PRODUCTION OF CHEMICALS/PETROCHEMICALS FROM NATURALGAS – A TECHNICAL STUDY

A Project Report submitted in partial fulfillment of the requirements for the Degree of
MASTER OF TECHNOLOGY
in
GAS ENGINEERING
(Academic Session 2003-05)

By

GANGAVELLI BHARATH KUMAR

Under the Supervision of

Dr.HIMMAT SINGH

COLLEGE OF ENGINEERING STUDIES
UNIVERSITY OF PETROLEUM & ENERGY STUDIES
DEHRADUN (U.A) 248007
May 2005

PRODUCTION OF CHEMICALS/PETROCHEMICALS FROM NATURALGAS – A TECHNICAL STUDY

A Project Report submitted in partial fulfillment of the requirements for
the Degree of
MASTER OF TECHNOLOGY
in
GAS ENGINEERING
(Academic Session 2003-05)

By
GANGAVELLI BHARATH KUMAR

Under the Supervision of

Dr.HIMMAT SINGH

COLLEGE OF ENGINEERING STUDIES
UNIVERSITY OF PETROLEUM & ENERGY STUDIES
DEHRADUN (U.A) 248007
May 2005

CERTIFICATE

This is to certify that the Project Report on *"Production of Chemicals/ Petrochemicals from Natural Gas – A Technical Study"* submitted to University of Petroleum & Energy Studies, Dehradun, by **Mr. Gangavelli Bharath Kumar**, in partial fulfillment of the requirement for the award of Degree of Master of Technology in Gas Engineering (Academic Session 2003-05) is a bonafide work carried out by him/her under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

Date: 24.8.2005

Dr.Himmat Singh

ACKNOWLEDGEMENT

I would like to express my most sincere gratitude to many people, notably among them are numerous scholars at UPES who have given guidance at various levels and gave me an opportunity to work with them. They provided me necessary impetus with all their zest, zeal and motivation and without their guidance, support and extremely helpful attitude; this project would not have seen the light of the day. They gave valuable suggestions to me and were considerate enough to share their knowledge and experience for the accomplishment of project work.

I express my deep sense of gratitude and indebtedness to my guide Dr.Himmat Singh, (Distinguished Professor, UPES) for his invaluable and efficient guidance.

I am highly grateful to Dr.B.P.Pandey (Dean, College of Engineering, UPES) for his kind cooperation during project.

GANGAVELLI BHARATH KUMAR

TABLE OF CONTENTS

Contents | Page No

Executive Summary

1. Introduction 1

2. Methanol 3

  2.1. Methanol applications and demand 4

  2.2 Basic Technology 7

  2.3 Synthesis gas generation 9

  2.4 Methanol synthesis 25

  2.5 Methanol Purification 28

3. Major technologies

  3.1 LURGI Mega-methanol technology 29

  3.2 SYNETIX Leading Concept Methanol (LCM) Process 49

4. Production of Olefins from Methanol 55

  4.1 LURGI MTP Technology 56

  4.2 UOP/HYDRO MTO Process 68

Conclusion 84

References

List of Tables

List of Figures

EXECUTIVE SUMMARY

It is a truism to observe that the world's hydrocarbon resources are not evenly distributed and in particular that a substantial proportion of known reserves are situated in locations remote from areas of high consumption. Transportation of liquid hydrocarbons from source to consumer is a task for which a large and flexible infrastructure exists. However, where natural gas deposits in remote locations are to be exploited, the transportation task becomes a major challenge - particularly if geography, economics or a combination of both precludes the possibility of a pipeline. This challenge can be met by conversion of natural gas into a transportable and saleable form or product.

The conversion of methane to olefins and other higher value products or derivatives which may be more cost effective to transport long distances from remote gas sources has therefore attracted renewed interest. Although a commercially viable process for the direct conversion of natural gas to olefins is not yet available, the production of methanol from natural gas is a well established technology and continues to advance in terms of thermal efficiency and production scale economy. The next step is the use of methanol as feedstock for the production of olefins which is one of the most promising new applications.

