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Abstract

Recent direction dealing with climate change has changed more to focus on carbon utilization rather than the direct carbon capture and storage. Conceptually converting CO$_2$ to sellable chemicals or fuels should be more benign to environment by substituting the fossil raw materials like oil, natural gas, or coal. Instead of converting CO$_2$ fully to valuable chemicals or fuels, it is much easier to employ a portion of CO$_2$ with existing raw materials in many natural gas conversion processes. Dimethyl ether (DME) and gas-to-liquids (GTL) are most prominent processes that can be modified to accommodate CO$_2$ as a reacting raw material. There are already several successful technology developments in using CO$_2$-rich natural gas for DME and liquid fuels, although they are not yet fully reached the commercialized level. This chapter highlights recent developments in utilizing CO$_2$-containing natural gas and landfill gas to yield valuable chemicals and fuels like diesel or DME.

Keywords: CO$_2$, chemicals, fuel, DME, GTL

1. Introduction

Carbon dioxide (CO$_2$) is widely used in process industries as its own form or feedstock for the production of bulk chemicals including methanol, dimethyl ether (DME), synthetic fuel, etc. Although chemical activity of CO$_2$ is low, CO$_2$ can be activated enough for chemical reactions with the presence of suitable catalysts and the appropriate operating conditions. The most of reactions involving CO$_2$ as reactants, except CO$_2$ insertion reactions, are based on reductions in which hydrogen or electrons are added. Cost-effectiveness of industrial manufacturing using CO$_2$ is heavily dependent on energy consumption required for the reaction, and hence it is very important to provide energy required for CO$_2$ conversion in a most economic and
effective manner. Various options for improving economics of reactions using CO₂ are possible, for example, reducing inherent energy requirement for the reaction from the development of new catalysts, saving energy cost through strategic utilization of renewable energy sources, etc. Another important aspect in the utilization of CO₂ from the viewpoint of carbon capture sequestration and utilization (CCSU) is provision of co-reactants for CO₂ utilization because of huge quantity of CO₂ available.

Methanol is the key feedstock for C¹ chemistry as it is used for producing formaldehyde, acetic acid, chloromethane, and other chemicals for chemical industries. Attention has been paid recently to methanol as a clean synthetic fuel because it can be converted to hydrogen-rich gas via the steam reforming which can be utilized in the fuel cell systems for generating electricity.

A breakthrough in the synthesis of methanol was made from the observation as methanol can be favorably synthesized at the presence of CO₂. The main reactions during hydrogenation of CO₂ are as follows:

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O}
\end{align*}
\]

The first reaction is a direct synthesis of methanol from CO₂, while the second reaction is reverse water gas shift one. These two reversible reactions are both exothermic. It should be noted that the cost of such CO₂ hydrogenation reaction is higher than that of reaction based on CO and CO₂ mixture. However, the CO₂ hydrogenation for methanol synthesis provides opportunity for utilizing CO₂ gases, which are often wasted in process industries.

Industrial catalysts for methanol synthesis are available for gases containing H₂ and CO, which normally come with small quantity of CO₂ presented. Therefore, it is required to develop a new catalyst for methanol synthesis that can deal with CO₂-rich feed.

A colorless, nontoxic, and environmentally benign DME is widely used as a solvent and propellant in aerosol products, of which physical properties are close to those of liquefied petroleum gas (LPG). As considerably fewer pollutants are generated from the combustion of DME compared to that of conventional diesel fuel, DME is regarded as a sustainable substitute for diesel fuel. DME has a structure of CH₃-O-CH₃ including oxygen between two CH₃s and thus can work as a clean fuel. DME can be produced from a wide range of feedstocks, including natural gas, coal, biomass, and waste plastics. Another benefit for DME is that DME can be the alternative to conventional diesel fuels and LPG because high cetane number can be achieved from DME and physical properties of DME is close to that of LPG. Furthermore, existing infrastructure for transportation and storage of conventional fuels can be readily adopted for DME once it is introduced to the market.

Ammonia (NH₃) and carbon dioxide (CO₂) produced from ammonia plant react as below and the urea and water are produced.

\[
2\text{NH}_3 + \text{CO}_2 \rightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}
\]

The intermediate products such as carbamate, non-reacted ammonia and CO₂ are separated and recycled as raw materials. The water generated as byproduct is removed during the process of condensing urea.
2. DME manufacturing using CO₂

DME is an ultra-clean burning alternative to LPG and diesel. It is easy to liquefy, making it a convenient fuel to transport and store. These properties make DME a versatile and promising solution in the worldwide consideration of clean and low-carbon fuels. And DME can be produced from various feedstocks like natural gas, Coal Bed Methane (CBM), shale gas, biomass, coal, and CO₂.

