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Development of GTL (Gas to Liquid) Technology

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Abstract

A GTL (Gas to Liquid) technology was developed by the authors under the JOGMEC project. This technology is anticipated to contribute to clean energy production processes in future. Nippon Steel was responsible for the development of FT synthetic technology. In the process of this development project a cobalt basis catalyst was developed. Its high performance and high strength were confirmed as being superior to other existing competitors, such as a catalyst at the Yufutsu pilot plant test (7BPD). As for the process development, a simulation model was developed as well as a scale up design method. A feasibility study of this developed technology was also developed to confirm the feasibility in its application to actual gas fields.

1. Introduction

In the fields of energy production and use, there is a serious and increasing need to preserve our natural environment on a global scale. Trends point to the fact that there will also be a continued increase in the demand for natural gas. Natural gas has less of a negative impact on our natural environment than that of other sources of energy, namely coal or petroleum. Furthermore, natural gas is a relatively evenly distributed resource. However, pipelines must be constructed, and there is a need for an LNG infrastructure (manufacturing, shipping/receiving, transport). Therefore, there are small reserves and many undeveloped gas fields that include impurities such as carbon dioxide gas that do not meet the criteria for large investments for their development. GTL technology converts natural gas into clean naphtha, kerosene and light oils thereby making it possible to ensure the same distribution routes as petroleum. Thus, this technology also contributes to preserving our environment and to the diversification of our resources. At the center of this technology are global corporations such as Shell, Sasol and Exxon Mobil. They are making efforts into the commercializing of this energy source. However, Nippon Steel Corporation has also promoted research into the practical application of this important technology with the features described below in the GTL technical development project known as JOGMEC (Japan Oil, Gas and Metals National Corporation). Nippon Steel Corporation is an active participant in the planning of this project.

2. The Significance and Scope of GTL Technical Developments

2.1 The significance of developments

The significance of developments can be described as falling into the following three Es categories. (Energy security, Ecology, and Economy)

(1) Energy security

A. This is the effective use of untapped natural gas resources, and diversification of fuel resources by ensuring substitutes for crude oil.

B. This is reduced dependence of resources from the Middle East by effectively utilizing untapped gas fields including carbon dioxide gas from Southeast Asia and Western Australia.

C. This is the suppression of future GTL enterprise monopolization and cost controls by major international oil company overseas.

(2) Ecology

A. This is to provide clean resources of flue gases (NO_X, PM) from the characteristics of the Sulfur component and aromatic sweet-free fuels in petroleum based fuels.

B. This is to promote the diffusion of highly efficient diesel-powered vehicles (with low carbon dioxide gas discharge) linked to GTL light oil introduction.

C. This is the reduction and effective use of associated gases

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(flaring) in oil and gas producing countries.

(3) Economy

A. This is the participation in the planning of a development project and contribution to technologies through independent and superior, domestic technologies.

B. This is the promotion of development of domestic company's gas fields and linking to gas producing countries that have superior technologies.

2.2 Trends of developments of the GTL technology at each company

Table 1 shows the syngas manufacturing technologies, FT synthesis technologies and the developmental stages at each company developing GTL technology.

(1) Syngas manufacturing technology

While there are a variety of methods undertaken in the development of syngas, many methods vary according to each company's developmental concepts and objective applications. As a general flow, there is a move toward ATR (Auto Thermal Reforming) that uses oxygen. However, because it requires an oxygen plant, thus incurring enormous costs, the issue of excess equipment costs becomes a problem.

(2) FT synthesis technology

Both BP and Shell employ a multi tubular fixed bed, but that method is considered to be better suited for a slurry bed because it is more efficient in removing the heat of the reaction in the FT synthesis, and because the equipment can be more compact. However, this method still has many unanswered technical issues, such as establishing a method for designing scaled-up systems.