In all the processes where natural gas is converted to higher value chemicals/ petrochemicals, the first step is the production of synthesis gas (syngas), a mixture of carbon monoxide and hydrogen. Various processing routes exist for this syngas. Then the next step is the production of methanol from synthesis gas.

Syngas production is very capital intensive and accounts for over half of the total capital cost in most processes. There is much research and development underway to reduce the cost of syngas production. Methanol is the basic feed stock for production of several chemicals and petrochemicals. The next step is production of olefins from methanol using MTO technology.

The MTO process primarily converts the methanol into ethylene and propylene. Ethylene and propylene are in increasing demand worldwide and have significant financial value in the marketplace. MTO projects are driven by the desire to monetize stranded gas and the market demands for ethylene and propylene and their derivatives. Stranded natural gas prices are generally independent of crude oil and naphtha market prices so MTO provides another means for olefin derivative producers to diversify the cost structure for their feedstocks. MTO can provide much lower costs of production and higher returns on investment. Methanol to olefins process provides an economical means to convert natural gas to olefins.

This report presents the various processing routes available for production of syngas and methanol. Syngas production is very capital intensive and accounts for over half of the total capital cost in most processes. Selection of syngas production process from available process is very important. This report also presents the major technologies available for production of Methanol and Olefins from Methanol (MTO). The selection of process for a particular location depends on the economics of that process and marketability of the products from that process.

CHAPTER-1
INTRODUCTION

Creating value from natural Gas:

Natural gas is the cleanest energy source. The global reserves of natural gas are estimated at some 5.000 trillion cubic feet (141 trillion cubic meters) of which 3000 trillion cubic feet can be classified as stranded gas or at least gas without direct access to a marked. The reserves of natural gas are also much more geographically wide spread than for oil. The main natural gas resources are located in remote areas. Due to the difficult and expensive transport of gas, a considerable amount of gas is currently just flared wasting energy and money and polluting the environment. Conversion of natural gas to transportable liquid fuels and valuable chemicals is essential for economical natural gas usage.

There are four main categories for use of natural gas:

1. Conversion of natural gas to transportable liquid fuels and valuable chemicals
2. Re-injection into oil reservoirs to enhance liquid production
3. Direct use, e.g. for iron ore reduction, fermentation etc.
4. Local production of heat and power

Gas to Liquids (GTL, incl. methanol) technology has gained increased interest world-wide because it opens the way to capitalise stranded gas into products which fits the market demand and may also enable the development of oil fields with associated gas outside established infrastructure. New business opportunities will materialize, especially in the field of new transportation fuels. Methanol is shown to be an excellent fuel for both fuel cells and gas turbines, and as a feedstock to the petrochemical industry.

There are about 95 methanol plants worldwide with a total capacity of 34 Mt/y. About 80% of methanol is produced from natural gas, and methanol production is concentrated in regions where natural gas is cheap and available.

The first step of natural gas usage is the conversion of the feed gas to synthesis gas. Various processing routes exist for this syngas. Then the next step is the production of methanol from synthesis gas. Methanol is the basic feed stock for production of several chemicals and petrochemicals.

