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Improving Gas to Liquid production by Associated Gases

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Abstract

Gas-to-Liquids (GTL) is a process for converting natural gas into synthetic oil, which can be further processed into fuels and other hydrocarbon-based products. The total GTL plant is self-sufficient. Therefore most of the required utilities provided, too. High energy cost is the main driving force behind currently increasing interest in the Fischer-Tropsch synthesis (FTS) for the conversion of GTL. The catalytic synthesis of hydrocarbons from CO and H_2 Syngas mixtures leads to a large variety of products such as paraffins, olefins, alcohols, and aldehydes. The process uses mainly natural gas. However, other gases fuels could also be employed. Three-fourths of Iraq's natural gas resources are associated with oil. Meanwhile, Majnoon oil production is generating significant amounts of associated gas that was usually flared while different options to abate flaring are under review. The current article presents using a 10 MM m^3 annually associated gases in the southern part of Iraq in 3000 BPD GTL plant. The simulation of the plant shows that the added associated gas which is currently flared could increase the productivity and there is no need to send it to the flares. Research Institute of Petroleum Industry has a license of the GTL process, both fixed-bed and slurry types.

Keywords: GTL (Gas to Liquid), Fischer-Tropsch synthesis; Associated Gases; Iraq's natural gas

1-Introduction

In the face of increasing oil prices and decreasing oil reserves, alternative routes for production of liquid fuels attract considerable attention in research and industrial application. Fischer-Tropsch synthesis (FTS) offers the possibility of the conversion of synthesis gas to a mixture of linear hydrocarbons. Fuels produced with FTS are of a high quality due to a very low aromaticity and near zero sulfur content. New and stringent regulations may promote replacement or blending of conventional fuels by sulfur and aromatic-free FTS products. Various types of reactors (fixed-bed, fluidized-bed, ebulliating-bed and slurry-phase) differ with respect to the most suitable particle size of the catalyst used. The range of catalyst sizes reflects the tradeoff between the desires to provide high catalyst utilization and maintain a manageable pressure drop across the reactor. If a fixed-bed mode of operation is envisaged, the FT catalyst will generally consist of particles with a few millimeters in size for reasons of pressure drop and heat transfer. Table 1 shows a brief history of commercial Fischer-Tropsch synthesis.

Table (1) Brief history of commercial Fischer-Tropsch synthesis

Year	**Description**
1902	Methanation reaction with Syngas over Ni catalyst. ▪
1923	Franz Fischer & Hans Tropsch reported hydrocarbon synthesis at higher pressure using Co, Fe Ru catalysts. ▪
1936	4 FT Plants commissioned in Germany ▪
1950	Hydrocol plant operated for sometime based on Fixed Fluidized Bed rector with Fe-K catalyst, Cap. 5000 bpd at Brownsville, Texas. ▪
1950-1953	In Germany, Koelbel set up 1.5 m dia. slurry phase reactor at Rheinpreussen and operated it successfully ▪
1955	German plants were shut down after brief operation using petroleum residue. Interest in FTS declined worldwide, when oil deposits were ▪

	discovered in abundance in the Middle East.
1970-1980	Renewed interest in FTS due to increased oil prices and fear of oil ▪ shortage ▪
1990s	Further revival of FTS or GTL due to discoveries of huge stranded natural gas reserves and requirement for clean fuels. ▪
1992	First natural gas based plant (Mossgas) set up in S.Africa, based on Sasol's Synthol reactor. ▪
1993	Shell Middle Distillate Synthesis (SMDS) plant (12,500 bpd) was set up in Malaysia (natural gas based) using TFB reactor and Co catalyst. ▪
2000	Worldwide environmental legislation requiring ultra low sulphur and aromatic levels in fuel will cost billions in oil refinery upgrading. ▪ Design, Engineering and Construction of a Sasol SPD Plant (Cost Effective FT GTL Plant) ▪
2001	Engineering break throughs and new advances in catalysis have led to cost reductions making the FT process viable. ▪
2002	Nearly every major oil company is developing their own F-T technology, forming joint ventures, or scrambling to do so. ▪ Exxon/Mobil and has spent over $500 MM ▪ Chevron formed a joint venture with Sasol ▪ Statoil has formed a joint venture with Mossgas ▪ Conoco built a $400MM test plant in Oklahoma ▪ BP completed its pilot/test plant in Alaska ▪

