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Conversion of Biomass to Liquid Fuels: Energy for the Future

Sri. S. R. K. Rao, Dr. Amalendu Sinha

***Abstract* – The rising exhaust emission standards & the increasing demand for cleaner and cheaper energy services prompt oil companies to develop technologies such as the so-called gas-to-liquid (GTL) technology, using natural gas, which showed great potential. In parallel to the GTL Technology there is strong research & development of the so called biomass-to liquid (BTL) production process. This process is envisioned to be more CO_2 neutral than using fossil fuels because the primary energy source is renewable plant matter. In the first process step of BTL, the biomass is broken down into a gaseous constituent & a solid constituent (organic semicoke) by low temperature gasifcation. The second process step involves producing the synthetic gas. The synthetic gas is then converted to fuel in a Fischer Tropsch Synthesis process with downstream fuel optimization by H_2 after treatment. So, here the major emphasis has been given on Fischer Tropsch synthesis process for producing liquid fuels from Biomass.**

***Keywords* – Biomass, Fisher-Tropsch, Synthesis Gas, Catalyst, Middle Distillates.**

I. INTRODUCTION

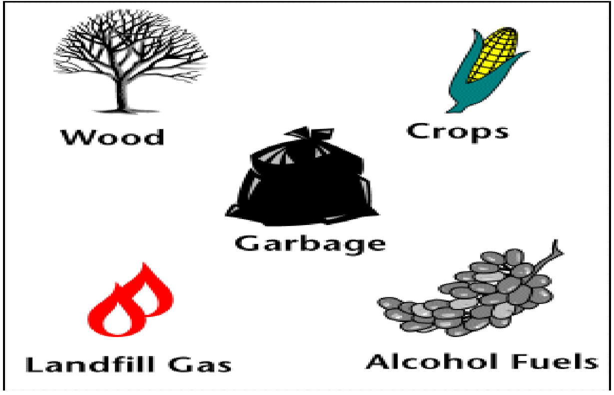
During World War II over a million gasifiers were built for the civilian sector while the military used up all the gasoline. Now that world oil supplies are being depleted and global warming is perceived as a threat to our environment, there is renewed interest in gas from Biomass.

"Woodgas" is the name for the various gases that can be easily made from wood or biomass. Various forms are: synthesis gas, typically 40% hydrogen, H2, 40% carbon monoxide, CO, 3% methane, CH_4 and 17% Carbon dioxide, CO_2; producer gas, made by gasifying biomass with air (and therefore containing ~50% nitrogen); pyrolysis gas, similar to synthesis gas, but including lots or water and tar and accompanied by production of 10-30% charcoal.

Biomass is one of the most promising renewable energy sources showing great variety through thermochemical processing routes.Through Biomass gasification via Fischer Tropsch (FT) synthesis transportation fuels can be produced to replace existing gasoline and diesel.In the course of the FT synthesis numerous products are formed, which consequently influence fuel characteristics.

Biomass resources include any organic matter available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crops, agricultural crop wastes and residues, wood wastes and residues, aquatic plants, animal wastes, municipal wastes, and other waste materials. Material handling, collection logistics and infrastructure are important aspects of the biomass resource supply chain.

Types of Biomass



Babool Wood used at CIMFR

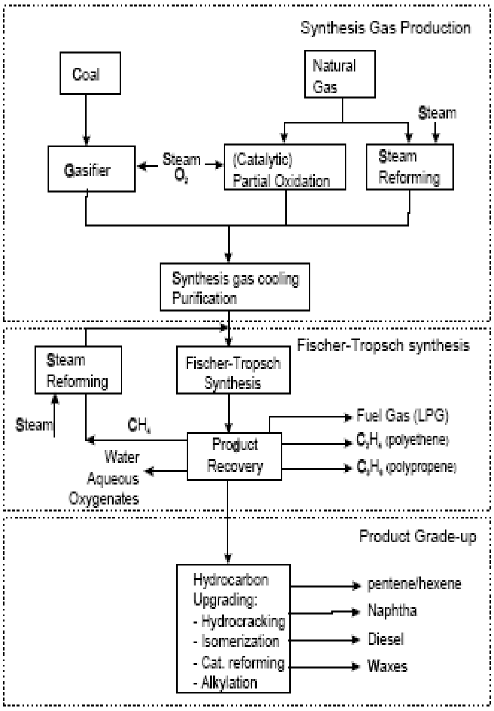
In CIMFR, various research works has resulted that using **BABOOL** wood as the BIOMASS gives many useful liquid fuel products.