In 2000, Korea Gas Co. (KOGAS) embarked the development of proprietary catalyst and process development with the ultimate goal of producing DME on a commercial scale. Central to the KOGAS DME technology is the one-step DME synthesis from synthesis gas compared to the conventional two-step process including methanol synthesis. Conceptually, the one-step technology offers a possibility to produce DME with a lower capital and production cost.

The KOGAS technology has progressed considerably toward commercialization. The technology has been undergoing extensive testing since 2008 in the 3000 metric tons/year demonstration plant at the KOGAS R&D Center in Incheon, Korea [1]. In 2011, KOGAS completed the Basic Engineering Package (BEP) of 300,000 metric tons/year. In parallel, the Korean Government had initiated market test studies in distributing DME to local end-users.

2.1. DME market (case study in Korea)

The demand and supply dynamics for DME in Korea are analyzed based on potential usage of DME in Korea. There are three market sectors in Korea where DME can be potentially used [2]:

- LPG replacement for domestic and transportation usage by diluting LPG with DME.
- Bunker-C oil replacement for district heating with industrial boilers.
- Diesel fuel replacement for diesel-fueled vehicles.

DME can be blended up to 20–30% with LPG [3]. The LPG replacement for domestic usage is estimated with the assumption that DME will replace 20% of LPG usage. Based on this analysis, it is expected that DME demand will decrease from 254 kilotons in 2013 to 163 kilotons in 2021. This is because LPG demand for domestic usage has been decreasing due to the introduction of more economical LNG for domestic use. It is projected that this trend will continue.

On the other hand, the demand of DME for transportation for LPG fueled vehicles is expected to increase from 265 kilotons in 2013 to 360 kilotons in 2021, when LPG is replaced with a 5-mol% DME/LPG mixture. When LPG-DME blended fuel is used, additional distribution and end-use infrastructures are not required. Thus, it is possible to establish a market for DME in a very short time. KOGAS also successfully carried out field tests for DME-LPG blends.

The potential demand for DME in replacing diesel for diesel vehicles is expected to increase from 105 to 1046 kilotons in 2021. This is because the diesel engine–based vehicles have been steadily increasing, and DME can provide advantages over diesel in terms of air pollution. Particulate matter and NOx have been two of the major problems of diesel engines despite their higher energy efficiency.
DME may also command a price premium with respect to diesel due to its cleaner burning properties. The emission requirements for diesel vehicles are getting tighter in many countries, and the use of DME will help vehicle manufacturers and end-users comply with the tighter regulations.

Diesel substitute and fuel for power generation could be a big market for DME in the future. Natural gas is a good fuel for power generation, but DME is comparable to natural gas in performance as a fuel for power generation. This has been approved by gas turbine manufacturers, and DME can be an efficient alternative fuel for medium-sized power plants, especially for remote or isolated locations where it is difficult to transport natural gas.

2.2. DME production technology

The KOGAS process represents the newest generation of DME production technology. At the most conceptual level, its distinguishing feature is that DME is synthesized directly from synthesis gas and hence called a “direct” or “one-step” process. By contrast, the conventional process is called the “indirect” or “two-step” process because DME is produced from an intermediate product, methanol. The Toyo process was used as a representative indirect process to compare to KOGAS DME as Toyo’s process is the most established conventional two-step DME technology.

Key technical comparisons between the KOGAS DME and Toyo processes are summarized in Table 1. KOGAS DME represents the first commercial-scale (demonstration) plant for KOGAS’ process, whereas Toyo’s process has several commercial-scale plants in operation. Based on demonstration plant data, KOGAS DME process was shown to be competitive to Toyo in terms of catalyst longevity, operations reliability, and similar number of equipment, which is an indicator of fixed capital costs. A fundamental advantage of the KOGAS DME process is that it needs just one reactor section to convert syngas to DME, whereas Toyo requires two sections. Another advantage is KOGAS’ proprietary catalyst, which can utilize high CO₂ content in the reformer feed, allowing it to handle a more diverse and economic source of feed gas. The estimation of energy efficiency for KOGAS process is comparable to that of the Toyo.

