

# ADVANCED CATALYSTS OF FISHER-TROPICH PROCESSES: A MINI-REVIEW

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## Abstract

Fisher Tropsch is the process of converting synthesis gas to liquid hydrocarbons is FTS. The FTS process has many feedstocks that are used such as natural gas, coal, and biomass. In the last few years, it has shown a big improvement in this technology, including improvement in the reactors' design and catalysts. In this review, an overview of the FTS process includes its history, mechanism, surface chemistry, and composition of catalyst. There is also discussion of the difficulties with FTS, such as selectivity issues, heat and mass transport restrictions, and catalyst deactivation. This review will cover the modified Fischer-Tropsch Synthesis (FTS), which is a crucial area of current research that converts CO<sub>2</sub> by hydrogenation into higher hydrocarbons. The reverse water-gas-shift reaction in this method turns CO<sub>2</sub> into carbon monoxide, which then proceeds down the standard FTS pathway to produce hydrocarbons. The selectivity and activity of the final product are mostly determined by the catalyst's nature. Therefore, this study will provide a thorough overview of current advancements for catalysts which are bimetallic, Co, and Fe-based catalysts. Furthermore, the impact of including promoters on the performance of catalysts such as Mn, Na, or K. Lastly, FTS's promise to produce sustainable fuels and chemicals is investigated.

**Keywords:** FTS, Commercial Applications, Carbon dioxide, FTS reactors, Catalyst, Mechanism.

## 1. Introduction

(FTS) originated in the early 1900s when Franz Fischer and Hans Tropsch made the initial discovery of the process (Fischer and Tropsch, 1913). Since coal was readily available and reasonably priced at the time, the FTS method was first created to create liquid fuels from it (Steynberg and I. Dry, 2004). When its access to crude oil was restricted during World War II, Germany employed the FTS technique to provide liquid fuels for their war vehicles (De Villiers, 2002). Following the war, South Africa adopted the FTS method to turn coal—which was cheap and plentiful there—into liquid fuels. (Dry, 2003). The necessity to minimize greenhouse gas emissions and the growing demand for alternative fuels has rekindled interest in the FTS process in recent years (Mahmoudi et al., 2017).

The dependence of the world on traditional fossil fuels endangers the globe. If current trends continue, the combined average temperature of the ocean surface and the world's land surface in 2100 will rise by 5° C. This will cause an increase in extreme weather occurrences, reductions in water and food, and an increase in sea levels. One of the greatest challenges to our future well-being is human-caused global warming (H. Mahmoudi et al., 2017). For more than a century, liquid fuels have been produced from a variety of carbon-based energy sources, such as coal, natural gas, and biomass, using the Fischer-Tropsch synthesis (FTS) process. The need to lower greenhouse gas emissions and the growing demand for alternative fuels has rekindled interest in it in recent years (H. Mahmoudi et al., 2017). A catalyst is used in the process to react hydrogen (syngas) with carbon monoxide to generate a variety of hydrocarbons, such as oxygenates, alkenes, and linear and branched alkanes. For the liquefaction of carbon-based energy sources for solid or gaseous (GTL and CTL) into liquid fuels transportable, fuel transfer technology (FTS) is a promising method (H. Mahmoudi et al., 2017). Three major obstacles to improving the LTFT process are catalyst suppression, the limiting of mass and heat transfer, and selectivity for a smaller product distribution (A. Steynberg and I. Dry, 2004). Furthermore, the need for sustainable and renewable energy sources has increased the importance of bioenergy and Second-Generation Biofuels (SGB) in recent years (M. Balat, 2010). Biomass may be transformed into liquid fuels using the FTS process, which can be utilized in place of fossil fuels (M. and H. Balat, 2008).

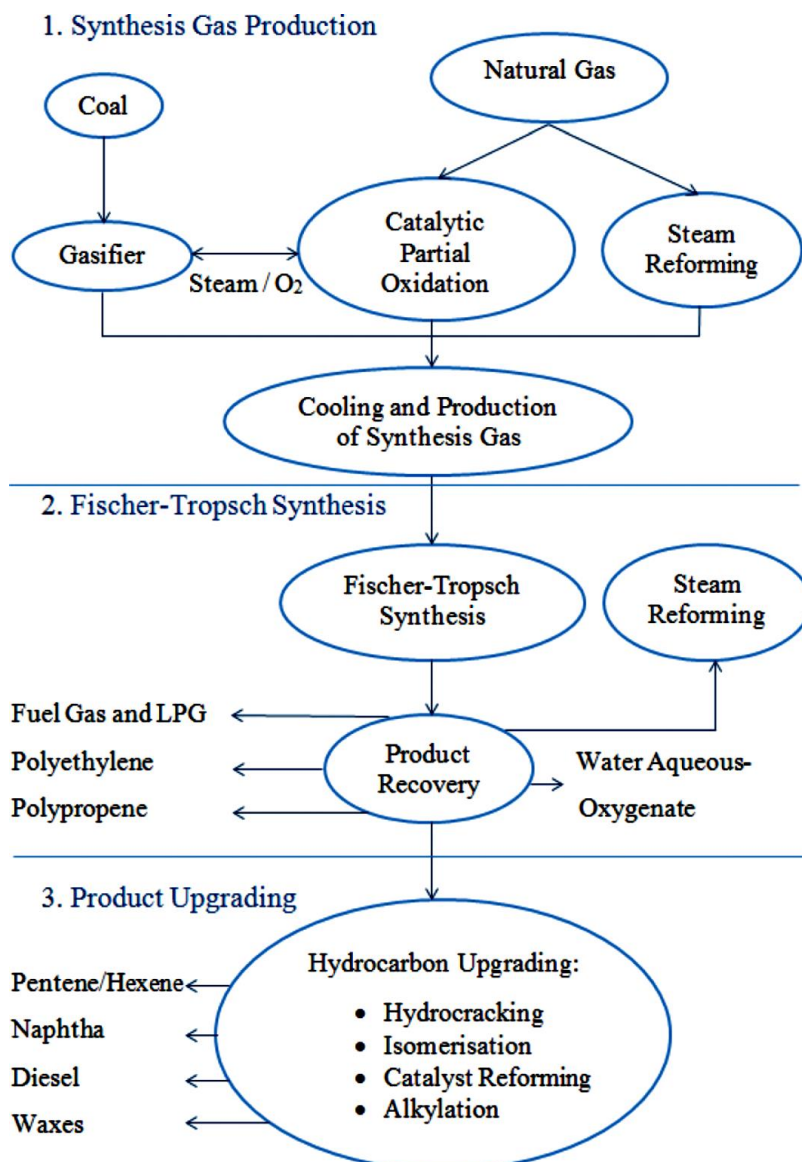


Figure 1: block diagram of the overall FT process configuration (Fahim et al., 2010)