2.3 JOGMEC/GTL technical characteristics (see Fig. 1)

The JOGMEC-GTL processes are compared in **Fig. 1** to the latest representative model of conventional GTL processes (ATR). The conventional process requires an oxygen plant and equipment for the removal of carbon dioxide gas in order to manufacture syngas. To derive syngas having an optimum mole ratio of 2:1 (hydrogen to carbon monoxide) in the FT synthesis, equipment that adjusts the hydrogen concentration in the synthesized gas is necessary. On the other hand, by employing carbon dioxide gas reforming, natural gas that includes carbon dioxide gas in the crude material can be utilized as it is. This makes it possible to obtain syngas having an optimum composition in the FT synthesis in one step. That capacity translates into lower construction and operating costs. This was achieved through the development of a stable catalyst that is operable even

Table 1 Comparison of GTL technology

	O_2 plant	Singes production	F T synthesis (cat)	Production
JOGMEC (Japan)	No need	Tubular reformer <Chiyoda>	Slurry bed (Co) <NSC>	7B/day Pilot
Sasol (South Africa)	Need	Auto thermal reformer <Topsoe>	Slurry bed (Co) <Sasol>	17,000B/day Commercial (× 2)
Shell (Malaysia)	Need	POX <Shell>	Fixed bed (Co) <Shell>	3,000B/day Commercial (× 4)
ExxonMobil (USA)	Need	Auto thermal reformer <ExxonMobil>	Slurry bed (Co) <ExxonMobil>	200B/day Demonstration
Conoco (USA)	Need	CPOX <Conoco>	Slurry bed (Co) <Conoco>	400B/day Demonstration
BP (USA)	Need	Compact reformer <BP>	Slurry bed (Co) <BP>	300B/day Demonstration

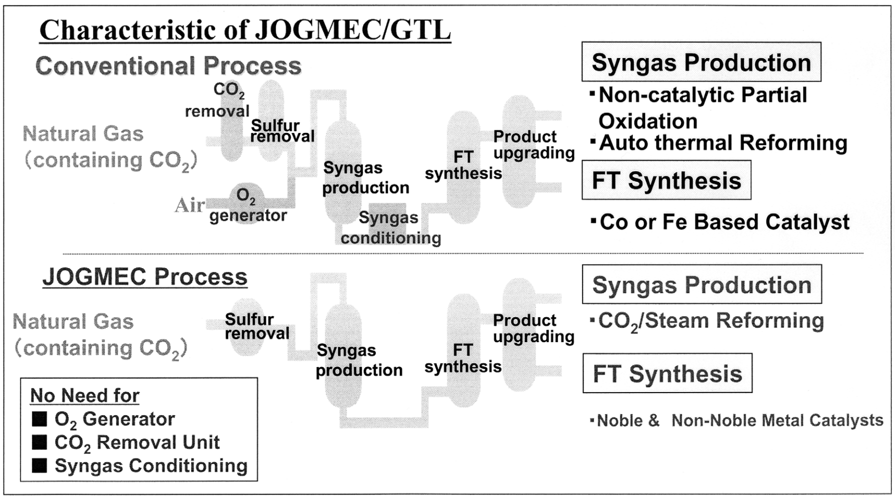

Fig. 1 Characteristic of JOGMEC / GTL

under the conditions where continued operations were impossible because of the precipitation of oxygen in the conventional technologies.

Using the FT synthesis developed by Nippon Steel, the following were possible. (1) Developed a catalyst (patent pending) that has high durability to wear, and high performance based on control of the boundary surface to an optimum structure; (2) Continuing from laboratory tests, verified performance that exceeds the prior technical level at a pilot plant in Yufutsu, Hokkaido; (3) Advanced development for a simple slurry bed reaction model that has superior heat transfer transmission characteristics and that is compact, studied the reactor structure that has heat transmission characteristics and that allows for uniform flow of catalyst slurry, and verified stable slurry circulation and processing capabilities even in the pilot tests. (Patent pending)

3. Details of Efforts Toward Developments and The Results

3.1 Details of efforts

From 2001, Nippon Steel planned together with JOGMEC and four other private companies (Japex, Chiyoda Corporation, Cosmo Oil, and Inpex Corporation) for the development of GTL technology, or the so-called gas-to-liquid technology. The research plans are outlined in **Fig. 2**. In the research plans of Nippon Steel, efforts focused on FT synthesis technologies for 1) pilot operation research; 2) development of an FT synthesis catalyst; and 3) an economic evaluation (Pertamina FS) and process research.

