer–Tropsch synthesis. J. Catal. 2012, 288, 104–114.
41) Hans, S. Short history and present trends of Fischer–Tropsch synthesis. Appl. Catal. A 1999, 186, 3–12.
42) Dry M. Chemical concepts used for engineering purposes. Stud Surf Sci Catal 2004; 152:196–257.

43) Iglesia E,Reyes S, Madon R, Soled S. Selectivity control and catalyst design in the Fischer–Tropsch.AdvCatal1993;39:221.
44) Van der Laan G. Kinetics, selectivity and scale up of the Fischer–Tropsch synthesis. University Library Groningen; 1999.

*****