## 2. The mechanism of Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis (FTS) mechanism is the reaction of carbon monoxide and hydrogen (syngas) over a catalyst to generate a variety of hydrocarbons, including oxygenates, alkenes, and linear and branched alkanes H. Mahmoudi et al. (2017). The FTS product chain consists of CH<sub>4</sub>, paraffins and olefins, oxygenate (mainly alcohols and ketones and aldehydes) and aromatics. This is indicative of the complex nature of the process. The FTS process is divided into three types (carbide mechanism, enol mechanism, and CO insertion mechanism) all assume the presence of a monomer in the chain and suggest schemes that include three major steps (Initiation, Propagation, and Termination) that cause carbon monoxide hydrogenation and carbon-carbon bonds forming, and the subsequent steps of the Fischer-Tropsch synthesis could be explained by the definition of complex reaction networks.

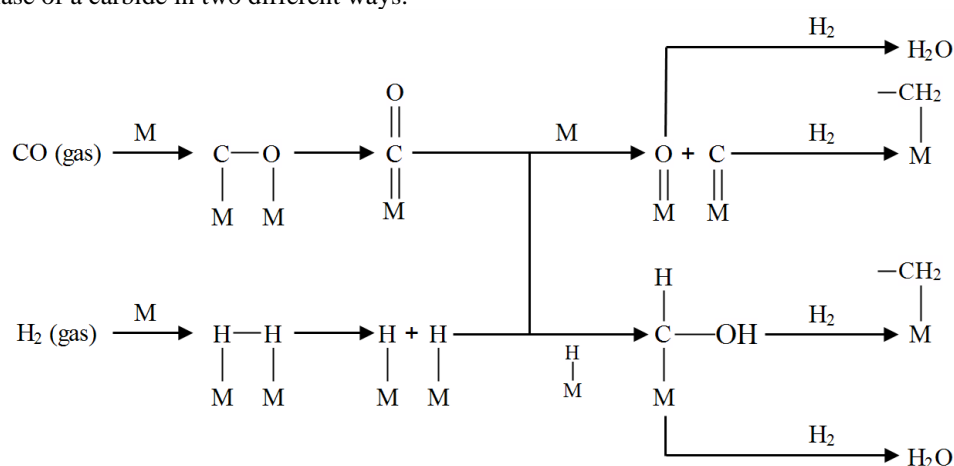
According to (Steynberg and Dry 2004), the reaction happens in two stages: first, surface-bound intermediates are created then hydrogenated of these intermediates to create hydrocarbons. Carbon monoxide and hydrogen adsorb on the catalyst surface to produce the surface-bound intermediates, which in turn generate a variety of species, including carbide species, surface-bound CO, and surface-bound H (De Villiers, 2002). A sequence of processes, including the creation of surface-bound hydrocarbons, their desorption, and the creation of new surface-bound intermediates, contribute to the hydrogenation of these intermediates (M. Dry, 2003). Research is currently being done to better understand the process as the precise mechanism of FTS is still not entirely understood (Schouten et al., 2011). Nonetheless, it is widely acknowledged that a combination of gas-phase and surface chemistry causes the reaction to occur (Kim et al., 2009).

**Table 1:** main reactions in an FTS reactor (Van Der Laan GP, Beenackers AACM, 1999).

main reactions	
Paraffin (alkane)	$(2n+1)H_2+nCO \rightarrow C_nH_{2n+2}+nH_2O$
Olefins (alkene)	$2nH_2+nCO \rightarrow C_nH_{2n}+nH_2O$
WGS reaction	$nCO+H_2O \leftrightarrow CO_2+H_2$
Methane Formation	$CO + 3H_2 \rightarrow CH_4 + H_2O$
Side reactions	
Alcohols	$2nH_2+nCO \rightarrow C_nH_{2n}+2O+(n-1)H_2O$
Boudouard reaction	$2CO \rightarrow C+CO_2$
Catalyst (Metals) oxidation/reduction	$MxOy+yH_2 \leftrightarrow yH_2O+xM$ $MxOy+yCO \leftrightarrow yCO_2+xM$
Bulk carbide formation	$yC+xM \leftrightarrow MxCy$

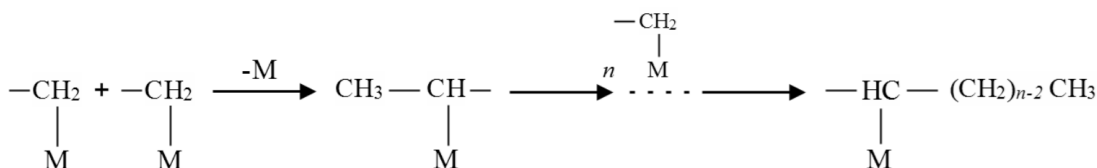
**2.1 Carbide mechanism**

This review will explain this mechanism in detail. In a carbide mechanism, the adsorption of CO from the surface of the catalyst causes the reaction of FT. During this step, gaseous carbon monoxide carbides the metal surface (M). At first, two catalyst surface sites are involved in the bridge mode of carbon monoxide chemisorbed. Afterward, it reaches equilibrium in a linear mode involving a single metal surface site. The C-O link then breaks apart into two types of surface O and C. Also the hydrogen is chemisorbed and separated on the surface site metal (X. Wang and M. Economides, 2013). Hydrogen is adsorbed weaker from CO on the surface sites of the catalyst (A. de Klerk, 2012). C<sub>1</sub> intermediate species are created when the surface of carbon reacts with the surface of hydrogen that is chemisorbed (MCH<sub>x</sub>). When hydrogenation of the carbon surface of carbides to the methane surface oxygen is removed as H<sub>2</sub>O and this was a probable process that Fischer and Tropsch proposed in 1926 (R.B. Anderson et al., 1984). The interactions between the adsorbed oxygen and hydrogen remove the oxygen from the metal surfaces. Figure 1 depicts the first mechanism phase of a carbide in two different ways.