3.2 Results of developments

Using the technical developments described above, predetermined developmental target values were reached at a pilot plant constructed in Yufutsu, Hokkaido. These were attained for characteristic and superior technologies for syngas manufacturing and FT synthesis as described in section 2.3. Applications to actual gas fields were evaluated. FS was studied with regard to cooperative FS with Pertamina in Indonesia which was promoted at the same time. The economics of development to a commercial plant were also verified. The following will describe in detail the area under control by Nippon Steel.

3.2.1 FT synthesis catalyst development, and testing evaluations

Nippon Steel Corporation optimized the properties of a silica-type carrier and cobalt holding method for the FT synthesis catalyst, and evaluated them in a laboratory to test at the pilot plant. In the development, the technologies of 1) Metal structure control; 2) Ceramic (carrier) control; and 3) Analysis and control of the boundary, were applied. By optimizing the structural controls, it was possible to link highly active, and strong catalysts to the development.

(1) Catalyst performance

Developmental targets for the catalysts were set at CO conversion rates (%), C5 + selection rates (%), and chain growth probability α(–). A variety of prototypes were made to develop a high performance catalyst that would satisfy these targets and realize high productivity (C5 + g/kg-cat·h)Laboratory evaluations followed, then evaluations on employing catalysts selected through screening on the pilot prototype catalysts.

(2) Pilot plant FT synthesis reactor

The pilot plant FT synthesis reactor is a slurry-bed type. **Fig. 3** shows the flow in the FT reactor at the pilot prototype.

The raw material of syngas is supplied from the spersier on the bottom of the reactor as air bubbles. It passes through the slurry composed of catalyst and catalyst oil and reacts in suspended state. The FT synthesis reaction generates heat so it is important for the reaction temperature to be efficiently controlled. For that reason, the heat removal tube inside the reactor is a heat exchanger type. As a cooling agent, BFW (or Boiler Feed Water) is supplied. Thus, steam is let off because of the exchange of heat. The heavy reaction generated product and catalyst exist in a slurry form in this slurry bed type reactor, so these elements must be separated. To that end, a sediment separation vessel is established outside of the reactor to separate these elements using the different gravity between the catalyst and the reaction generated product. Separated catalyst is returned