Acacia Arabica popularly known as **'Babool'** is originated from the Sind province of Pakistan. It occurs wild the India subcontinent & tropical Africa. It is also cultivated for its bark. The leaves, the bark, the pods & the gum of the tree have medicinal virtues. It is medium sized tree with blackish-grey to brown fissured bark.

The reference literatures define the vegetable gum, as a group of plant product resembling carbohydrates. They are composed of carbon, hydrogen and oxygen with small quantities of mineral matter ash constituents and sometimes a little nitrogen, small quantities of tannin may also be present in some gums. But the gums contain more than these that cannot be detected by modern analytical methods. They are not aware of its chemical constituents and properties but well aware of its unique medicinal properties and utilities.

Products and their uses

Products	**Uses**
CH_4, C_2-C_4 hydrocarbon.	Industrial and Household Uses.
Naptha – C_5-C_{10} (low octane number)	Gasoline Blending
Middle distillate c_9-c_{20}	Jet and diesel fuel
Medium gas oil C_{16}-C_{25}	Marine diesel fuel
Heavy gas oil C_{22+}	Lube oil, waxes



Synthesis gas production

The initial reactants (synthesis gases) used in the Fischer-Tropsch process are hydrogen gas (H_2) and carbon monoxide (CO). These chemicals are usually produced by one of two methods:

1. <u>The partial combustion of a hydrocarbon:</u>

   $$\mathbf{C_nH_{(2n+2)} + ½\, nO_2 \rightarrow (n+1)H_2 + nCO}$$

   When n=1 (methane),the equation becomes :-

   $$\mathbf{2CH_4 + O_2 \rightarrow 4H_2 + 2CO}$$

2. <u>The gasification of coal, biomass, or natural gas:</u>

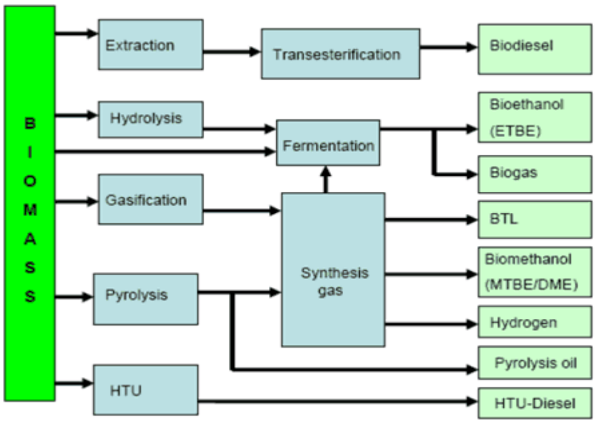
   $$\mathbf{CH_x + H_2O \rightarrow (1+0.5x)H_2 + CO}$$

The value of "x" depends on the type of fuel. For example, natural gas has a greater hydrogen content (from x=4 to x≈2.5) than coal (x<1).

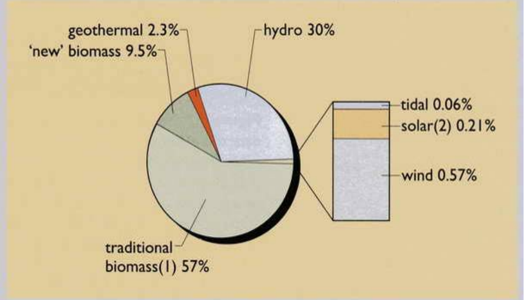
The energy needed for this endothermic reaction is usually provided by the (exothermic) combustion of the hydrocarbon source with oxygen. The mixture of carbon monoxide and hydrogen is called synthesis gas or syngas. The resulting hydrocarbon products are refined to produce the desired synthetic fuel.

The carbon dioxide and carbon monoxide is generated by partial oxidation of coal and wood-based fuels. The utility of the process is primarily in its role in producing fluid hydrocarbons from a solid feedstock, such as coal or solid carbon-containing wastes of various types. Non-oxidative pyrolysis of the solid material produces syngas which can be used directly as a fuel without being taken through Fischer-Tropsch transformations. If liquid petroleum-like fuel, lubricant, or wax is required, the Fischer-Tropsch process can be applied.