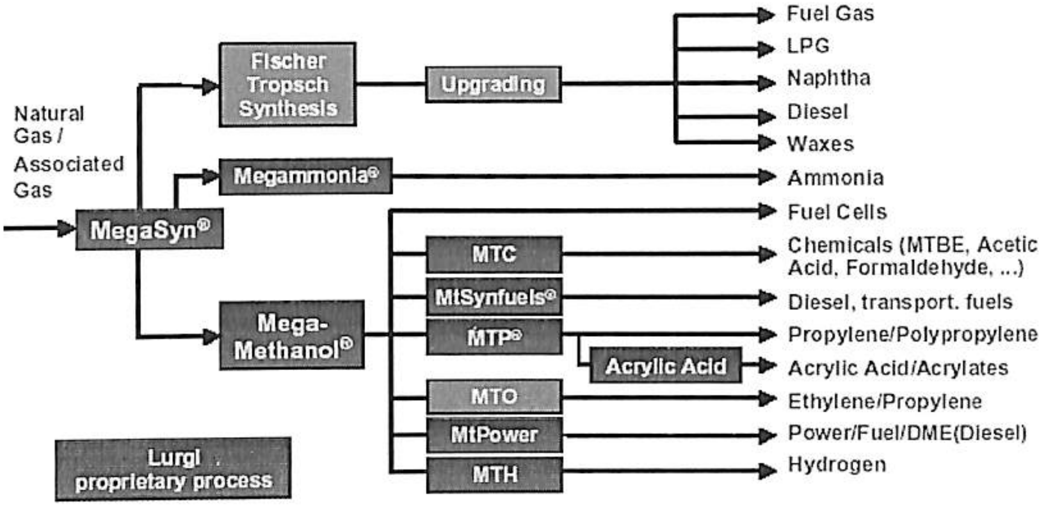
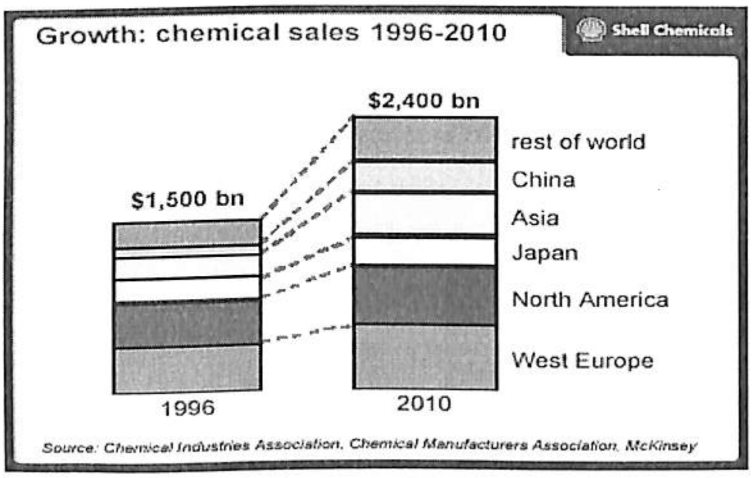


Fig 1.1 Gas processing routes

Source: Lurgi Oel Gas Chemie GmbH\32SCHL copy.doc

Methanol is easily processed further to chemicals such as MTBE or acetic acid. The MTO process primarily converts the methanol into ethylene and propylene. Ethylene and propylene is an important petrochemical base material for plastics. Methanol can also be used as hydrogen carrier. Conversion of methanol to hydrogen is an alternative to naphtha reforming.



Source: Chemical Industries Association, Chemical Manufacturers Association, McKinsey

As the demand for the chemicals is going to increase in future , it is important to find the alternative routes to meet the future demands .Production of chemicals and petrochemicals through natural gas has several advantages. The main advantage is the creating value for the natural gas .The other advantage is meeting the future demand.

CHAPTER-2

METHANOL

Methyl alcohol (methanol) is the first member of the aliphatic alcohol family. Methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production. Currently, it is mainly produced from synthesis gas generated from natural gas.

As a chemical compound, methanol is highly polar, and hydrogen bonding is evidenced by its relatively high boiling temperature (65°C), its high heat of vaporization, and its low volatility. Due to high oxygen content of methanol (50 wt %), it is being considered as a gasoline blending compound to reduce carbon monoxide and hydrocarbon emissions in automobile exhaust gases. It was also tested for blending with gasoline due to its high octane (RON = 112).Methanol is a potential fuel for gas turbines because it burns smoothly and has exceptionally low nitrogen oxide emission levels.