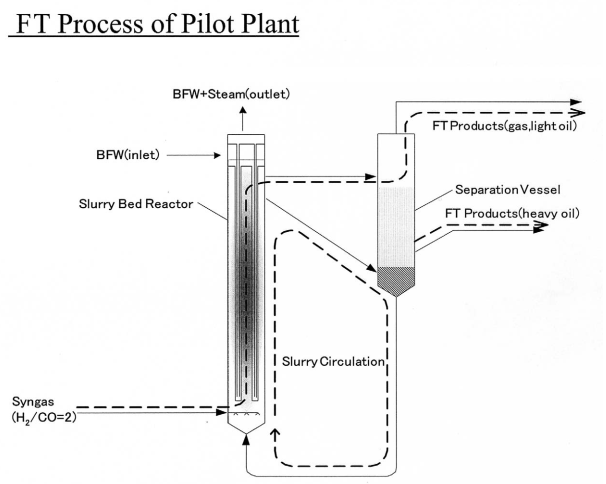

Fig. 3 Flow sheet of FT reactor

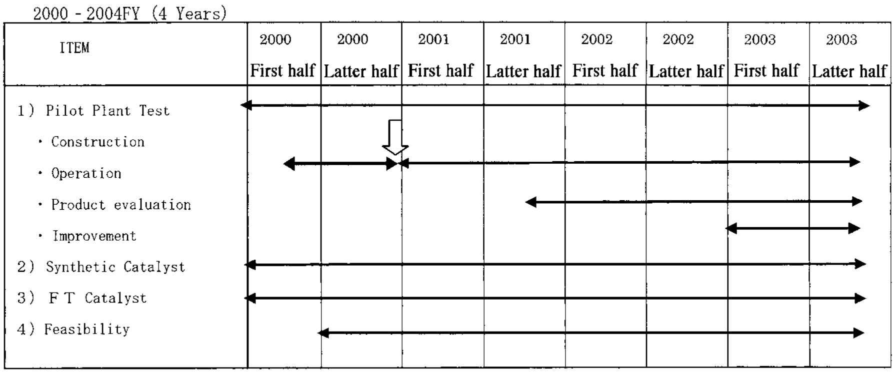

Fig. 2 JOGMEC GTL R&D schedule

to the reactor bottom. As a catalyst applied to a slurry bed, not only the development of a catalyst that exhibits such performance, but also the development of one that is unaffected by mechanical damage in the circulation of the slurry and that has high durability was pursued.

(3) Pilot test results

Table 2 summarizes the general results of performance verified in the pilot test. The target values for the development at the Yufutsu pilot plant were set to CO conversion rate at one pass, C5 + selection rate, and chain growth probability α. Evaluation was conducted by adjusting the temperature and W/F (g·h/mol) conditions.

Evaluations were conducted with the low W/F conditions, holding down the amount of catalyst filled. The test is outlined in line 1 of the Table. While these conditions make it difficult to achieve performance targets, the results verified that each of the targets for CO conversion rates, C5 + selection rates and chain growth probability α surpassed their targets. Also, it was verified that C5 + productivity (C5 + g/kg-cat·h) resulted in higher values exceeding conventional technical levels, as disclosed in research reports and patents, when these conditions were applied.

In the tests of line 2 of the table, the temperatures were lowered with the same amount of catalyst as disclosed in Table 1. The amount of syngas infused was reduced to evaluate using high W/F conditions. Under these conditions, it was verified that each of the target values (CO conversion rates, C5 + selection rates and chain growth probability α) were even more easily cleared.

Line 3 shows the evaluations wherein catalyst amounts were increased. Data was taken under high W/F conditions. The data disclosed in lines 1 and 2 verify that development targets have been cleared. Under these conditions, the pilot plant was run to verify its maximum productivity of GTL oils. In the tests, it was possible to record values that exceed 7BPD of the nominal rating of the design capacity. Total operating hours reached approximately 1,500 hours in the tests.

(4) FT synthesis catalyst performance stability

It is extremely important to develop catalysts that enable stable performance under these operating conditions in order to apply catalysts in a slurry bed reaction process for commercialization. Oxidation of active metal that causes moisture to form (increased according to the increase in CO conversion rates) by the reaction is assumed. Oxidation is thought to be a cause of decreased catalyst action in the slurry bed. This is handled by considering the scope of attaining appropriate CO conversion rates by adjusting the reaction conditions. The rate of the minute decrease caused by these conditions was evaluated in an appropriate manner. Damage to and powdering of catalyst grains caused by their mutual collisions in the reaction at the slurry bed run in a flow region having large synthetic gas superficial velocity are assumed. This was handled by adjusting the catalyst using spherical silica type carriers having high moisture resistance and high strength.

3.2.2 Research of the process

An objective of the research of the processes was to establish a scaled-up design technology for that slurry bed reactor. To that end, simulator introductions were studied for the arrangement of the development inside the slurry bed reactor and the reactor design. That was evaluated, then the accuracy was verified, and the linking method was studied to compare with the data from the pilot tests.

(1)Arrangement of internal development of the slurry bed which affects performance

Three elements can be considered to affect the performance of the slurry bed reactor. They are: 1. The characteristics of the reaction of the catalyst itself; 2. The macro-physical movement speed such as the fluid mixing inside the reactor; and 3. The boundary film physical movement (micro-physical movement speed) in the air bubbles and catalyst boundary.