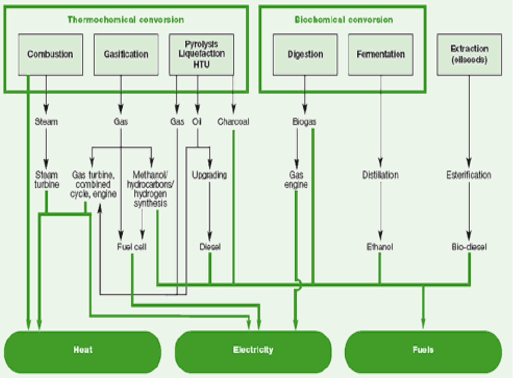
Biomass Conversion Processes



Renewable Energy in Use



Bio Energy Conversion



II. PROCESS CONDITIONS

Generally, the Fischer-Tropsch process is operated in the temperature range of 150-300°C (302-572°F). Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favour methane production. As a result the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favours formation of long-chained alkanes both of which are desirable. Typical pressures are in the range of one to several tens of atmospheres. Chemically, even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.

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 promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2: CO ratios (<1).

Predominant source of world's fuel and chemical is petroleum crude oil and estimated reserves of methane & coal exceeds that of crude oil by factors of about 1.5 and 25, respectively. Production of syngas from methane or coal and conversion of the syngas to a range of fuels and chemicals could become increasingly of interest as the reserves of crude oil are depleted and/or the price of crude rises. The industrial application of the FT synthesis started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660 X 103 t per year [1]. These plants ceased to operate after the World War II; however interest in the FT process remained because at this stage there was the persistent perception that the reserves of crude oil were very limited. Based on syngas produced from methane, an FT plant with a capacity of 360 X 103 t per year was built and operated in Brownsville, TX, during the 1950s but a sharp increase in the price of methane caused the plant to be shut down. During the same time period, based on the world-wide prediction of increasing crude oil prices an FT plant based on coal came on stream in Sasolburg, South Africa. Even before construction of this plant was completed, however, the huge oil fields of the Middle East were discovered and consequently the predicted rise in the price of crude oil did not materialize and interest in the FT process all but disappeared.

The economic viability of the FT synthesis depends on the price of crude oil and as it has varied considerably over last three decades (Fig. 1), the decision to construct an FT plant is always associated with risk. The oil crises of the mid 1970s prompted Sasol to construct two much larger coal-based FT complexes and this time things worked out better as the two plants came on-line in 1980 and 1982 when the price of crude exceeded US$ 30 per barrel. At that stage the combined capacity of the three Sasol plants was about 6000 X 103 t per year. Based on methane, the Mossgas plant in South Africa and the Shell plant at Bintuli, Malaysia, came on stream in 1992 and 1993, respectively. At that stage, however, the price of crude had dropped to about US$ 15 per barrel and so the timing of these two plants, with capacities of about 1000 X 103 and 500 X 103 t per year, respectively, was not as fortunate as had been the case for the two new Sasol plants. Crude oil prices continued to decline to about US$ 10 per barrel, but in 1999 there was a dramatic increase and at the time of writing the price is again above US$ 30 per barrel. Environmental/political considerations are also factors. Thus, for instance, certain large new oil fields are associated with high levels of natural gas the flaring of which is prohibited. In order to recover the crude oil the construction of FT plants to convert the methane to oil is being considered.

The FTS is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt. The principal purpose of this process is to produce a synthetic petroleum substitute for use as synthetic lubrication oil or as synthetic fuel. FTS involves three process steps: (1) the generation of the synthesis gas, a mixture of CO and H_2; (2) the conversion of the syngas to a mixture of hydrocarbon and oxygenate products; (3) hydroprocessing of synthesis products to produce transportation fuel products, today with emphasis on diesel.

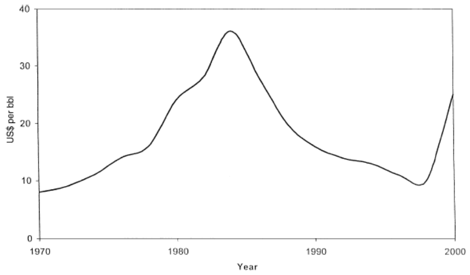


Fig.1. Change in Global Crude Oil Price

A number of approaches are available for the conversion of synthesis gas. Two catalysts—iron and cobalt based—have been widely used and these are the only ones receiving serious consideration today. The major difference between these two catalyst types is the formation of the oxygen containing products: with cobalt the oxygen in the syngas is rejected as water and with iron the oxygen is rejected as carbon dioxide. Since cobalt catalysts do not have water-gas-shift (WGS) activity, the feed gas must have a H_2/CO ratio of about 2.0–2.3. Iron based catalysts have significant WGS activity so that much lower H_2/CO ratio feed gas can be utilized. Thus, the perception has developed that the iron catalyst is preferable for syngas with a low (0.5–1.3) H_2/CO ratio, typical of those produced from coal as the carbon source, and that the cobalt based catalyst is preferred for high (2.0+) H_2/CO ratios, typical of those produced from natural gas. Since natural gas usage is the primary driving force for FTS today, cobalt has been receiving much attention. However, utilization of coal indicates that iron catalysts should not be automatically eliminated from consideration for syngas derived from natural gas.