**Figure 1:** start step in the mechanism of carbide through FTS reaction (R.B. Anderson, 1984; H. Mahmoudi, 2015).

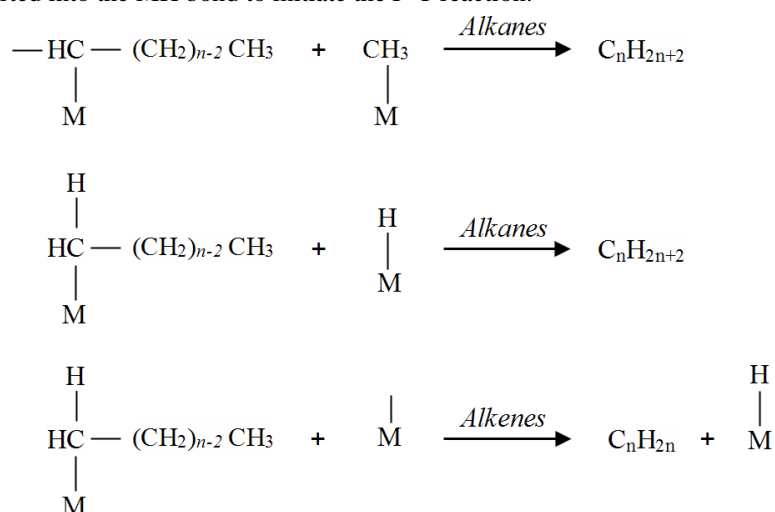
After the synthesis of hydrocarbon molecules begins, many mechanisms may regulate the process's growth and chain termination. While an HTFT reaction works to assist the reaction to take the first way, an LTFT reaction causes oxygenate the enol groups with additional reaction (X. Wang and M. Economides, 2013). The M-CH<sub>2</sub> surfaces then engage with another M-CH<sub>2</sub> to undergo polymerization, producing an intermediate M-CH<sub>2</sub>-CH<sub>2</sub>-M. We are in a period of chain expansion. Insertion into the M-CH<sub>2</sub> bonds results in the production of the cycloalkanes and cycloalkanes, respectively, which are then desorbable and hydrogenated. According to A. de Klerk (2012), this procedure describes how cyclic aliphatic hydrocarbons are created during F-T synthesis. The long-chain hydrocarbons with CH<sub>x</sub> are the ones that are recommended groups added to carbon-metal bonds. The proliferation of the monomer units is seen in Figure 2.



**Figure 2:** The FTS process involves the chain diffusion of units of monomer in the mechanism of carbide (R.B. Anderson et al., 1984).

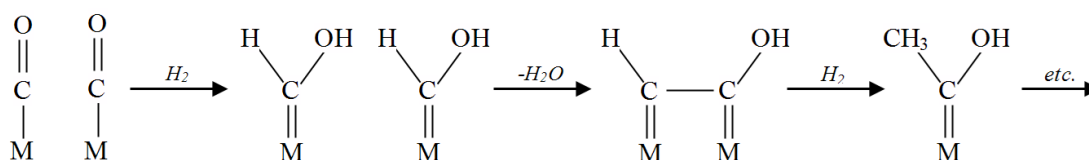
The alkyl groups that Adsorbed surface (-HC- (CH<sub>2</sub>)<sub>n-2</sub>-CH<sub>3</sub>) either mix with adsorbed surface CH<sub>3</sub> to induce the chain termination, or are hydrogenated to generate paraffins (Figure 3). The products of alkenes and Olefin are manufactured

when removing the hydrogen at the alkyl groups surface (X. Wang and M. Economides, 2013). CO insertion into the metal-carbon bonds summarizes the main chain growth pattern of the CO insertion mechanism in the FTS process. In this method, CO is inserted into the MH bond to initiate the F-T reaction.



**Figure 3:** Routes in the carbene mechanism's termination step for the production of alkanes and alkenes (X. Wang and M. Economides, 2013).

Chains are created by decreasing the acyl group after homogeneous catalysis inserts CO into bonds of metal alkyl. The control of acyl group hydrogenation that is produced from oxygenate (G.H. Olivé and S. Olive, 1984) or from other hydrocarbons. This procedure is illustrated in Figure 3. The 3rd development of FT process production is the way of hydroxycarbene (Figure 4), at this way depends on the generation of the hydroxycarbene intermediates. Hydroxycarbene is produced on the metal surface when chemisorbed carbon monoxides are hydrogenated by atomic hydrogen. When two hydroxy methylene groups condense and remove water, carbon-carbon bonds are formed. The expansion of the chain occurs by the collaboration of the intermediates of oxygenated surface (G.H. Olivé and S. Olive, 1984).



**Figure 4:** Mechanism schematic of the intermediates creation of hydroxycarbene and the expanded chain pattern throughout the fatty acid production process (G.H. Olivé and S. Olive, 1984).

### 2.2 The Enol mechanism

Storch's 1950s suggest the enol mechanism (Table 2), which functions as the monomer after CO is partly hydrogenated to a CHOH (ox methylene). Chain growth happens when water is removed by a condensation process. Also, distinct termination pathways select the ultimate product molecule that is generated. (Sølvi Storsaeter et al., 2006)

### 2.3 The CO insertion mechanism

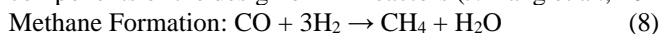
The mechanism of CO insertion (Table 2) was developed by Pichler and Schultz in the 1970s and is based on the supposition that the carbide mechanism's starting stage is identical. The method by which chain development is thought to happen—direct CO insertion into the developing intermediate, followed by hydrogenation to eliminate the oxygen atom—is where the differences lie. (J. Yang et al., 2014).