In the laboratory tests, it is important to have a quantitative grasp of the affects of the aforementioned causes that accompany a scaled-up version when designing a larger-scaled apparatus based on the data attained using the pilot tests. In a comparison of the pilot plant and commercial plant, it can be conceived that 1) in a commercial plant, the catalyst and reaction conditions (temperature, pressure, and crude gas composition), the gas superficial velocity, and the diameter and pitch of the heat removal pipes are the same. Thus, among the causes of 1. to 3. above, the actual plant would have the same conditions as 1 to 3 in the micro-scaled version, and that it should be possible to predict using the conventional testing method. 2) It is thought that the causes in 2. relating to scale will be different on the actual plant, in relation to the increased diameter of the reactor along with the increase in scale.

Predicting these affects is not easy because of the complex flow of gas liquid solid multiple phase flow. Also, because there are few equations for predicting the affect of these causes, the important points in designing a commercial scale FT reactor must be considered. 1) Establishing internal fluid dynamics analysis technologies for the reactor using CFD (Computational Fluid Dynamics) which can simulate the changes that occur with the increased scale of the macro-physical movement speed of the mixing of fluids inside the reaction tower. 2) Combine with the developed reaction model based on the

Table 2 Operation results of Yufutsu pilot plant

	Temp. (°C)	Press. (MPaG)	W/F (g·h/mol)	CO conv. (%)	C5 + sel. (%)	α	Productivity (g/kg-cat·h)	BPD (bbl/day)
Target			-	≥ 60	≥ 85	≥ 0.9	-	-
1	240	2.2	1.8	62.3 (60.0)	85.2 (82.6)	0.91	1325 (1243)	5.0 (4.6)
2	230	2.2	4.5	75.3 (75.6)	88.7 (88.0)	0.91	689 (668)	2.6 (2.5)
3	234 - 239	2.4	4.2	87.5	79.5	0.92	761	7.2

( ) : Lab. date at same condition

pilot actual test results, and develop a process simulation for designing that enables evaluation of commercial scale FT reactor performance.

(2) Study of the simulation model

An efficient and reliable method was developed by combining the two simulation tools below, in view of the discussion above. **Fig. 4** summarizes the basic philosophy.

1) FT reactor design tools

A study was undertaken on the simulator that combined an FT composite reaction model based on the results of the Yufutsu pilot plant tests, to the tank model that uses conventional design means. There are many calculations that do not require heavy calculations to handle this, but a precise correlating equation for the fluid parameters (gas hold up, levels) is required. To compliment that, high precision was attempted using fluid dynamic analyses tools using the following CFD.

2) Process fluid dynamics development analysis tools (CFD)

CFD technology was applied to analyze the state of the air bubbles' fluid dynamics inside the reactor. The tools above were used to estimate the fluid dynamic parameters necessary in a commercial scale. There is little available in CFD for air bubble fluidity so we are still at the development stage. Therefore, the technical infrastructure of Nippon Steel Corporation will be applied to advance precision verification using demonstration tests in the future. The flow of precision verification of the model and the linking of that and CFD are discussed below.

1. Fluid dynamic simulation using CFD: A precision verification of a calculation method using a comparison to cold model testing results
2. Using simulations that reflect physical properties at the time of the actual reaction, using these methods whose precision is verified
3. Comparing with actual operational data (Yufutsu pilot plant test results) to verify the model during reaction, and to improve prevision through corrections
4. A process fluid dynamic analysis tool that has improved precision calculates fluid dynamic parameters in FT reactor design tools
5. In the reaction model, reaction speed analyses were conducted based on the results of the laboratory test conducted under wide testing conditions. This was applied on the Yufutsu pilot plant test results to build the reaction model.
6. Simulation calculations were made for combining the aforementioned fluid dynamic parameters and reaction models to the tank model, and then increasing the scale of the reactor.
7. The results of the calculations were verified and corrected in light of the Yufutsu pilot plant test results.