The Central Institute of Mining & Fuel Research, Dhanbad being the premier Coal Research organization in the country, has been working on FTS for last five decades. Initial research on FTS was aimed for liquid fuel synthesis from coal derived syngas and iron based catalysts was studied for this purpose. However, during last one decade, attention has been focused towards the utilization of vast natural gas reserve of India hence cobalt based catalysts are studied for conversion of natural gas derived syngas for synthesis of liquid hydrocarbon or wax (Fig 2).

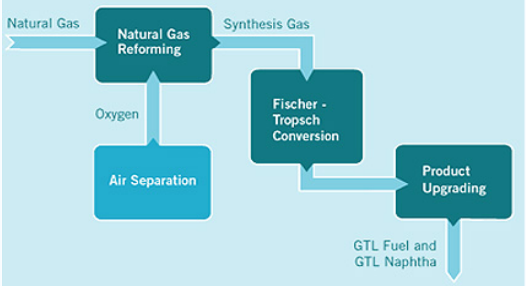


Fig.2. Pathway of conversion of natural gas to liquid fuels through FTS

III. REACTION CHEMISTRY OF FTS

The original Fischer-Tropsch process is described by the following chemical equation:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$

The initial reactants in the above reaction (i.e., CO and H_2) can be produced by other reactions such as the partial combustion of methane (in the case of gas to liquids applications):

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO$$

OR by the gassification of coal or biomass:

$$CH + \tfrac{1}{2}O_2 \rightarrow 1/2H_2 + CO$$

The mixture of carbon monoxide and hydrogen is called synthesis gas or syngas. The resulting hydrocarbon products are refined to produce the desired synthetic fuel. Chain growth pathways and possible secondary reactions of olefins in the FT-Synthesis are shown in Fig 3.

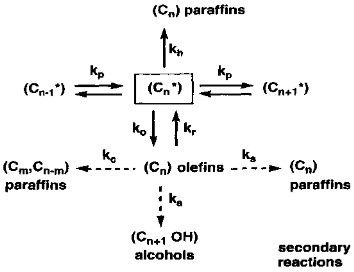


Fig.3. Chain growth pathways and possible secondary reactions of olefins in the **Fischer Tropsch Kinetics**

F-T chemistry is often modelled by a simple power law equation:

$$-r_{CO} = Ae^{-E/RT}\, p_{H2}{}^{m} p_{CO}{}^{n}$$

where:

r_{CO} = rate of conversion of CO

p_{H2}, p_{CO} = partial pressure of H_2 and CO, respectively

In general m is positive (~ 1.0) and n is negative (-0.1 – -0.35).

Energy of activation is generally found in the range of 20 –25 kcal/gmol.