<table>
<thead>
<tr>
<th></th>
<th>KOGAS DME process</th>
<th>Toyo process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process development stage</td>
<td>10 metric tons/day DME production plant</td>
<td>30 metric tons/day DME production plant</td>
</tr>
<tr>
<td></td>
<td>Demonstration plant</td>
<td>340 metric tons/day commercial scale</td>
</tr>
<tr>
<td>Catalyst life expectancy</td>
<td>Tri-reformer: 1 year</td>
<td>ISOP reforming: 3 years</td>
</tr>
<tr>
<td></td>
<td>DME reactor: 1 year</td>
<td>Methanol conversion: N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methanol dehydration: N/A</td>
</tr>
<tr>
<td>Number of reaction steps</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Tolerance for high CO₂ in NG feed</td>
<td>Can use natural gas with as much as 30-mol% CO₂</td>
<td>Not known</td>
</tr>
<tr>
<td>Total number of major equipment</td>
<td>80 plus ASU</td>
<td>90 plus ASU</td>
</tr>
<tr>
<td>Process energy efficiency</td>
<td>60%</td>
<td>55%</td>
</tr>
</tbody>
</table>

Table 1. Comparison of KOGAS DME process and Toyo process.
2.3. Description of KOGAS DME process

A schematic process flow diagram (PFD) of KOGAS’ commercial scale DME plant is shown in Figure 1.

The four major sections of the KOGAS DME process and their functions are as follows:

(1) Reforming section

Synthesis gas, a mixture of H$_2$ and CO, is produced from natural gas, steam, O$_2$, and CO$_2$ using tri-reformer, an adiabatic auto-thermal reformer based on KOGAS’ proprietary catalyst, KDN-1. This KOGAS proprietary catalyst involves pre-coating Ce-ZrO$_2$ onto a commercially available Al$_2$O$_3$ substrate before impregnating with Ni.

The tri-reformer consists of a homogeneous section and a fixed-bed catalyst section, in which the pre-reformed natural gas (mainly methane) is reacted with steam, oxygen and carbon dioxide for producing synthesis gas. Maintaining right amounts and ratio of carbon monoxide and hydrogen for the reaction is important. Auto-thermal nature in the reaction compensates heating requirement for reforming reactions with exothermic combustion reactions. The resulting temperature for the exit stream from the tri-reformer is around 1080°C, and the pressure is 3.1 MPa.

The global reactions taking place in the tri-reformer can be summarized as

\[
\text{CH}_4 + \text{O}_2 + \text{CO}_2 \rightarrow 3 \text{H}_2 + 3\text{CO} + \text{H}_2\text{O} + \text{Heat} \quad (4)
\]
\[
2 \text{CH}_4 + \frac{5}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 5 \text{H}_2 + 2\text{CO} \quad (5)
\]

The composition of the product syngas (in particular the H$_2$:CO ratio) is a function of the three key molar feed ratios: steam, oxygen, and CO$_2$.

Figure 2 shows the tri-reformer reforming reactor and KDN-1 catalyst for reforming process. Compared to other traditional reforming catalysts, the KDN-1 catalyst provides better conversion of CH$_4$ and CO$_2$ both initially and over time. The KDN-1 enables the production of
syngas with the desired H₂ to CO ratio for optimum performance in the DME synthesis for a wide range of compositions in the natural gas feedstock, including high CO₂ content.

(2) Syngas treatment section

The raw syngas produced by KOGAS’ tri-reformer has a carbon dioxide content of around 15 mol%. This CO₂ content must be reduced to around 1.3 mol% to meet the 4 mol% requirements of KOGAS’ DME reactor feed. KOGAS BEP design uses a UOP SELEXOL absorption column to remove CO₂ from the raw syngas down to the desired level.

(3) DME synthesis section

The H₂ and CO in the syngas are catalytically reacted to produce DME, and a small amount of methanol and water in a single-step DME reactor goes through the synthesis according to the following set of global reactions:

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 &\rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO} + \text{H}_2\text{O} &\rightarrow \text{CO}_2 + \text{H}_2 \\
2\text{CH}_3\text{OH} &\rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}
\end{align*}
\]

Figure 3 shows the DME synthesis reactor and KD-540-27 catalyst for DME synthesis. This proprietary reactor consists of a multiple tubular reactor configuration filled with KD-540-27, a hybrid bifunctional catalyst consisting of Cu/ZnO, which is catalyzing methanol synthesis and γ-Al₂O₃ catalyzing methanol dehydrogenation to DME.