Using the reaction model parameters attained through the process fluid dynamic development analysis tool (CFD), and those attained from the fluid dynamic parameter and laboratory tests, and the Yufutsu pilot plant tests, results for reproduction calculations of CO conversion rates in the Yufutsu pilot plan. An example of these

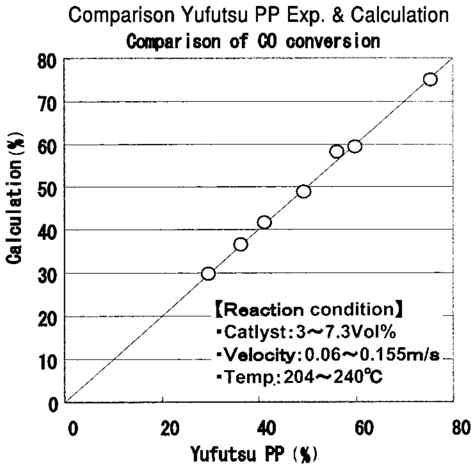

Fig. 5 Verification results of simulation

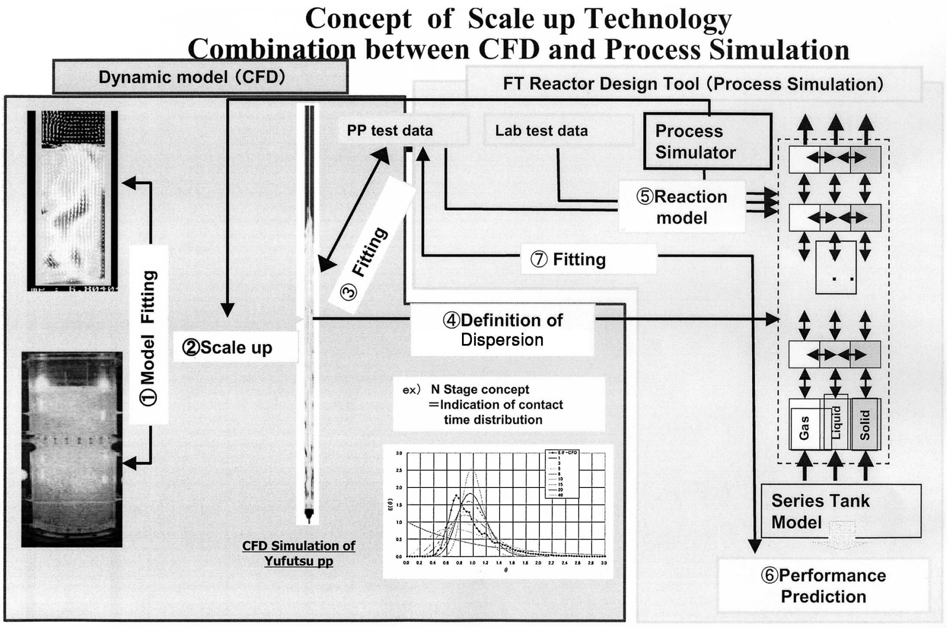

Fig. 4 Concept of scale up simulation technology

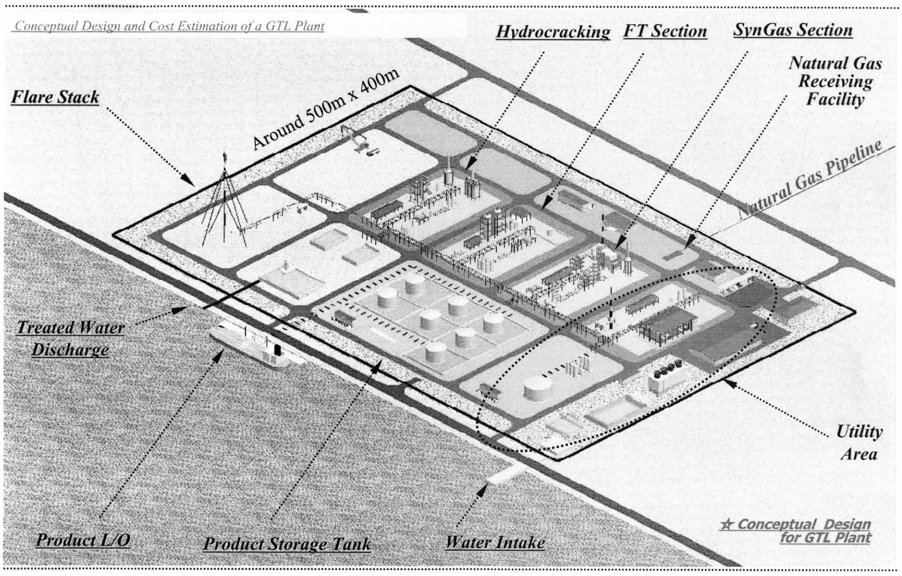

Fig. 6 Commercial GTL plant

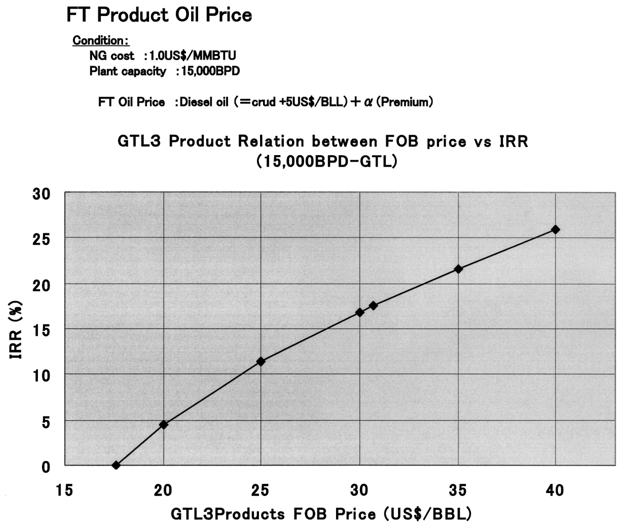

Fig. 7 Feasibility study result of GTL

is summarized in **Fig. 5**. These design tools reproduced highly precise CO conversion rates with wide reaction conditions, and evaluated that the FT reactor design tools are of an applicable level.

3.2.3 Economic evaluation (pertamina FS)

A commercial prototype plant was designed in view of Southeast Asia, based on the data attained in the development stage (see the facility of the plant in **Fig. 6**). Under calculations of the JOGMEC-GTL process based on crude natural gas conditions of actual gas fields in Southeast Asia, a plant of the scale of 15,000 bbl/day can produce approximately 440,000 Nm^3/h of syngas from approximately 200,000 Nm^3/h of crude natural gas (H_2 and CO (H_2/CO = 2.0). This syngas can be converted to approximately 74 t/h of FT synthetic oil.