IV. INTERNATIONAL STATUS

Since 1955, F-T synthesis is being exploited commercially by SASOL in South Africa. Sasol is a synfuel technology supplier established to provide petroleum products in coal rich but oil poor South Africa. The firm has built a series of FT coal to oil plants, and is one of the world's most experienced synthetic fuels organizations and now marketing a Natural Gas To Oil Technology. It has developed the world's largest synthetic fuels project, the Mossgas complex at Mossel Bay in South Africa that was commissioned in 1993. To increase the proportions of higher molecular weight hydrocarbons, Sasol has modified its Arge reactor to operate at higher pressures. Sasol has commercialized four reactor types with the Slurry Phase Distillate process being the most recent. Its products are more olefinic than those from the fixed bed reactors and are hydrogenated to straight chain paraffins. The slurry phase distillate converts natural gas into liquid fuels, most notably superior quality diesel. Another technology uses the Sasol Advanced Synthol (SAS) reactor to produce mainly light olefins and gasoline fractions. Sasol has developed high performance cobalt based and iron based catalysts for these processes. The company claims a single module or sasol slurry phase distillate plant which converts 100 MM scfd of natural gas into 10,000 barrels/day of liquid transport fuels can be built at a capital cost of US $ 25,000 including utilities, off-site facilities and infrastructure units. Due to steeply growing market demand and for the utilization of large natural gas reserves many new players has came in GTL market which are now licensing their GTL technologies. SASOL, SHELL & SYNTROLEUM are the major licensing companies and other companies like Exxon, Statoil, Rentech are also spreading their business worldwide. Shell has carried out R&D since the late 1940s on the conversion of natural gas, leading to the development of Shell Middle Distillate Synthesis (SMDS) process, a modified FT-process. This process aims on maximizing the yield of middle distillates. First commercial SMDS project started in 1993 at Bintulu-Malayasia. In this process natural gas is first partially oxidized into syngas (CO + H_2) in Shell gasifier. This syngas is then converted into heavy paraffins in a fixed bed multi-tubular reactor. This heavy paraffin is then selectively hydrocracked & isomerized for getting the middle distillates. The product obtained by this process is free from contaminants, sulphur, aromatics and heavy metals.Syntroleum Corporation is the developer, user and licensor of the Syntroleum Process, which is a proprietary process for converting natural gas (or synthesis gas from coal) into synthetic liquid hydrocarbons. The Syntroleum Process produces synthetic liquid hydrocarbons, also known as synthetic crude oil, that are virtually free of contaminants that are normally found in products made from conventional crude oil. These synthetic liquid hydrocarbons can be further processed into higher margin products through conventional refining techniques, including Syntroleum's proprietary Synfining Process. These products include: Ultra-clean liquid fuels for use in internal combustion engines and fuel cells; specialty products such as synthetic lubricants, process oils, waxes, etc. Costs to produce these products using GTL technology are increasingly competitive with conventional process technologies. Moreover, the ultra-clean properties of GTL fuels meet or exceed the new and proposed environmental requirements that will soon go into effect for the U.S. and Europe.

Key advantages to the Syntroleum Process include its use of air in the conversion process, which is economically competitive and inherently safer than the requirement for pure oxygen in other GTL technologies; and Syntroleum's proprietary catalysts, which enhance conversion efficiency of the catalytic reaction. These features help to reduce capital and operating costs of plants, and permit smaller plant sizes, including mobile plants that can be mounted on barges for offshore service. Research indicates that the Syntroleum Process can be economically applied in plant sizes from less than 20,000 to over 100,000 barrels per day.

RENTECH proposed electrical power and FT fuels project in West Australia as announced October 29, 1999. Rentech Inc. is the developer and licensor of a patented and proprietary Fischer-Tropsch, gas-to-liquids process, for conversion of synthesis gas made from natural gas, industrial off-gas, or solid or liquid carbon-bearing materials into high-value fuels, products and chemicals. These products include cleaner burning, sulfur- and aromatic-free diesel fuel, naphtha, waxes and fuel for fuel cells.

Preliminary project sizing is for a 200-megawatt electrical power plant and a 6,000-barrel per day Fischer-Tropsch plant. It is expected that Texaco's gasification technology will be used to gasify the lignite to product a syngas consisting of hydrogen and carbon monoxide. The syngas will in turn be used to produce electricity and feed the Rentech-designed Fischer-Tropsch reactor.

With its large gas reserves, Norway’s STATOIL has been developing catalysts and process reactors for the FT-process to produce middle distillate from natural gas. This process employs a three-phase slurry type reactor in which syngas is fed to suspension of catalyst particles in a hydrocarbon slurry, which is a product of the process itself. The process continues to be challenged by catalyst performance and the ability to continuously extract the liquid product.

EXXON has developed a commercial FT system from natural gas feed stock. They claim for the slurry reactor and proprietary catalyst systems result in high productivity and selectivity along with significant economy of scale benefits. Exxon employs a three-step process: fluid bed synthesis gas generation by catalytic partial oxidation; slurry phase FT-synthesis; and fixed bed product upgrade by hydro isomersation. The process can be adjusted to produce a range of products. More recently they have developed a new chemical method based FT-process to synthesize diesel from natural gas. Exxon’s better catalysts and improved oxygen–extraction technology have reduced the capital cost of the process and is actively marketing the process internationally.

One GTL-Microsystems of UK claims to have developed a process -GTL Microsystems modular Process Intensification (PI) reactors for Steam Methane Reforming (SMR) and Fischer-Tropsch process, by using micro reactor technology. This has reduced size of about one tenth of conventional GTL plants, which uses a unique metallic substrate catalyst with high conversion of C_{5+} hydrocarbons. This process has low capital cost and superior economics, compact in design, high efficiency and no compressed air, oxygen or water is required for its operation.