	Shell has announced 7 new projects ▪
2004	As of July 2004, 50 new Fischer-Tropsch projects have been ▪ announced. These projects total over 900,000 BPD capacity ▪ Some of these projects are pilot plants, some are feasibility studies for ▪ clients, and some have started construction.
2005	These projects include: ▪ Chevron/Sasol: 100,000 BPD GTL Qatar ▪ Shell: 140,000 BPD GTL Qatar ▪ Conoco/Phillips: 130,000 BPD GTL Qatar ▪ Exxon-Mobil: 150,000 BPD GTL Qatar ▪ Chevron/Sasol: 33,000 BPD GTL Nigeria ▪ Shell: 6 projects worldwide with 72,000 BPD each ▪ Sasol 2 : 80,000 BPD CTL China ▪ Shell 70,000 BPD CTL China ▪
2007	Sasol, 35,000 bbl/d GTL Plant Qatar (two additional 35,000 bbl/d ▪ expansions planned)
2008-10	Shell Oil 140,000 bbl/d GTL Plant Qatar ▪
2014-Present	RIPI-GTL: 3000 BPL Gheshm/Iran (Under construction) ▪

1.GTL- Process

Gas-to-Liquids is a process for converting natural gas into synthetic oil, which can be further processed into fuels and other hydrocarbon-based products. In the simplest of terms, the GTL process tears natural gas molecules apart and reassembles them into longer chain molecules, like those that comprise crude oil. The technology used is based on the Fischer-Tropsch synthesis. Nowadays GTL mostly refers to gas conversion, which results in an extremely pure synthetic crude oil that is virtually free of contaminants such as sulphur, aromatics and metals. This synthetic crude can be refined into products such as diesel fuel, naphtha, wax and other liquid petroleum or specialty products.

The Fischer-Tropsch Synthesis Unit is the heart of GTL Plant where long chain molecules are formed. The Fischer-Tropsch Synthesis includes several Fixed Bed Fischer-Tropsch (FT) Multi Tubular Reactors, which contains Fe-based FT catalyst. Within the Fischer-Tropsch reactor the synthesis gas is converted to the various hydrocarbon products, mainly from C_1 to C_{30}. The FT products usually include LPG, Naphtha, Kerosene, Diesel, Lube Oil and Wax.

The unconverted synthesis gas and FT Tail Gas leaves the unit and is routed to Tail Gas Recovery (TGR) Unit, and after condensate recovery, it is recycled to the Reformer. Also the FT products will be routed to Product Degassing and Distillation Unit for further separations and purifications.

Since the FT reactions are highly exothermal, therefore the released heat of reaction could be utilized in a waste heat recovery system for the purpose of MP steam generation.

Considering that separation of the Oily Water from the other FT products takes place through thermal separation, inter-stage cooling is used. An overview of the GTL process is shown below.

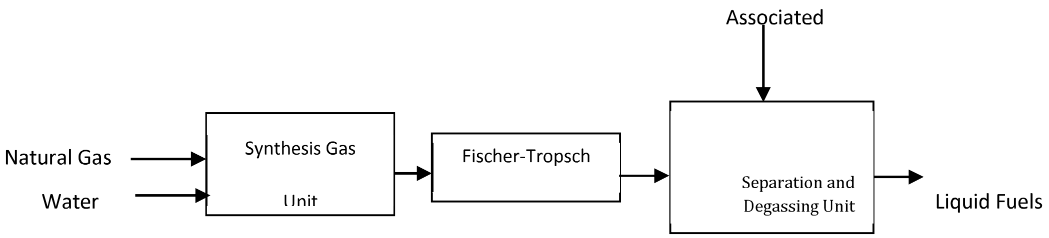


Fig. (1) Overview of the GTL process

RIPI has several experiences about each parts of the plant. Both experimental and modeling and simulation tests could help for new designs and different product distributions. For instance, Detail modeling of the syngas (steam reformers) could predict the reactor and furnace behavior which is integrated inside the plant [1, 2, 3].