Methanol Properties

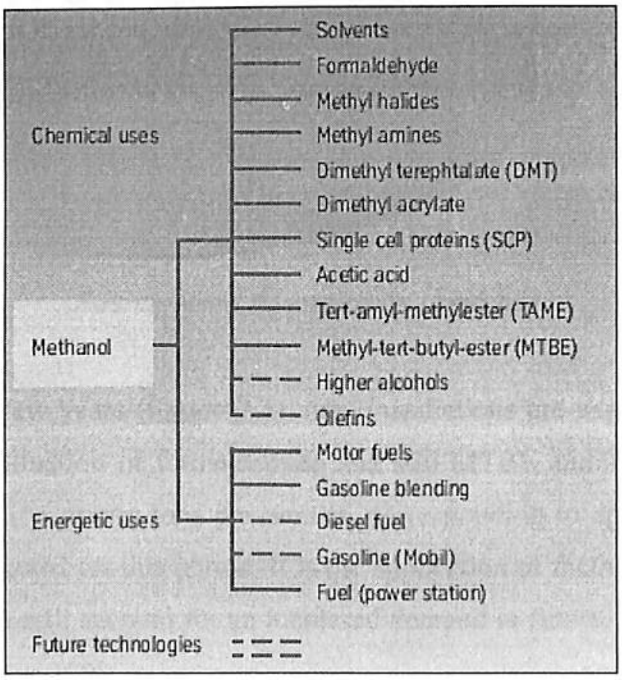
Molecular weight	32.04
Freezing point	-143.7°F (-97.6°C)
Boiling point	148.3°F (64.6°C)
Specific gravity	0.792 (lighter than water)
Weight per gallon	6.59 lbs./gal.

Due to the high reactivity of methanol, many chemicals could be derived from it. It could be oxidized to formaldehyde, an important chemical building block, carbonylated to acetic acid, and dehydrated and polymerized to hydrocarbons in the gasoline range (MTG process). Methanol reacts almost quantitatively with isobutene and isoamylenes, producing methyl t-butylether (MTBE) and tertiary amyl methyl ether (TAME), respectively. Both are important gasoline additives for raising the octane number and reducing carbon monoxide and hydrocarbon exhaust emissions. Additionally, much of the current work is centered on the use of shape-selective catalysts to convert methanol to light olefins as a possible future source of ethylene and propylene.

2.1 METHANOL - APPLICATIONS AND DEMAND

Methanol is one of the most important chemical materials produced today. Methanol has many important uses as a chemical, a fuel and a building block. Technical applications are shown in fig2.1.Its traditional use is in the production of chemicals, solvents, acetic acid, single cell protein and oxygenated compounds. Approximately 35% of methanol production is oxidized to formaldehyde. As a methylating agent, it is used with many organic acids to produce the methyl esters such as methyl acrylate, methylmethacrylate, methyl acetate, and methyl terephthalate. Methanol is also used to produce dimethyl carbonate and methyl-t-butyl ether, an important gasoline additive. It is also used to produce synthetic gasoline using a shape selective catalyst (MTG process). Olefins from methanol are the future route for ethylene and propylene in competition with steam cracking of hydrocarbons. The use of methanol in fuel cells is being investigated. Fuel cells are theoretically capable of converting the free energy of oxidation of a fuel into electrical work.

Fig. 2-1
Methanol applications



Source: www.thyssenkrupp.com/uhde

About 35% of the methanol produced today is used as feedstock for the production of formaldehyde and 27% is used for the production of MTBE and TAME. A further potential use of methanol (fuel grade) is in fuel cells, e.g. for Advanced Automotive Technologies (AAT).

The current world demand for methanol by end use 2001 is shown in figure 2.2.All major automobile manufacturers the world over are pursuing the development of fuel cell vehicles with onboard hydrogen generation from methanol to meet the low emission requirements expected in the future.