Another company VELOCYS of USA is also claiming for the micro channel reactor technology application to FT synthesis reactions.

A group of Japanese companies intent on making gas-to-liquids (GTL) fuels a commercially viable overseas business by 2011 plans to start building a trial GTL plant in Niigata. This facility is targeted to begin operation in 2008 with a daily output capacity of about 500 barrels per day of synthetic fuels and chemicals using natural gas.

The partners include Nippon Oil, Nippon Steel, Japan Petroleum Exploration, Inpex, Cosmo Oil, Chiyoda and the government-owned Japan Oil, Gas and Metals National Corp (JOGMEC), along with support from the Ministry for Economy, Trade and Industry (METI).

JOGMEC has been researching GTL technology since 1998, with an emphasis on the efficient production of the syngas used in the Fischer-Tropsch (FT) process that actually produces the end products.

Working in partnership with Chiyoda (which developed the catalyst), JOGMEC is developing a GTL process that eliminates the need for three units usually found the syngas section of a conventional GTL operation, thereby potentially significantly reducing the cost. There shall be no CO_2 removal unit, oxygen plant and syn gas conditioning unit. The JOGMEC process has only been tested in very low production pilots (7 bpd). This trial is designed to help perfect in support of building an overseas plant (likely in Indonesia) with a production capacity of 15,000 barrels per day. The major GTL Technology overviews are shown in Table-1.

It is evident that continuous developmental work on F-T synthesis is being carried out since the beginning of this century to develop alternative source of liquid fuels for particular situation and to meet the need of coming decades.

It is found that fundamental work F-T process development is being carried out in Universities & Institutes and application part is being carrying out by Multinational & Large Companies.

V. CIMFR STATUS

The research work on F-T synthesis in India is considered to have begun within two decades of the invention of the process in 1913 in Germany. The first Indian research paper was published in 1935. Since then, investigational studies on F-T synthesis is continuing. Most of these studies were to examine the effectiveness of catalyst and obtain data on adsorption kinetics and mechanism aspects of F-T synthesis. These studies were initially started at Universities of Bengal and followed up by IISC (Bangalore), CIMFR (Dhanbad), IIT (Kharagpur).

In the early 1960s, IIT (Kharagpur) put up a pilot plant of considerable size (product capacity: 100 gals per day) and operated the same. This was by far the biggest F-T synthesis unit in the country. However, this unit used fixed bed reactor of Pre-World War II period, was not suitable for engineering developmental studies.

CIMFR, which started investigations on F-T synthesis from 1952 put up a fluidized bed reactor of maximum catalyst capacity of 1.2 liter by the end of 1950s and operated the same for about a decade. By the end of 1960s, studies on F-T synthesis practically stopped at IIT (Kharagpur) and IISC (Bangalore). Studies at CIMFR, however, continued on low-key basis till the middle of 1970s.

In the early 1970s, when the oil crisis occurred, interest on F-T synthesis was revived and IICT (Hyderabad), IIT (Bombay) took up projects on F-T synthesis. In the early 1980s, IIT (Madras) also started working on F-T synthesis. From 1976, CIMFR started working on the design of scaled up F-T synthesis unit with fixed bed reactor system to install the same and study the catalysts developed at CIMFR.

Since the above studies were taken up institution wise, the contributions to the science of F-T synthesis were diverse in nature.

Table 1: The major GTL Technology

S. No.	Company (Location)	O_2 Plant	Syn gas Production (Catalyst source)	FT-Synthesis (Catalyst/ Source)
1.	GTL-Microsystems (UK)	None	Steam-Methane-Reforming in PI Reactor (Microsystems)	Micro Channel reactor (Microsystems)
2.	VELOCYS (USA)	None	SMR (Velocys)	Micro Channel reactor (Velocys)
3.	JOGMEC (Japan)	None	Tubular reformer (Chiyoda)	Slurry bed (Co/NSC)
4.	SASOL (SA)	Reqd.	Auto thermal reformer (Topsoe)	Slurry bed (Co/Sasol)
5.	SHELL (Malayasia)	Reqd.	POX (Shell)	Fixed bed (Co/Shell)
6.	SYNTROLEUM (USA)	None	Auto thermal reformer (Syntroleum)	Slurry bed (Co/Syntroleum)
7.	Exxon Mobil (USA)	Reqd.	Auto thermal reformer (ExxonMobil)	Slurry bed (Co/ExxonMobil)
8.	Conoco (USA)	Reqd.	CPOX (Conoco)	Slurry bed (Co/Conoco)
9.	BP (USA)	Reqd.	Compact reformer (BP)	Slurry bed (Co/BP)