2.1. Synthesis Gas Unit

The objective is to produce synthesis gas for the Fischer Tropsch Unit with a molar H_2/CO ratio of 1 to 2. In summary, the following basic process steps are included:

Hydrogenation and desulphurization of the natural gas feedstock (a

Saturation with water, CO_2 adding and preheating of feedstock (b

Catalytic Reforming of the natural gas feedstock (c

Synthesis gas cooling and heat recovery (d

a) Hydrogenation and Desulphurization of the Natural Gas Feedstock

Hydrogenation and desulphurization of the natural gas feed operate at about 380°C. The gas is heated up to this temperature in two steps. After preheating to 380°C, the natural gas enters the hydrogenation Reactor, filled with Co/Mo catalyst for the hydrogenation of organic sulfur compounds contained in the natural gas to H_2S. Finally all H_2S is adsorbed on the zinc oxide catalyst bed in the Zinc Oxide Vessel, according to the following equation:

$$ZnO + H_2S \longrightarrow ZnS + H_2O$$

The Zinc Oxide Vessels are operated in series, which allows optimum sulfur pick-up and catalyst lifetime.

b) Saturation, CO2 Adding and Preheating of Feedstock

After hydrogenation and desulphurization, the natural gas feedstock is mixed with proper quantity of steam and CO2 and then heated up to 550°C. The Required CO2 is provided from Recycled CO2 from Amine unit. The required steam is supplied from MP steam produced in this unit. After adding required steam and CO2, the feed is heated up to 550°C.

c) Catalytic Reforming of Natural Gas Feedstock

Natural gas feed with proper molar steam/carbon ratio and CO2/carbon ratio enter in a number of reformer tubes. The vertical reformer tubes are filled with catalyst and arranged in the furnace. The required heat is supplied by combustion of fuel in burners.

Prior to the start-up the reformer catalyst has to be reduced with hydrogen. The reactions are:

Methane reforming: $CH_4 + H_2O \Leftrightarrow CO + 3\,H_2 - \text{heat}$

Shift reaction: $CO_2 + H_2 \Leftrightarrow CO + H_2O - \text{heat}$

d)Synthesis Gas Cooling and Heat Recovery

Between synthesis gas and Amine units, the synthesis gas has to be cooled from 900°C to 50°C. Simultaneously, approx. 99% of the steam contained in the synthesis gas leaving the reactor has to be condensed, resulting in a high amount of sensible heat to be recovered or annihilated by cooling. Synthesis gas cooling and heat recovery are performed in heat exchangers.

Also, the flue gas which exits from radiation section of the furnace has temperature about 1000°C. This flue gas must be cooled up to 150°C and then vent to atmosphere, so there is considerable amount of sensible heat, which has been removed in convection section of the furnace. The heat exchangers are designed in convection section of furnace for this purpose.

The Waste Heat Boilers is connected to these exchangers for steam production. The Waste Heat Boiler is equipped with an internal bypass to control the gas outlet temperature at fouled and clean tube surfaces as well.

2.2. FT reactor

The syngas is sent to the FT reactor. The FT synthesis with cobalt catalyst produces mostly n-alkanes and 1-alkenes. The FT reaction is briefly presented as below (using cobalt catalyst)

$$nCO + 2nH_2 \rightarrow (\text{-}CH_2\text{-})_n + nH_2O$$

2.2. Separation and Degassing

The hydrocarbon products produced in the FT reactor consist of a mixture of:

- Light hydrocarbons
- Olefins
- Liquid hydrocarbons
- Waxy, long-chain paraffinic molecules that cannot directly be sold as products

These products are further processed in the product-upgrading unit to primarily produce naphtha, kerosene, and diesel. There is a variety of specialty products that can be produced from FT products such as:

- Solvents
- Wax
- Lube oils

Catalyst 2.3

High energy cost is the main driving force behind currently increasing interest in the Fischer-Tropsch synthesis (FTS) for the conversion of natural gas to liquids (GTL). The catalytic synthesis of hydrocarbons from CO and H2 syngas mixtures leads to a large variety of products such as paraffins, olefins, alcohols, and aldehydes. Several metal catalysts can be used for the

FTS; however, only iron and cobalt catalysts (Fig. 2) appear to be economically feasible on an industrial scale [4].