In overall, heat removal is made via a cooling jacket for the vertical tubes containing the catalyst with which the temperature of reacting gas is maintained at 260°C.

(4) DME separation & purification section

The stream leaving the DME reactors will contain unreacted syngas, which needs to be separated from the condensable DME, methanol, and water. There is also a significant amount of
CO₂ present. The unreacted syngas needs to be recompressed and recycled to the DME reactor feed, and most of the CO₂ needs to be removed.

Figure 4 shows the KOGAS’s 3000-metric tons/year demonstration plant. The KOGAS DME commercial design calls for the exit stream from the DME reactor to be cooled in stages: first with heat recovery against boiler feed water, process condensate, cooling water, chilled condensate, and finally refrigeration to −68°C. The condensing methanol is expected to be sufficient to remove most of the CO₂ in a single step. Therefore, no CO₂ absorption column is required. The DME/methanol/water/CO₂ condensate is sent to a CO₂ stripping column with three sections of packing equivalent to 30 theoretical stages that operates at 4.68 MPa. The stripped CO₂ from the DME exit stream is combined with the CO₂ removed from the raw syngas and sent back to the tri-reformer inlet.

Figure 4. KOGAS’ 3000 metric tons/year demonstration plant.
3. Fertilizer (ammonia/urea) manufacturing using CO$_2$

Manufacturing fertilizers (ammonia/urea) is one of the ways of increasing added value of the natural gas and CO$_2$. The fertilizers in modern society are inevitable for enhancing agricultural productivity. The main elements used for plant growth are nitrogen, phosphorus, potash, and sulfur. Among them, the nitrogen is the most consumed fertilizer and is easily produced by using nitrogenous in air and natural gas. Phosphorus and potash are provided from minerals, and sulfur is produced as byproducts in refineries and gas plant. Ammonia containing nitrogen is a toxic gas at room temperature and cannot be used directly as fertilizer. Therefore, ammonia should be converted into other chemicals such as urea, diammonium phosphate (DAP) and ammonium nitrate, which are suitable for plant applications. Urea is produced by combining ammonia and carbon dioxide generated from production of ammonia. It is a solid, and it can be granule or prill form. The 80% of ammonia used worldwide as fertilizer is converted into urea. The present chapter deals with manufacturing and selling the urea in granule form by producing ammonia with natural gas.

3.1. Production process and characteristics of facilities

The production process consists of following facilities, and its overall block diagram is represented in Figure 5.

- Ammonia plant
- Urea plant
- Granulation unit
- Warehouse
- Utilities & offsite

![Figure 5. Block diagram of ammonia/urea plant.](image-url)
3.2. Ammonia plant

Figure 5 shows the block diagram of ammonia/urea plant. This plant manufactures ammonia by use of natural gas and air. The ammonia and carbon dioxide (CO$_2$) generated as byproduct are used as raw materials for manufacturing urea. For enhancing operational flexibility and the possibility of direct sale of ammonia to customers, the ammonia storage tank is required. Block diagram of ammonia plant is shown in Figure 6.

![Block diagram of ammonia plant](image)

The existence of sulfur substances in gas reduces the activity of catalyst. For this prevention, the sulfur substances shall be removed from the gas. And then the produced gas is supplied to reformer. The synthetic gas is generated in passing through various reaction steps of the reformer. In reaction steps, the air is supplied for providing nitrogen needed in producing ammonia. After these reactions, the main substances of hydrogen (H$_2$), carbon dioxide (CO$_2$), and nitrogen (N$_2$) are produced.

The produced CO$_2$ is separated by using amine in CO$_2$ removal unit and then sent to urea plant. The CO$_2$ and CO that are not eliminated in the CO$_2$ removal unit are removed in methanation unit. N$_2$ and H$_2$ are reacted in ammonia reactor, and then the ammonia (NH$_3$) is finally produced.

3.3. Urea plant

Ammonia (NH$_3$) and carbon dioxide (CO$_2$) produced from ammonia plant reacts as below, and the urea and water are produced.

$$2 \text{NH}_3 + \text{CO}_2 = \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$$ (9)

The intermediate products such as carbamate, nonreacted ammonia, and CO$_2$ are separated and recycled as raw materials. The water generated as byproduct is removed during the step of condensing urea. Figure 7 shows the block diagram of urea plant.