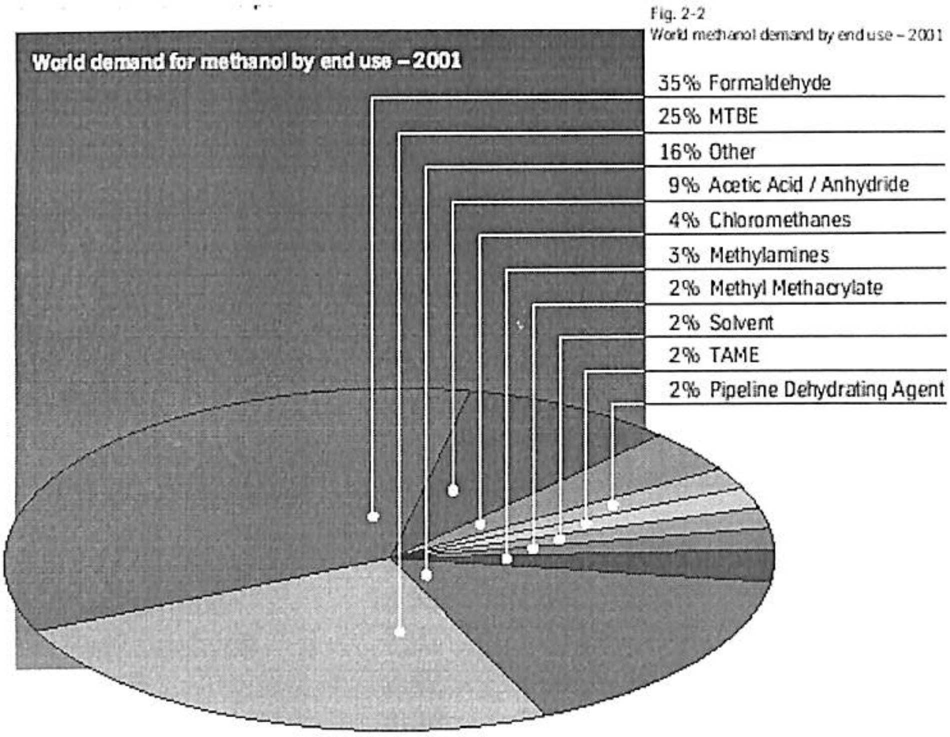
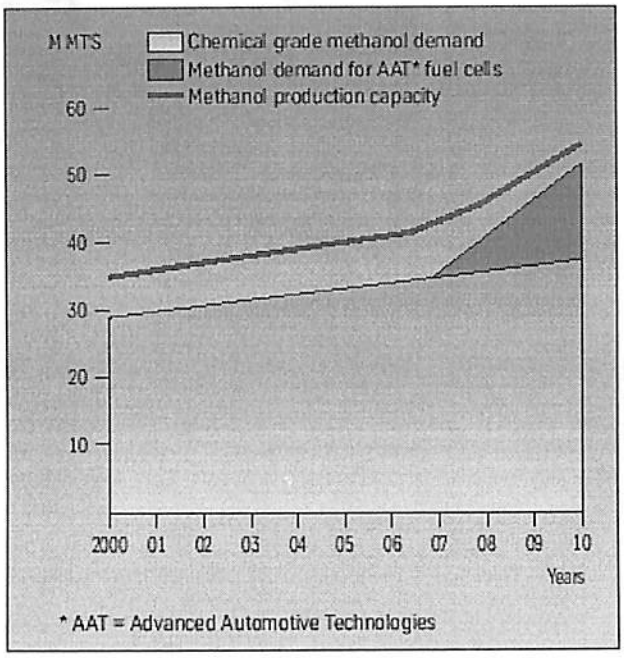


Fig. 2-2
World methanol demand by end use – 2001

Source: www.thyssenkrupp.com/uhde

In the next few years (Figure 2.3), new installations are expected to contribute primarily to the production of formaldehyde and still MTBE and TAME. An average increase of 0.8 million metric tons per annum, corresponding to approx. 2,400 metric tons per day, is expected for this period. It is the application of methanol in the fuel-cell vehicle industry that will account for an increased demand in future. Such an increase is expected after the year 2005.