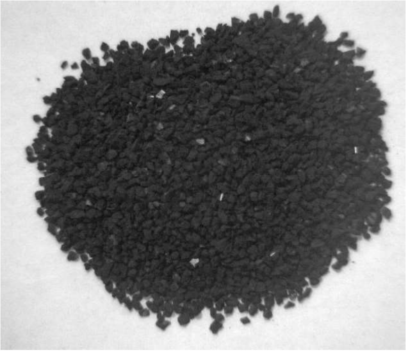


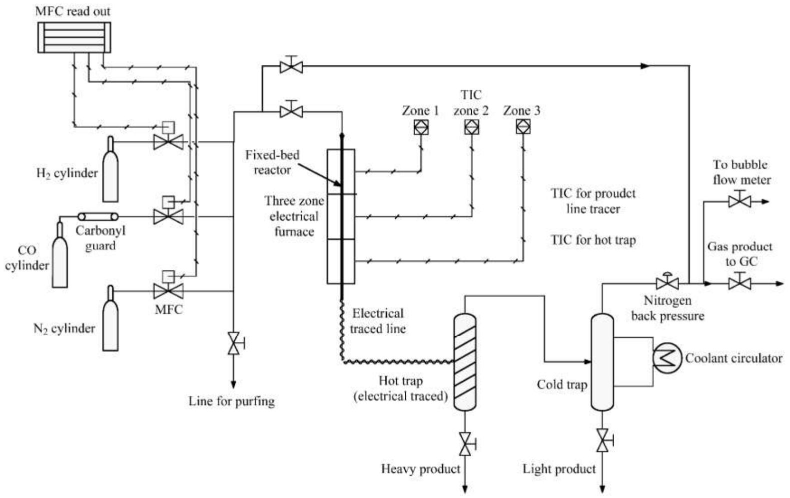
Fig. (2) Appearance photographs of the prepared catalyst pellets (0.5 mm)

Nanostructured iron catalysts were prepared by a microemulsion method. A series of unpromoted and CaO-promoted iron nanocatalysts were studied using different characterization techniques. The effect of calcium oxide on the Fischer-Tropsch synthesis activity and selectivity was investigated in a fixed bed reactor. It was shown that the activity and C5+ selectivity increased, but methane selectivity decreased with increasing the amount of calcium oxide, which was attributed to the increased reducibility. The changes in the catalytic performances could be ascribed to the effect of the promoter on H2 and CO adsorption, which further affected the FTS performances of the catalysts significantly. Using small pellets resulted in higher CO conversion, FT reaction rate and C5+ productivity as compared with larger pellets [5].

Fe-HZSM-5 bifunctional catalyst activity and products selectivity in Fischer–Tropsch synthesis (FTS) were investigated. HZSM-5 addition to FT catalyst suppressed the formation of oxygenates, which are converted to hydrocarbons on the zeolite acid sites [6]. Kinetic parameters are determined using the genetic algorithm approach (GA), followed by the Levenberg–Marquardt (LM) method to make refined optimization, and are validated by means of statistical analysis. Also, the performance of the catalyst for Fischer–Tropsch synthesis and the hydrocarbon product distributions were investigated under different reaction conditions [7, 8, 9].

2.2. Experimental tests

Several experimental tests have been performed to prove the FT-catalysts. The following set-up presents one of the tests.



Fig(3) Experimental set [10]

The experimental facility Figure (3) consists feed cylinders including N2, H2, CO, fixed bed reactor, hot and cold traps for gathering the products. More details about the facility could be found in literature [10] (Tavasoli et al., 2007).

3.Iraq-Associated Gases (AG)

Current proven Iraq's gas reserves are in the order of 128 TCF of which 92 is associated gas and 36 non-associated. The probable gas reserves are estimated to the order of 325 TCF 164 associated and 161 non-associated [11].