![Block diagram of urea plant](image)

The produced urea liquid in high temperature is solidified by cooling. The urea is solid state in atmospheric conditions, and it can be a form of prill or granule. The size of prill is smaller than granule. The investment cost for granulation processing is higher than that of prilling, but the granulated urea is more suitable as fertilizer. The granulated urea is packed in various sizes of bags for storage in warehouse.

For the operation of above plants, the following utility & offsite facilities are required:

- Water treatment including demineralization unit
- Cooling water system
- Boiler system
- Wastewater treatment system
- IA/PA
- Nitrogen
- Flare system
- Warehouse for Urea
- Ammonia storage tank

4. Gas-to-liquid using CO₂

4.1. What is GTL?

Gas-to-liquid (GTL) is the processing of converting natural gas to synthetic oil. This synthetic oil will be the fuel or the product based on hydrocarbon. Liquefied Natural Gas (LNG: for city gas and bunkering fuel), Pipeline Natural Gas (PNG: for city gas), and Compressed Natural Gas (CNG: for vehicles) are classified by their respective transportation technology, but GTL in liquid state at room temperature is the long-chain hydrocarbon products identified by transformation technology of chemical conversion. Figure 8 shows the transformation technology of GTL production.

Coal, natural gas, and biomass are used as raw materials in Fischer-Tropsch (FT) process while the meaning of GTL is based on conversion of natural gas to pure synthetic oil in removing
impurities such as sulfur, aromatic compounds, and metal substances. By refining this synthetic oil, it can produce diesel, naphtha, wax, and other liquid compounds based oil or other special products. This transformation technology is based on FT process, which was developed ca. 100 years ago. Technology of pre-treatment of gas, reforming, and upgrading process is in the mature stage, but FT process has been in the stage of commercialization. New technology is continuously developed, and the already developed technology is applied to conversion process for enhancing efficiency. Also mini GTL technology to be applied to small-scaled gas fields is being developed. The factors influencing on competitiveness are enumerated as investment cost, operation cost, materials price, plant dimension, and technology enhancing usability of products.

In comparing with history of coal-to-liquid (CTL) process, GTL is relatively a new technology and globally commercialized facilities are actually very rare. Table 2 shows the global GTL project status (see Figure 9).

Even when a plant in Nigeria is completed, total production capacity of GTL is only 260,000 barrels per day. On the contrary, daily consumed oil in the world is 87 million barrels. Thus, GTL production is not subject to restriction of consumption.

<table>
<thead>
<tr>
<th>Project</th>
<th>Country</th>
<th>Scale (bbl/day)</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell Bintulu GTL</td>
<td>Malaysia</td>
<td>14,700</td>
<td>1993</td>
</tr>
<tr>
<td>PetroSA Mossgas GTL</td>
<td>South Africa</td>
<td>36,000</td>
<td>1993</td>
</tr>
<tr>
<td>Sasol/QP ORYX GTL</td>
<td>Qatar</td>
<td>34,000</td>
<td>2007</td>
</tr>
<tr>
<td>Shell Pearl GTL</td>
<td>Qatar</td>
<td>140,000</td>
<td>2011</td>
</tr>
<tr>
<td>Chevron Escravos GTL</td>
<td>Nigeria</td>
<td>34,000</td>
<td>2013</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>258,700</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Worldwide GTL project status.
4.2. Production processing and facility features

GTL Process is composed of next four main steps.

4.2.1. Step 1: gas pre-treatment (gas clean-up)

The gas pre-treatment in GTL process is generally to dehydrate and remove sulfur compounds, mercury, and hydrocarbon C3+. It is similar to the requirements of LNG process, but it needs no stage of removal of CO₂.

4.2.2. Step 2: synthesis gas generation

The production of synthetic gas covers the conversion into CO and H₂ mixture by autothermal reforming (ATR) and steam carbon dioxide reforming (SCR). The oxygen needed in ATR is supplied by air or pure oxygen. When using the air, there are some advantages by eliminating the cost of air separation unit (ASU) and electricity cost but finally become obstacles to process due to large volume of nitrogen. By using reformed steam methane, we supply necessary oxygen. However, this method has disadvantage of producing synthetic gas of H₂ to CO ratio by 4:1 against the required H₂ to CO ratio by 2:1.