Fig. 2-3
Worldwide methanol supply and demand



Source: www.thyssenkrupp.com/uhde

Table . World consumption of methanol and forecasted demand (10^6 tpy)

	1990	1991	1992	1993	1994	1995
Consumption	18.35	19.50	20.50	21.50	22.65	23.90
Formaldehyde	7.03	7.27	7.49	7.73	7.85	7.98
MTBE	2.42	2.95	3.57	4.05	4.70	5.50
Acetic acid	1.36	1.51	1.55	1.63	1.72	1.87
Solvents	1.34	1.38	1.41	1.45	1.50	1.55
DMT	0.65	0.66	0.67	0.67	0.68	0.68
Methyl methacrylate	0.49	0.54	0.57	0.59	0.61	0.63
Gasoline	0.26	0.27	0.20	0.23	0.24	0.24
Others	4.80	4.92	5.04	5.15	5.35	5.45
Nameplate capacity	22.50	23.19	24.00	24.77	25.50	26.00
% utilization	82	84	86	87	89	92

Note: It is interesting to note from the last line of the table that the consumption in the next years will approach too closely the nameplate capacity of existing plants. Unless new capacity is added, the methanol market will suffer price tension.

Source: www.thyssenkrupp.com/uhde

2.2 BASIC TECHNOLOGY

Today, methanol is manufactured using a proven technology based predominantly on natural gas, with a small portion of the world capacity being based on petroleum fractions and process off gases. The technology used in natural-gas-based methanol plants has reached a high standard in terms of both energy efficiency and plant reliability, with constant improvements based on practical experience.

Methanol is produced by the catalytic reactions of carbon monoxide and hydrogen (synthesis gas).Because the ratio of CO: H_2 in synthesis gas from natural gas is approximately 1:3, and the stoichiometric ratio required for methanol synthesis is 1:2, carbon dioxide is added to reduce the surplus hydrogen.

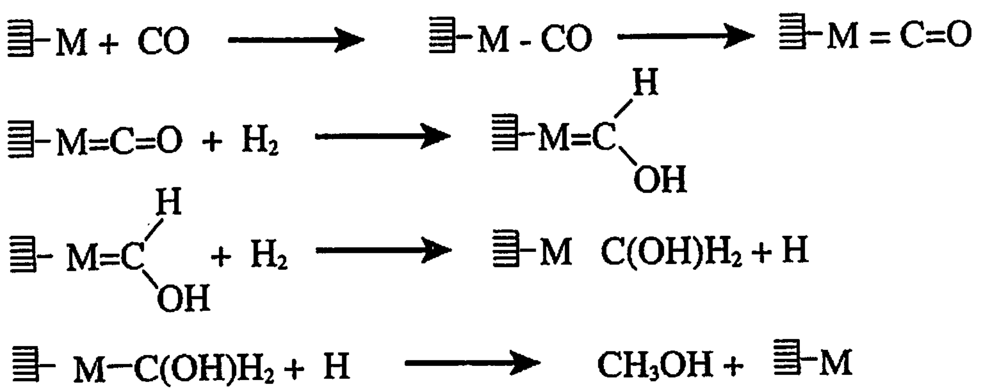
The following reactions are representative for methanol synthesis:

$$\mathbf{CO+2H_2 \rightarrow CH_3OH}$$

$$\mathbf{CO_2 + 3H_2 \rightarrow CH_3OH + H_2O}$$

Methanol synthesis over the heterogeneous catalyst is thought to occur by a successive hydrogenation of chemisorbed carbon monoxide.

This is represented as follow:



The basic concept (Figure 2.4), when processing natural gas to be used as the feedstock, comprises the following process steps:

- Desulphurisation of natural gas,
- Synthesis gas generation,
- Synthesis gas compression,
- Methanol synthesis
- Methanol distillation.