Around 70% of estimated gas reserves is solution gas, primarily associated with the giant oil fields in the southeast of the country. Reserves of 15-20 tcf of nonassociated gas are in seven fields mainly in northern Iraq [12].Gas Production In January 2013, Iraq’s gas production reached 2.234Bcf/day.

The MOO gas production reached 1.9Bcf/day of mostly associated gas produced from the southern fields. Currently, only 400 MMcf/day is captured from the south and 300MMcf/day is captured from the north (outside the Kurdistan Region), leaving 1.2 Bcf/day wastefully flared because of the lack of infrastructure and other persistent challenges. In addition to the gas produced by MOO, 340MMscf of free gas (non-associated gas) was commercially produced from the MNR-controlled northern field of Khor Mor.

All crude oil production generates some natural gas as a byproduct. In the modern oil industry, this so-called "associated gas" is typically captured and processed. In Iraq, however, where the oil sector has been ravaged by decades of underinvestment, huge volumes of associated gas are simply burned off as waste.The BGC would capture and process associated gas from the Rumaila, Zubair, and West Qurna 1 oil fields — a reduction in the project's scope, which originally covered all associated gas production in Basra. Still, the contract anticipates that those fields, whose crude oil production is set to skyrocket, will eventually reach a production plateau of 2 billion scf/d of associated gas [13].Geographically, gas reserves are concentrated in the Southern Mesopotamian region, mostly as the associated gas in the giant fields of Rumaila, West Qurna, Majnoon, Nahr Umr and Zubair. These fields account for around two-thirds of country’s total gas reserves and have relatively high content of natural gas liquids. The major resources of non-associated gas are in the Northern regions of the country. Table 1 provides some facts on Iraq’s gas reserves and production projections [14].

4.Results and Discussion

Below tables shows natural gas feed and associated gases employed in the current work.

Table (1) Feed (Natural gas) composition

NG-Feed	% mole
CO2	0.6
Nitrogen	6.7
Methane	86
Ethane	3.35
Propane	1.9
n-Butane	0.6
i-Butane	0.4
n-Pentane	0.15
i-Pentane	0.15
n-Hexane	0.15

Table (2) Associated gas composition

AG	% mole
CO2	2
Methane	68
Ethane	16
Propane	8.5
n-Butane	3.5
n-Pentane	2

Table (3) Operating conditions for two feeds

Parameter	NG	AG
Temperature, C	38	40
Pressure, barg	43.574881	21
Flow, kmol/hr	1587.0993	42
Flow, bbl/d	13120	411

Based on the results obtained from the simulation of all parts including syngas, CO2 separation, FT-reactor, and product separation and upgrading which was performed in HYSYS software, the following table presents product distribution:

Table (4) Comparison of the products obtained from two cases: with and without addition of associated gas

GTL-Products, BPD	**Without AG**	**With AG**
LPG	450	510
Naphta	730	740
Diesel	1320	1360
Kerosene	440	460
sum	2940	3070

The tables show that from 411 BPD added AG there is 130 BPD liquid fuels obtained from the product.

5. Conclusion

In the RIPI-GTL process the catalytic synthesis of hydrocarbons from CO and H2 syngas mixtures leads to a large variety of products such as paraffins, olefins, alcohols, and aldehydes. The process uses mainly natural gas. However, other gases fuels could also be employed. The current article presents employing a 10 MM m3 annually associated gases in the southern part of Iraq in 3000 BPD GTL plant. The simulated plant shows that the added associated gas which is currently flared could increase the productivity and there is no need to send it to the flares. Research Institute of Petroleum Industry has a license of the GTL process, both fixed-bed and slurry types. The results show that about 30% of the AG could be converted to the liquid products including LPG, naphta, diesel and kerosene. The remained part is used for the furnace, boilers, power, and utilities.So, the AG gas currently purged to the atmosphere could be linked to the current RIPI-GTL plant and produces a lot of liquid excellent sulfure –free product.

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List of Symbols:

AG: Associated gas

NG: Natural gas

GTL: Gas to liquid

FT: Fisher-Tropsch

RIPI: research Institute of Petroleum Industry

BPL: Barrel per day