investigation, nickel, cobalt and iron based catalysts were studied. These studies were aimed to examine the yield of liquid hydrocarbons, activity aspect of the catalyst, role of promoters as well as basic studies like adsorption of CO and H_2 over these catalysts. After the Second World War, emphasis was put to develop iron catalyst for F-T synthesis as iron had some advantages over cobalt and nickel. From mid-50s, investigations, therefore, concentrated on the development of iron based F-T synthesis catalysts. Considerable amount of studies had been carried out metals of group I, II, III, IV, VI and VII of periodic table as promoters for iron catalysts.

At IISc (Bangalore), investigation to understand the mechanism of FTS reactions were carried out using carbon balance method, in addition to chemisorption studies on cobalt and iron catalysts. Such carbon balance method helped to understand the product distribution pattern and reaction mechanism in respect of intermediate complexes had also been studied.

At IIT (Kharagpur), Fe based F-T catalyst was tested in the pilot plant and sufficient product was obtained for characterization. However, only one catalyst was studies and because of using obsolete type of reactor, the plant was not suitable for engineering development studies. Further, bench scale slurry phase reactor system was studied for some time.

At IIT (Bombay), some studies on the preparation technique and nature of supported mono and bimetallic catalysts using metals of group VIII had been carried out. It was reported that these catalysts, however, did not produce higher hydrocarbons during synthesis.

At IIT (Madras), some studies on the basic aspects of F-T catalysts was done using modern instrumental technique. These studies were related to the role of support and promoter in F-T catalysts and also mode of carbon monoxide activation and adsorption.

At IICT (Hyderabad), some studies on F-T catalysts have been carried out recently. Different methods of preparations of supported F-T catalysts and characterization of these catalysts have been carried out and studied. Synthesis over multi-metallic catalyst system has been reported.

At CFRI, extensive studies on iron catalysts from basic and applied angles had been carried out. Three different types of F-T synthesis reactors, viz., fixed bed; fluidized bed and slurry phase had been tested. The emphasis was mainly on fluidized and fixed bed type of reactors. Fluidized bed reactor system has been found to be suitable for olefins, gasoline and chemicals like alcohols and ketones production. The fixed bed reactor is suitable for paraffinic and high molecular weight hydrocarbons, like middle distillate and waxy products. The studies in lab scale slurry phase reactor showed production of low molecular weight (C_1-C_4) gas phase hydrocarbons.

In the field of catalysis, catalysts preparation technique, role of promoter and changes in catalyst phases during their use have been studied. Based on such studies, CIMFR has developed catalyst for the production of liquid fuels with high yield of middle distillate from synthesis gas. The results of iron based FT catalysts studied at CIMFR are presented in Table-2.

Table2: Previous GTL Runs of Iron catalyst in Liquid Fuels Section

Catalyst Name	H_2/CO	Pressure Kg/cm2	Rxn. Temp. °C	GHSV	Run time (h)	Yield Aqs / Oil / Wax
FT/CS- 23/151	1.56-1.70	15-15.5	200-205	450-460	129	108.2/ 148.5 /18.69
FT/CS-14/77/167	1.70	15-16	200-215	450	119	134 /84 /---
USA Catalyst	1.70	15-16	220	450	48	8 / 4/-----
FT/CS/15/79	1.70	15-16	200	300	134	153 /93/----
FT/CS- 23/151	1.56-1.70	15-16	200-205	450-460	53	137.5 /56.5/ -
FT/CS/23/B3/181	1.55	10-13	205-210	450	76	41 / 51/---

The laboratory scale studies of catalysts were translated into scale-up studies. For this purpose, Fixed Bed Tubular Reactor (Catalyst Capacity 150 ml) and Process Development Unit (Catalyst Capacity 3.20 liter) have been installed at CIMFR. The promising catalysts developed earlier were undergone large scale testing in the Process Development Unit.