SCR reformer has a homogeneous section and a fixed-bed catalyst section and reacts the pre-reformed natural gas (primarily methane), steam, and carbon dioxide to produce synthesis gas containing the correct amount and ratio of carbon monoxide and hydrogen. The SCR reformer uses exothermic combustion reactions to off-set the endothermic reforming reactions. The resulting exit temperature is around 870°C, and the pressure is 2.5 MPa. The composition of the product syngas (in particular the H₂:CO ratio) is a function of the three key molar feed ratios previously described (steam, oxygen and CO₂). The ratio of hydrogen to carbon monoxide in the SCR outlet is currently targeted to be 2.0 to provide the correct H₂:CO ratio in the mixed feed into the FT synthesis reactor. The advantage of SCR process is to enable the development of low-quality natural gas fields containing CO₂ or reuses efficiently CO₂ emitted from various processes (CO₂ removal and FT process, etc.). Figure 10 shows the simplistic integrated GT schematic process.
4.2.3. Step 3: FT synthesis and refining

FT synthesis is to convert synthetic gas into long-chain hydrocarbons. This conversion is made by catalyst. As for catalyst, cobalt is generally applied. For extracting substances for shipping as final products, fractional distillation is required.

4.3. Mini GTL

For successful mini GTL technology, it is required to develop compact and high-efficient GTL process and modularization techniques for being competitive even as small scaled. It will be efficient technology to be applied to small and medium gas field, associated gas of oilfield, and landfill gas on land and at sea. Figure 11 shows the example of roadmap toward modular GTL plant.

GTL technology for developing small and medium gas field and associated gas requires following conditions: (1) minimization of plant construction cost for economic feasibility as small-scaled hundreds to thousands barrels/day, (2) compact and mobility for installation in places without infra such as frozen zone of Siberia, (3) easy installation in limited space for application to offshore, and (4) compactification and modularization of compressor and related equipments for simple process and high efficiency.

Further study is to be progressed for small and medium gas fields that are expected to have potential application by mini GTL technology. From long-term point of view, the development of gas-to-liquids-floating production storage and offloading (GTL-FPSO) linked to shipbuilding technology will be applied to small and medium-scaled offshore gas fields as well as the strategy of launching high value-added shipbuilding market is to be established.

Figure 10. Simplistic integrated GTL schematic.
The micro reactor (synthetic gas + FT synthesis) was developed by CompactGTL Ltd., a manufacturer leading compact GTL technology, and its pilot operation was completed by applying to 20-barrels/day plant with Petrobras in 2011 [4–6]. Figure 12 shows the example of compact GTL roadmap toward modular GTL plant.

Figure 11. Example of roadmap toward modular GTL plant (source: S.A. Petrobras).

Figure 12. Example of compact GTL roadmap toward modular GTL plant (source: Compact GTL Limited).
Also by adopting micro channel technology, Velocys is developing mini GTL plants and reported that a pilot plant of 2.5 gallon per day has been developed. They constructed 6 BPD plant in Brazil under cooperation with Petrobras, MODEC and Toyo Engineering and plan the pilot operation in 2012.

Since micro reaction technology had advantages in its small volume, high heat transmission, and large reactive surface and control of exact reaction time, it will enhance high integration of chemical process, response selectivity, and stability.

5. Summary

The conversion of CO₂ to chemicals and energy products that is currently produced from fossil fuels is also promising due to the high potential market and promising benefits. Methanol is the key feedstock for C1 chemistry, as it is used for producing formaldehyde, acetic acid, chloromethane, and other chemicals for chemical industries. Also, industrial catalysts for methanol synthesis are available for gas containing H₂ and CO, which is applied with small quantity of CO₂ presented.

The utilization of CO₂ to produce chemicals like urea and cyclic carbonates is promising and can be a solution to reduce CO₂ emission. However, CO₂ still has certain disadvantages as a chemical reactant due to its inert, non-reactive, and low Gibbs free energy properties. DME is versatile and promising solution in the worldwide consideration of clean and low-carbon fuels. It has potential to solve forward problem of certain disadvantages as chemical reactant. Similar application of reaction schemes using CO₂ as applied to DME manufacturing is also possible in GTL fields, especially for low-value gas fields involving high CO₂ contents and for landfill gas fields.

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