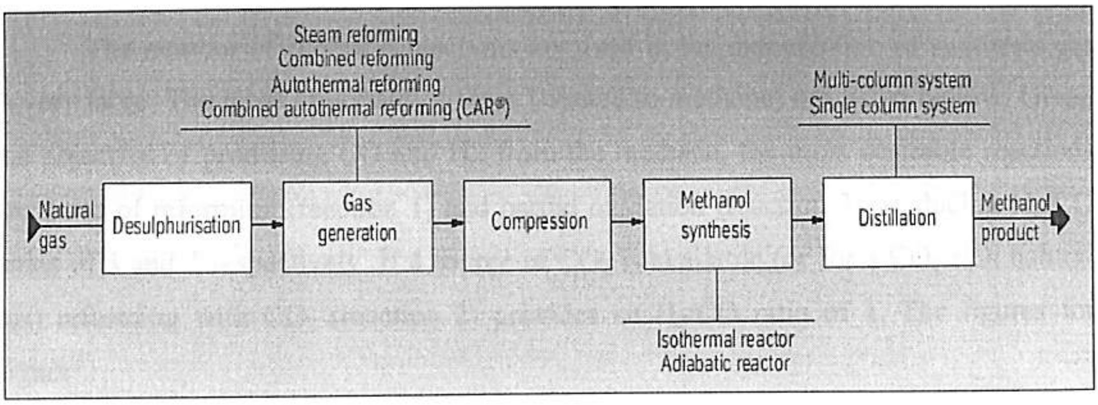


Fig 2.4 Methanol from Natural gas , *Source: www.thyssenkrupp.com/uhde*

Figure 2.4 shows the various options available for the individual process steps. The option selected as the most suitable and, consequently, the plant configuration depends on the customer's requirements and local conditions.

Methanol synthesis and syngas generation represent major areas for further development. As regards methanol synthesis, several developments have been reported in literature. But virtually all of them are presumably in an early phase of development. This applies to the development of new catalysts as well. The low-pressure (40 - 110 bar) synthesis process represents state-of-the-art technology. Recent developments of synthesis units seem to be more in connection with advanced reactor design.

However, the incentives in the area of syngas generation are greater. In a conventional natural-gas-based methanol plant with a capacity of 2,500 mtpd and more, syngas generation accounts for 55% of the investment required for process units. Distillation accounts for 12%, whereas approx. equal shares of the balance go to compression and synthesis. New concepts for syngas generation with the aim of reducing investment costs are of great interest

2.3 SYNTHESIS GAS GENERATION

In all the processes where natural gas is converted to higher value chemicals, the first step is the production of synthesis gas (syngas), a mixture of carbon monoxide and hydrogen. Various processing routes exist for this syngas. Syngas production is very capital intensive and accounts for over half of the total capital cost in most processes. There is much research and development underway to reduce the cost of syngas production.

The number of chemical reactions involved in the manufacture of synthesis gas is very large. The most important of these (limited to methane) are listed bellow. Given the objective of producing CO and H2 from the methane, the most desirable reactions are those of reforming (reaction 1) and partial oxidation (reaction 3) producing H_2/CO ratios of 3 and 2 respectively. If a source of CO_2 is available (or for a CO_2 rich natural gas) reforming with CO_2 (reaction 2) provides an H_2/CO ratio of 1. The figures for higher hydrocarbons in the natural gas are correspondingly lower. The final H_2/CO ratio is influenced further by the CO shift reaction (5). The reforming reactions (1 and 2) are strongly endothermic and must be supported by the strongly exothermic reactions of partial oxidation (3) and/or complete combustion (4). The latter reaction is, however, in principle less desirable since neither H_2 nor CO is produced.

Reforming (strongly endothermic)
$CH4 + H2O \leftrightarrow CO + 3\,H2$ (1)
$CH4 + CO2 \leftrightarrow 2\,CO + 2\,H2$ (2)
Combustion (strongly exothermic)
$2\,CH4 + O2 \rightarrow 2\,CO + 4\,H2$ (3)
$CH4 + 2\,O2 \rightarrow CO2 + 2\,H2O$ (4)
Shift conversion (mildly exothermic)
$CO + H2O \leftrightarrow CO2 + H2$ (5)
Carbon
$CH4 \rightarrow 2\,H2 + C$ (6)
$2\,CO \rightarrow CO2 + C$ (7)

Synthesis Gas Production – Principal Reactions

Steam methane reforming (SMR)