**Table 2:** FT reaction mechanism (Loosdrecht et al., 2013)

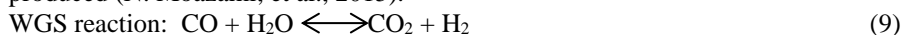
	<i>Carbide mechanism</i>	<i>Enol mechanism</i>	<i>CO insertion mechanism</i>
Initiation	CO → C + O O + 2H → H <sub>2</sub> O C + xH → CH <sub>x</sub>	CO + 2H → CHOH	CO → C + O O + 2H → H <sub>2</sub> OH
Propagation	R + CH <sub>x</sub> → R-CH <sub>x</sub> R-CH <sub>x</sub> + (2-x)H → R-CH <sub>2</sub>	R-C-OH + CHOH → R-C-COH + H <sub>2</sub> O R-C-COH + H → R-CH <sub>2</sub> -COH	R-CH + CO → R-CH-CO R-CH-CO + H → R-CH <sub>2</sub> -CH + H <sub>2</sub> O
Termination	R-CH <sub>2</sub> + H → R-CH <sub>3</sub> R-CH <sub>2</sub> -CH <sub>2</sub> -H → R-CH=CH <sub>2</sub> R + CO → oxygenates	R-CH <sub>2</sub> -COH + 4H → R-CH <sub>2</sub> -CH <sub>3</sub> + H <sub>2</sub> O R-CH <sub>2</sub> -COH + nH → oxygenates	R-CH + 2H → R-CH <sub>3</sub> R-CH-CO + nH → oxygenates

**2.4 Methane and WGS mechanisms**

The procedure that leads to the production of methane, an undesirable byproduct of F-T synthesis, is outlined below. This reaction is thought to be unique and irreversible. Since methane production (equation 8) increased as process temperature climbed, controlling the reactor temperature, and extracting heat from exothermic processes are crucial components of the design of F-T reactors (J. Yang et al., 2014).



Another key reaction in the process of FTS is the (WGS) reaction which the water produces as a byproduct. Especially, that reaction is critical in reactors where reactions take place over an iron-based catalyst, and carbon dioxide is produced as an undesired byproduct. In general, when the H<sub>2</sub>/CO ratio is higher, more H<sub>2</sub>O is produced; in contrast, CO<sub>2</sub> is produced (N. Moazami, et al., 2015).



A micro-kinetic model was developed by (Sølvi Storsaeter et al., 2006) for the generation of C<sub>2</sub> and C<sub>1</sub> through the support of cobalt catalysts. CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub> were suggested to be produced by two types of fundamental processes based on the hydrogenation of CO and CO dissociation by assist of hydrogen. These two reaction pattern types were merged to produce a model of micro kinetics.

The rate constant, pre-exponential variables, and activation energy of the basic processes in the carbide and CO insertion procedures were calculated. The bulk of carbon monoxides, according to the study's findings, were transformed and then dispersed, creating C<sub>2</sub> products through the CO insertion and metal-methyl bond pathways, respectively.

(Martin Kollar et al., 2010; J. Yang et al., 2013) were studied the mechanism process of the FTS, as well as the CO activation and the generation of CH<sub>4</sub> over a supporter of a cobalt catalyst.

FTS is defined as catalytic hydrogenation and polymerization of CO to yield hydrocarbons (heavy hydrocarbons) and oxygenate compounds (Rofer-DePoorter, 1981). This definition is based on the detailed analysis of FTS reaction processes. In this study, an explanation of the basic processes that take place along the many routes involved in FTS has been given. The main field of attentiveness was heterogeneous reactions of FT catalytic. The process has been described that formed Co<sub>2</sub> and H<sub>2</sub>O as byproducts. Also, the paper includes information about the mechanism of the CH<sub>4</sub> reaction, which is a step in FTS.

**Commercial applications**

the leading company in the market is Sasol in the commercialization of FTS (iron catalyst). Early, in the 1950s, Sasol employed Arge Tubular Fixed bed reactors to commercialize FTS of Fe catalyst, which was dependent on the process of Ruhrchemie and generated a different product of artificial petroleum see (Table 1) and (Figure 3). Then developed the Arge and the slurry bed reactor, which is utilized to produce high Mwt hydrocarbons that are used in the wax industry (A. Steynberg and I. Dry, 2004). Also in 1950, Sasol installed a reactor of circulating-fluidized beds in its Sasolburg facility and used it on the commercial side. Utilizing melted iron as a fluidized catalyst with high temperatures, this reactor produces lightweight hydrocarbons and is ideal to use as chemical feedstock and fuel.

In 1970 Sasol built the second plant and in 1980 used the technology of circulating fluidized-bed In 1990 changed by the improved fixed fluidized bed technology. After Sasol successfully commercialized the FTS iron catalyst, PetroSA, the national company of oil in South Africa, successfully sold a GTL plant using Sasol-licensed HTFT technology from the previous generation. A high temperature (330–350 C) melt iron catalyst operating in a reactor of fluidized beds forms the basis of this process. As of 2010, FTS was the largest refinery of GTL in the world, where it produces around 22,000 barrels of premium fuels every day. Rentech, a US corporation with its headquarters located in Colorado for a long time advocates the research of iron-based FTS. The technology that irons-based FTS was shown by Rentech in 2008. About ten barrels of aviation fuel, naphtha, and ultra-clean diesel are produced daily by the PDU (Davis, 2001). Nowadays, a big player in the Fischer-Tropsch market is Synthetic Fuels in China. (31) They have brought innovations to the market with their iron-based catalyst and high-temperature slurry-phase technology (HTSFTPTM). The best technology promises increased heat efficiency as well as a highly active catalyst. This method is proved in the semi-commercial YiTai CTL Company in Mongolia, which has a daily capacity of 4,000 barrels.

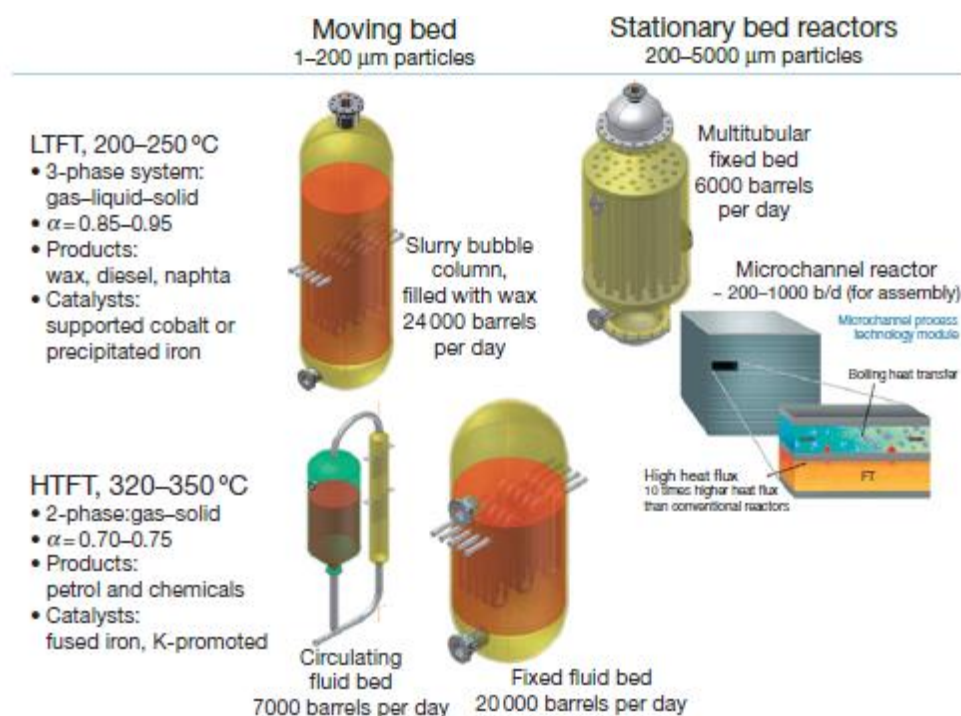
**Table 2:** Fischer–Tropsch synthesis, current commercial plants, and under-construction plants