Most of the FTS studies were performed under the in-house projects of CIMFR but in 1998, a project titled **“Fischer-Tropsch (F-T) Synthesis: Development of Catalysts for Wax Production”** was sponsored by Dept. of Science and Technology, Govt. of India under the Indo-Russian collaboration scheme (ILTP).This study was done in the temperature range of 180 – 220°C. It iwas observed that although pressure increases the selectivity for higher alkanes, due to limitations by the material construction of the STR, it was kept at 1.2 – 1.25 MPa. The work on the conversion of syngas to wax was initiated with iron catalyst. Three iron-based catalysts – two supported on clay having different proportion of promoter and the third with silica support were prepared by precipitation technique. One Fe-based clay supported catalyst showed appreciable wax yield which was tested for 208 h at GHSV $450h^{-1}$ and 1.2 MPa of pressure. At 205°C and H_2/CO ratio of 1.7, wax yield was 15% whereas for H_2/CO ratio of 1.6 and 210°C, wax yield was 32%. The wax yield for the Fe-catalysts was low so cobalt-based catalysts, which are known for its selectivity towards high molecular weight compounds, were taken up. Two cobalt-based catalysts (CIMFR/C1 and CIMFR/C2) which were prepared differently and showed maximum activity, were compared with one Russian catalyst (cobalt-based). The wax yield for CIMFR/C1 was 18.3 wt% of C_{5+} fraction at 195°C, H_2/CO =1.7 and GHSV~$550h^{-1}$ and the other catalyst CIMFR/C2 showed maximum wax selectivity 58.3 wt% C_{5+} fraction at 1.2 MPa, 200°C, GHSV~ $650h^{-1}$ and feed H_2/CO = 2.0. Analysis of the wax component by simulated distillation showed the maximum carbon number of wax was 62.

Very recently extensive investigations have been carried out on alumina supported Cobalt catalyst under the Taskforce Project of CSIR, India, titled, **“**Development of Gas to Liquid Technology for Fischer-Tropsch & DME Fuels**”**. Three different formulations of Cobalt based catalyst (FT-Cat12, FT-Cat12A and FT-Cat14) for middle distillate synthesis have been prepared, characterized and its activity evaluated. All the catalysts have been tested at 500-1000 h^{-1} GHSV’s, 20 bar reaction pressure, H_2/CO ratio 2.0, and at 220-250^{0}C reaction temperature.

FT-Cat 12, FT-Cat 12A and FT-Cat 14 have been tested for 125 Hrs, 122 Hrs and 78.5 Hrs of continuous operation respectively. FT-Cat 12, FT-Cat 12A and FT-Cat 14 have yielded 207 ml, 147 ml and 101 ml of C_{5+} Hydrocarbon Liquid respectively, which was characterized in GC-FID-SIMDIST. The SIMDIST results show the yield of naphtha (b.p up to 140^{0}C) varies from 4-25 %, middle distillate (b.p 141-360^{0}C) varies from 61-83 % and waxy oil (> 360^{0}C) varies from 8-33 % of total liquid product. The CO conversion varies from 73-95%. The selectivity of C_{5+} hydrocarbon at 500 h^{-1} GHSV of FT-Cat 12, FT-Cat 12A and FT-Cat 14 were 77, 72 and 66% respectively.

It has been observed that CO conversion increases and C_{5+} hydrocarbon liquid selectivity decreases with increase in space velocity of feed. The C_{5+} Hydrocarbon Liquid selectivity is maximum at low space velocities, which may be due to larger residence time.

Also, as per SIMDIST result, IBP of liquid hydrocarbons of product varies from 70-75 ^{0}C and FBP varies from 400-450 ^{0}C. As per the yield and selectivity pattern of the developed catalyst system it can be emphasized that these may be successful formulations leading to commercialization for converting the huge Natural Gas Reserves of our country and adding up in the current oil pool.

VI. CONCLUSION

As transportation accounts for a significant share of CO_2 emissions the use of biomass should be extended beyond heat and power production. Through biomass gasification transport fuels such as gasoline and diesel can be produced to replace existing transport fuels. While the latter represents proven technologies, the production of liquid fuels via Fischer Tropsch synthesis has received growing interest.

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AUTHOR'S PROFILE

Sri. S. R. K. Rao

is Chief Scientist at CSIR-Central Institute of Mining & Fuel Research, Dhanbad.

Born on 30th August, 2013 at Jamshedpur (Jharkhand State), the author has Master's Degree in Science (Chemistry); Post Graduate Diploma in Business Administration and Master's Degree in Intellectual Property Law.

The Author has bagged Life Time Achievement Award in Research from International Science Congress Association, held at Brindavan on 8-9th December, 2012 in its 2nd International Science Congress.