Based on that, calculations were done on FT oil prices, assuming a cost of $.1.00/MMBTU of natural gas (see **Fig. 7**). Adding the costs for refining and transport ($5 US/BBL) for the price of the FT oil, it should be compared to the environmental premium depending on products such as naphtha. The results of the study organized the average FOB price for three GTL products with a relationship to an estimated IRR. If the average prices is between 30 and 35 US$ per BBL, investment IRR can be expected to be around 20%. Also, because of the limitations on paper, this could be given up, but sensitive analyses were conducted on several important parameters, beginning with the cost of natural gas.

4. Conclusion

This reported on the concepts of GTL technical developments advanced under the JOGMEC framework, and reported on the results of developments made thus far. It is important to promote the development of technologies that have characteristics and superiority over overseas technologies, in the development of new energy technologies of the future. This GTL technical development should be advanced as a national project with links to the main players of each industry and country from the viewpoint of measures for the degree of further dependence on Middle Eastern oil, the atmospheric environment that is linked to the diffusion of diesel vehicles and to measures against carbon dioxide issues. Currently, progress is being made toward the next step of commercialization, in view of the results of the developments at the Yufutsu pilot plan. Efforts will be made toward the development of technologies related to fossil fuels and natural gas and technologies that have competitive power until presently we have followed in the footsteps of technologies from overseas.