Company	Carbon feedstock	Catalyst type	Reactor type
Sasol	Initially coal, currently natural gas	Fused Fe/K Precipitated Fe/K Precipitated Fe/K (spray-dried)	HTFT circulating fluidized bed LTFT multitubular fixed bed LTFT slurry phase
Sasol	Mostly coal, now supplemented by natural gas	Fused Fe/K	HTFT circulating fluidized bed
Shell	Natural gas	Co/SiO <sub>2</sub> Co/TiO <sub>2</sub>	LTFT multitubular fixed bed

PetroSA	Natural gas	Fused Fe/K	HTFT circulating, fluidized bed
Sasol-QP (Oryx)	Natural gas	Co/Al <sub>2</sub> O <sub>3</sub>	LTFT slurry phase
Shell (Pearl)	Natural gas	Co/TiO <sub>2</sub>	LTFT multitubular fixed bed
Chevron-Sasol	Natural gas	Co/Al <sub>2</sub> O <sub>3</sub>	LTFT slurry phase
SIMPRA	Natural gas	Co/TiO <sub>2</sub>	LTFT slurry phase
Essar Oil, Fulcrum Bioenergy	Municipal solid waste	TRI steam reformer	JM/BP FT technology
British Airways/Shell/Velocys	Municipal solid waste is 500 ktonnes, 70% reduction in GHG compared to ordinary jet fuel, 90% reduction in particulate matter from engine exhausts	TRI steam reformer	Velocys technology, Haldor Topsoe upgrading
University of Manchester, Argent Energy, TU/e, TNO innovation for life, CSIC, vito, CiaoTech, Siirtec Nigi AND INERATEC, C&CS	Bio-based glycerol	ATR/gasification	

**4. F-T Reactors**

Fixed bed reactors are the most used technology for Fischer-Tropsch synthesis (FTS) due to their high efficiency in maximizing the synthesis driving force in the absence of heat transfer limitations (Basu, 2010). On the other hand, significant pressure drops, poor catalyst usage, inadequate removal of heat, and restricted diffusion are some of the disadvantages reactors of fixed bed (Basu, 2010). Different kinds of FTS reactors, such as slurry-phase reactors, fluidized bed reactors, and microchannel reactors, have been created to get around these restrictions (DECC, 2013). In comparison to fixed bed reactors, slurry-phase reactors provide superior heat and mass transmission since they suspend catalyst particles in a liquid media (Wang and Economides, 2013). In comparison to fixed bed reactors, fluidized bed reactors employ a fluidized bed of catalyst particles, which improves mixing and heat transmission (Davis, 2001). In comparison to other reactor designs, microchannel reactors have higher surface area-to-volume ratios thanks to a network of tiny channels, which improves mass and heat transport (de Klerk, 2012). The creation of sophisticated multiphase FTS reactors that can function in near- or supercritical environments has attracted increasing attention in recent years (Taylor, 1957). To increase the FTS process's efficiency, these reactors combine gas, liquid, and solid phases (Anderson, 1984).



**Figure 5:** Overview of Fischer-Tropsch technology with reactors



#### 4. FTS Catalysts

Nowadays, the synthesis of hydrocarbons involves a variety of metals. Iron, cobalt, and bimetallic catalysts are a few of them. Although iron-based catalysts have been employed in several tests, cobalt-based catalysts are more resilient against water's ability to deactivate them. Water has a less noticeable effect on the rate at which carbon monoxide is converted (B.H. Davis, 2001; H. Taylor, 1957). Conversely, iron in copper catalysts can increase the stability of the thermal Cu particles in reactions of HTFT and the activity of the catalyst of the hydrogenation process. Moreover, the iron is likely to promote enormous surface areas that result from the dispersion of copper. Particle size is the catalyst parameter that may affect the behavior of the catalyst (Bezemer et al., 2006; Rane et al., 2012), also the phase composition, texture, and support type (Borg et al., 2007; Cheng et al., 2015).

Therefore, everything needs to be correctly controlled to make catalysts that work. The production of fixed metal sites which is a significant concentration is the main goal for the preparation of any catalyst in modified FTS (Khodakov, 2009). For feasible industrial applications, the catalyst must be able to sustain stable properties like selectivity of required product and high conversions over a prolonged length of time. It is important to keep in mind that the stability of catalysts should be evaluated.

(Iglesias et al., 2015; Zhang et al., 2015; Liu et al., 2018a) were able to achieve stabilities surpassing 100 hours for catalysts of iron-based by promoters' application in several investigations. Iron catalysts are used in the synthesis of hydrocarbons because of their great selectivity for primary olefin creation (Zhang et al., 2015). Catalysts of iron-based are special in the CO<sub>2</sub> hydrogenation process because of the activity for FTS and RWGS reactions (Visconti et al., 2017). The reduced form of the Hägg iron carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>) phase provides active sites for CO hydrogenation and chain growth, while the Fe<sub>3</sub>O<sub>4</sub> phase catalyzes the RWGS process in CO<sub>2</sub> hydrogenation over Fe-based catalysts (Kim et al., 2020b). Moreover, the methods of production and addition of the promoter have an impact on the catalytic activity and have been widely studied. The catalyst of Co is used in the industrial context to convert FTS synthesis gas to alcohols and hydrocarbons. Nonetheless, because of its high hydrogenation capacity and low RWGS activity, methane dominates the product selectivity. (Chakrabarti et al., 2015) looked at the action of CO<sub>2</sub> on the CoPt/Al<sub>2</sub>O<sub>3</sub> the system of catalyst with the conditions of FTS. The principal product produced when CO<sub>2</sub> was passed over the CoPt/Al<sub>2</sub>O<sub>3</sub> catalyst was methane. The remaining goods were all C<sub>1</sub>-C<sub>3</sub> hydrocarbons. Visconti et al. (2016) also reported that methane is the principal product of the successful hydrogenation of CO<sub>2</sub> over an unpromoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

However, alternate catalyst preparation techniques, support, and promoters can be used to circumvent the process of CH<sub>4</sub> and provide substitute products. According to (Wang et al., 2018) Co catalysts are made from layered Co/Al dual hydroxide (LDH) which is used to selectively hydrogenate CO<sub>2</sub> to ethanol. The resulting alumina-supported Co particles (CoAlO<sub>x</sub>) were subsequently reduced and calcined. The perfect performance of the catalyst was at 600°C, at 140°C, it exhibited 92.1% ethanol selectivity. The scientists believe that this increase in performance is probable because of the ideal existence of surface oxide types with coexisting Co-CoO phases, which encourage the \*CH<sub>x</sub> creation for converting HCOO into CH<sub>3</sub>COO by injection of a critical intermediate for the generation of CH<sub>3</sub>CH<sub>2</sub>OH. Moreover, C<sub>5</sub>+ ethanol hydrocarbons may be produced using cobalt catalysts. The chemisorption of CO<sub>2</sub> increases while the adsorption of H<sub>2</sub> decreases with the addition of alkali metals. Subsequently, it reduces CO<sub>2</sub> conversion while enhancing C<sub>5</sub>+ selectivity and inhibiting CH<sub>4</sub> synthesis. (Shi et al., 2018a) looked at the effect of alkali metals promoting on activity of catalysts also physical and chemical properties of (CoCu-TiO<sub>2</sub>) catalysts. The Na-modified CoCu/TiO<sub>2</sub> catalyst showed the strongest basicity and the lowest H<sub>2</sub> desorption among the study's promoters, resulting in the highest CO<sub>2</sub> conversion (18.4%), the best selectivity (42.1%), and the largest C<sub>5</sub>+ output (5.4%).

Monodisperse CoFe<sub>2</sub>O<sub>4</sub> nanoparticles (NPs) were created by (Kim et al., 2020b) for hydrogenation of CO<sub>2</sub>. The exceptional performance of the bimetallic catalyst can be attributed to the formation of the bimetallic alloy carbide (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>5</sub>C<sub>2</sub>. Higher CO<sub>2</sub> conversion, selectivity of C<sub>2</sub>+ hydrocarbons, and light olefins were the outcomes of this. CoFe<sub>2</sub>O<sub>4</sub> was first reduced to a single phase of the Co-Fe alloy and then to a bimetallic carbide alloy with a Hägg carbide structure (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>5</sub>C<sub>2</sub>.

#### 4.1 Supports

Most research has concentrated on utilizing support oxides. Different supports can be utilized to alter the dispersal of metal, the size of particles, and the reactions of metal support because of the physical and chemical properties of the supports. The supports of metal or nonmetal oxide like silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), titania (TiO<sub>2</sub>), and carbon materials are used exceedingly in catalysts of CO<sub>2</sub> FTS with promoters of alkali to yield mixtures of olefinic hydrocarbon (Hwang et al., 2020).

(Owen et al., 2016) looked at the effects of the supports which are inorganic oxide (SiO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and ZrO<sub>2</sub>, and ZSM-5) Co, Na, and Mo-based catalysts in the immediate conversion of CO<sub>2</sub> to hydrocarbons. SiO<sub>2</sub> and ZSM-5-based catalysts exhibit greater values of CO<sub>2</sub> conversion and equivalent selectivity for carbon monoxide and hydrocarbons. The Co Na and Mo catalysts based on CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> demonstrated a similar CO<sub>2</sub> conversion of around 15% under the examined conditions. Conversely, ZrO<sub>2</sub> < Al<sub>2</sub>O<sub>3</sub> < TiO<sub>2</sub> < CeO<sub>2</sub> is the order in which the hydrocarbon selectivity/CO ratio decreases. (Liu et al., 2018c) looked at several supports, potassium modified in physical combination with pure Fe<sub>5</sub>C<sub>2</sub> catalyst. The scientists found that the alkaline Al<sub>2</sub>O<sub>3</sub> promoted the development of light olefins and C<sub>5</sub>+ hydrocarbons because, through the reaction, K migrated to Fe<sub>5</sub>C<sub>2</sub>, which improved the creation

of C<sub>5+</sub> value-added hydrocarbons and C<sub>2-4</sub> = olefins. Piriyasurawong et al. (2021) used a one-step FSP (flame spray pyrolysis) procedure to generate Fe/Ce-Al<sub>2</sub>O<sub>3</sub> catalysts. This research found that cerium accelerated the process of carbonization also iron carbide synthesis, making the activity of catalyst and selectivity of hydrocarbon.

Moreover, to these other features, the size distribution of pores of supports has an important impact on the performance of catalyst and product dispersion. Reducibility, metal dispersion, and mass transport performance are all significantly impacted. In this way, the bigger pore sizes of the catalyst enhance product diffusion, which lowers the olefins hydrogenation that re adsorbed to paraffin and increases olefins/paraffins ratios. A very small pore size is harmful to reaction because the pore size produces a minimum size of particle that is inadequate to produce carbon-carbon bonds, according to (Xie C. et al., 2017; Numpilai et al., 2019).

Furthermore, (Wang S. et al., 2020) estimated the materials of carbon-based. The researchers used single-walled and multi-walled carbon nanotubes, FeK/MWNTs, and FeK/SWNTs to enable the creation of iron-potassium catalysts. In contrast to the catalyst of FeK/SWNTs, which prefers C<sub>5+</sub> olefin selectivity (39.8%), the catalyst of FeK/MWNTs prefers C<sub>2-4</sub> olefin selectivity (30.7%), according to the study. Apart from achieving high productivity in the production of olefins which is heavy, the FeK/SWNTs catalyst gives markedly decreased selectivities towards undesired carbon monoxide and CH<sub>4</sub>. The great propensity of the SWNTs to contribute electrons, which aid in the breakdown of the C-O bond, may account for some of its remarkable catalytic activity. Encouraging the synthesis of monomers of carbon also raises the C-H surface ratio, it aids in the production of olefins.

## 2. Promoters

Additives known as promoters are used with catalysts to increase their stability, selectivity, or activity. Promoters like K, Na, Mn, Zn, and others have been investigated concerning the performance of catalysts concerning the selectivity of olefins and higher hydrocarbons in the context of Modified Fischer-Tropsch Synthesis. K inhibits secondary reactions, increases the possibility of chain extension, encourages the adsorption of CO and CO<sub>2</sub>, and enhances the synthesis of olefins. It can also maintain the microstructure of the Fe-Al-O spinel, increase CO<sub>2</sub> adsorption, and raise the surface Fe<sub>5</sub>C<sub>2</sub> concentration (Iglesias et al., 2015). Only K may improve the selectivity of the olefins, according to Ramirez et al.'s (2018) examination into the promotion to Fe-C composition (41 weight percent) which results in Mo, Cu, Li, K, Na, Ca, Mg, Ni, Zn, Mn, Co, Pt, Fe and Rh.

Thus, iron oxide and iron carbides boost the absorption of CO and CO<sub>2</sub> lowering the closeness of H<sub>2</sub>, increasing the olefins selectivity. nevertheless, the yield selectivity and activity of the catalyst, including the properties of the CO or CO<sub>2</sub>-containing reacting mixture, are greatly influenced by its concentration and the conditions of the reaction (Visconti et al., 2017).

**Table 3:** The major catalysts and promoters that are used at modified FTS, along with their selectivity and reaction conditions.

Catalyst Conditions Selectivity (%) Reaction Conditions

Metal	Promoter	Support	Pore (nm)	Particle Size(nm)	KCO <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2-</sub> C <sub>4</sub>	C <sub>2-</sub> C=	C <sub>5+</sub>	H <sub>2</sub> /CO	T (°C)	P (MPa)	
Co	Na, Mo	SiO <sub>2</sub>	5,000		43.9	6.9	45.5	31.3	12.8	10.4	3/1	370	0.1	Owen et al. (2013b)
	Pd	Al <sub>2</sub> O <sub>3</sub>	1.9		33.0		94.7	4.8		0.5	3/1	220	2.0	Chakrabarti et al. (2015)
	Na	SiO <sub>2</sub>	20		16.0		80.0	19			3/1	220	1.9	Gnanamani et al. (2015)
	Na, Mo	SiO <sub>2</sub>			30.0	21.5	57.1	30.4	0.1	12.3	3/1	200	0.1	Owen et al. (2016)
	Pt	mSiO <sub>2</sub> , CeO <sub>2</sub>			3.0	75.0	60.0	40.0			3/1	250	0.6	Xie T. et al. (2017)
	Pt	Co <sub>3</sub> O <sub>4</sub>	26.5		27.8		60.0	25.2	14.8		3/1	200	2.0	Ouyang et al. (2017)
	Mn				15.3	0.4		46.6		53.4	1/1	200	8.0	He et al. (2019)
	Na	Ac	0.6	6.2	67.2	0.1	96.0	3.6		0.4	3/1	250	5.0	Zhang S. et al. (2020)
Fe	K	ZrO <sub>2</sub>			43.0	15.0	18.0	9.2	44.0	28.8	3/1	340	2.0	Wang et al. (2013)
	K			20–50	38.0	7.3	21.0	14.0	34.0	30	3/1	340	2.0	You et al. (2013)
	K	Al <sub>2</sub> O <sub>3</sub>	7.9		54.4	14.0	26.7	10.3	26.7	36.2	3/1	400	3.0	Ding et al. (2014)
	K				29.0	8.0	63.0	31.0		6.0	3/1	330	1.0	Iglesias et al. (2015)
	K				41.0	2.0	27.2	50.3		22.5	5/1	300	1.1	Fischer et al. (2016)
	K	Al <sub>2</sub> O <sub>3</sub>		5–8	42.5	23.9	30.0	40.5		29.6 <sup>f</sup>	3/1	400	3.0	Xie T. et al. (2017)
	K		6		45.0	13.0	18.4	5.7	41.4	34.5	3/1	300	0.5	Visconti et al. (2017)
	K		6.5		72.0	1.0	13.5	33.7		52.8	3/1	320	2.0	Landau et al. (2017)
	K	K/a-Al <sub>2</sub> O <sub>3</sub>			44.8	23.2	30.1	6.3	29.8	33.9	3/1	400	3.0	Liu et al. (2018c)



	K	HSG	14.9				25.0	12.0	59.0	4.0	3/1	340	2.0	Wu et al. (2018)
	K	C			40.0	21.0	16.5	11.4	46.8d	25.3g	3/1	350	3.0	Ramirez et al. (2018)
	K	K <sub>2</sub> CO <sub>3</sub>			44.0	13.0	16.1	9.2	72.4e	2.3	3/1	350	3.0	Ramirez et al. (2019a)
	K	MPC	8.1	15	50.6	8.2	16.8	34.7		48.5	3/1	300	2.5	Hwang et al. (2020)
	K	SWNTs		4.6	52.7	9.6	13.5	8.6	22.5	55.4	3/1	340	2.0	Wang S. et al. (2020)
	K	C			24.0	40.0	25.0	41.7		33.3	2/1	350	2.0	Pokusaeva et al. (2020)
	K				41.9	8.9	22.7	8.3	42.7	26.4	3/1	320	3.0	Liu et al. (2021b)
	K	C-1EDA		7.4	20.1	31.7	17.2	5.6	37.7	39.5	3/1	300	1.0	Kosol et al. (2021)
	K, Cu	SiO <sub>2</sub>			27.0	35.0	12.0	33.0		55.0	3/1	250	2.0	Gnanamani et al. (2013)
	K, Cu, La	TiO <sub>2</sub>			27.0	32.0	10.3	30.9		58.8	3/1	300	1.0	Rodemerck et al. (2013)
	K, Mn	Al <sub>2</sub> O <sub>3</sub>			33.4	11.0	26.4	52.4		21.1	3/1	300	1.8	Drab et al. (2013)
	K, Mn	Al <sub>2</sub> O <sub>3</sub>			60.0	13.4	25.9	74.1			3/1	300	1.8	Willauer et al. (2013)
	K, Cu, Al		4.3		77.0	2.0	14.6	6.7	30.3	48.3	4/1	300	1.0	Landau et al. (2014)
	Mn		19.1		30.0	7.7	29.3	63.2		3.9g	3/1	340	2.0	Al-Dossary et al. (2015)
	K, Zn		27.7		51.0	6.0	34.9	7.8	53.6	3.7	3/1	320	0.5	Zhang et al. (2015)
	K, Cu, Al				51.0	16.0	79.8	20.2			3/1	325	15	Mokou et al. (2015)
	Na	CNT			24.0		21.0	7.0	45	27.0	3/1	370	0.8	Mattia et al. (2015)
	K, HZSM-5		26.8		43.9	6.1	10.1	11.5		78.4	3/1	300	2.5	Geng et al. (2016)
	K, Zn, Cu		9		8.90	19.5						220	3.0	Visconti et al. (2016)
	Na		16.7		40.5	13.5	15.8	7.5	46.6	30.1	3/1	320	3.0	Wei et al. (2016)
	Na, HZSM-5			13.1	34.0	13.0	9.0	24.0		67.0	3/1	320	3.0	Wei et al. (2017)
	K, Mn	Macrolite®			36.0	8.4	27.2	72.8			3/1	320	2.0	Bradley et al. (2017a)
	K, Mn	NCNT			30.1	72.1	23.0	57.8		19.1	3/1	360	2.5	Kangvansura et al. (2017)
	K, Zn, Cu		11.6		15.1	23.4	13.2	25.5		61.4	2/1	230	1.6	Ning et al. (2014)
	K, Cu	Al <sub>2</sub> O <sub>3</sub>			41.0	5.7	6.8	93.2			3/1	300	2.0	Bradley et al. (2017b)
	K, Zr			25	45.0	7.0	14.0	37.2			3/1	320	2.0	Samanta et al. (2017)
	Zn, Na			2,500	34.0	11.7	9.7	31.8		58.5	3/1	340	1.0	Choi et al. (2017b)
	biopromoters	C		6–8	31.0	23.2	11.8	63.9	33.2	50.3	3/1	320	1.0	Guo et al. (2018b)
	Ni	Al <sub>2</sub> O <sub>3</sub> - HZSM-5			81.7	9.3	20.5	0.3		79.2	3/1	300	1.0	Bashiri et al. (2018)
	Ru	BMI-NTf <sub>2</sub> IL			12.0		2.0	57.0		41.0	4/1	150	0.9	Qadir et al. (2018)
	K, Zn	NC		6	34.6	21.2	24.2	7.1	40.6	28.0	3/1	320	3.0	Liu et al. (2018a)
	K, Zr, Ce		2.43	21.2	54.3	3.1	20.6	7.9	55.6	15.9	3/1	320	2.0	Zhang et al. (2018)
	Rb				27.3		27.8	66.3		5.9	3/1	270	1.2	Gnanamani et al. (2018)
	K, Mg	Al <sub>2</sub> O <sub>3</sub>			33.5	24.9	68.1	27.8		4.1	27/10	400	3.0	Tarasov et al. (2018b)
	Na, Mn				27.9	24.1	13.1	5.3	33.9	47.6	3/1	320	0.5	Liu B. et al. (2018)
	Ni			8.4	94.1	0.7	78.2	19.7		2.1	5/1	300	0.3	Puga and Corma, (2018)

### 5. Conclusions and future challenges

Today, there is a daily need for crude oil around 90 million barrels, of which 85% are wanted to yield fuels for transportation. Nowadays, more than 5% of liquid transport fuels are produced by other processes like waste-to-liquid (WTL), BTL, and GTL. Crude oil is an energy source that cannot be used continuously. Additionally, it is predicted that over the next 50 years, countries will produce less crude oil than they would require for energy transportation. This will not meet all the necessities of the country's energy, but it will decrease the dependence on crude oil. This is one of the results of the international economy growing, which is why it is so important to do research into sustainable alternative energy sources. To convert lignocellulose biomass, a component of agricultural products that does not belong in the food chain of humans to desired liquid fuel, a lot of research is being done in this area. While meeting the country's energy needs might not be possible, this proposal could reduce the country's need the crude oil. The FTS synthesis is one route in the non-immediate liquefaction process. Hydrogenation of CO yields a different of compounds with a wide range of carbon numbers like oxygenates, hydrocarbons, and H<sub>2</sub>O, also the carbide metal polymerization.

The study offered a comprehensive review of the literature on the FTS process, addressing a range of subjects with the development of FT technology for the production of liquid hydrocarbons, the importance and advantages of second-

generation biofuels for the transportation of energy in the future, and the organic materials properties of used like a feedstock in the FT process to produce hydrocarbons of long chain. Additionally, this study provided the polymerization surface procedures for the Fischer-Tropsch process, which yields a range of hydrocarbons. The silanol functional groups are illustrated together with an attempt to understand the mechanics of the re-hydroxylation, dehydration, and dehydroxylation of the surface of silica. Included is also a review of catalyst composition and reaction engineering in FTS.

The prospect of reducing CO<sub>2</sub> emissions and inserting renewable energy in the cars and chemical sectors has made utilizing CO<sub>2</sub> and H<sub>2</sub> as clean hydrocarbon sources more popular, albeit it is still an issue. Various techniques have been contemplated to transform CO<sub>2</sub> into hydrocarbons. This study describes the FTS path of a CO<sub>2</sub> hydrogenation catalyst. It utilizes a modified form of the FT reaction, where CO<sub>2</sub> instead of CO reacts.

The reaction happens in two stages. In the RWGS, CO<sub>2</sub> and H<sub>2</sub> first mix to create CO. Subsequently, hydrocarbons are created when CO and H<sub>2</sub> react in the traditional FT reactions. To reach high selectivity to the specified heavy hydrocarbons rather than an undesired carbon monoxide product, the synergistic development of RWGS and growth of carbon chain reaction coupling is required.

So, the reaction wants an active catalyst in each of the FT and RWGS reactions. Fe-based catalysts are preferred over Co-based catalysts because of the high activity in RWGS, these catalysts are frequently doped with alkali metals.

Many financial and technological problems still need to be resolved. Large-scale CO<sub>2</sub> conversion to value-added hydrocarbons still requires economically feasible advances in both technology and catalysis. Research on producing more efficient catalysts, however, might be aided by societal and economic incentives.

**List of abbreviations**

BBL	Barrel
BPD	Barrels Per Day
BTL	Biomass to Liquid
FT	Fischer-Tropsch
FTS	Fischer-Tropsch Synthesis
GTL	Gas to liquid
HTFT	High-Temperature Fischer Tropsch
LTFT	Low-Temperature Fischer Tropsch
WGS	Water Gas Shift
CTL	Coal-to-liquid
WTL	Waste to Liquid
RWGS	Reverse Water Gas Shift reaction

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