Background:-

The steam methane reforming (SMR) process can be described by two main reactions:

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta h = +206 \text{ kJ mol}^{-1}, \qquad (1)$$

$$CO + H_2O = CO_2 + H_2, \quad \Delta h = -41 \text{ kJ mol}^{-1}. \qquad (2)$$

The first reaction is reforming itself, while the second is the water-gas shift reaction. Since the overall reaction is endothermic, some heat input is required. This is accomplished by combustion of natural gas or other fuels in a direct-fired furnace. Reaction (1) favors high temperature and low pressure, and proceeds usually in the presence of a nickel-based catalyst. The first patents on steam methane reforming were awarded to BASF in 1926 and the first reforming plants were built in the 1930s. Large-scale production has began only in the beginning of 1960s following the discovery of large gas fields in Europe and the subsequent change-over from use of coal to natural gas as a feedstock. In the early days, reforming proceeded at atmospheric pressure, later the process parameters were increased to pressures of up to 30 bar and temperatures of up to 1000°C. The increased pressure saves compression energy in the downstream synthesis stage, however, the high temperature necessitates an extensive heat recovery system.

Process description:-

In a direct-fired furnace a pre-heated mixture of natural gas and steam is passed through catalyst- filled tubes, where it is converted to hydrogen, carbon monoxide and carbon dioxide (Fig. 2.5). It is of a great importance to control the maximum tube temperature and heat flux in the reformer to maintain a reliable and prolonged performance. To obtain this, several burner arrangements are employed: top-fired, bottom-fired, side-fired, terrace-walled, and cylindrical type. Of these, the side-fired and terrace-wall types provide a better temperature control. Due to the endothermic nature of SMR, 35-50% of total energy input is absorbed by the reforming process, of which half is required for temperature rise and the other half for the reaction itself. The produced syngas leaves the reformer at a temperature of 800–900°C. The heat of the flue gases is usually utilised in the convective part of the reformer by generating steam and preheating the feedstock, thus bringing the overall thermal efficiency to over 85%. Only a portion of the steam generated in the boiler is required for the reforming process, while most of the steam (about 60%) is consumed elsewhere. There are also arrangements to recover the heat of the syngas such as the regenerative burners developed by United Technology Corporation, KTI, and Haldor Topsoe. To avoid catalyst poisoning a de-sulphurisation stage is usually required. In addition to the usual nickel-based catalysts, cobalt and noble metals are often used in SMR processes. Non-metallic catalysts have not proved their feasibility due to their low activity.

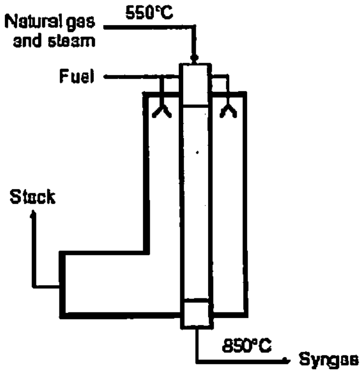


Fig. 2. 5 *Steam methane reforming.*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Another catalyst problem is carbon deposition, which is especially present when processing higher hydrocarbons. In this case, ruthenium, which can effectively resist carbon formation in steam reforming, can be used.

Typical operating parameters of the SMR process are:

Pressure	20-26 bar
Temperature	850–950°C
H_2/CO ratio	2.9–6.5
Plant capacity	0.4 to 21 mln Nm3/day

Complete conversion cannot be obtained in the SMR process, typically 65% of methane is converted, at best it is about 98%, so secondary reforming must be used if a higher conversion rate is desired. In view of the high H_2/CO ratio, steam reforming is the most effective means for hydrogen production. The carbon monoxide then is oxidised to CO_2 in the shift reaction, thus producing even more hydrogen, which is subsequently purified in a pressure-swing adsorption (PSA) unit.

The advantages of the SMR process are that this is the most proven technology with a great deal of industrial experience, it requires no oxygen and produces syngas with a high H_2/CO ratio. It also has relatively low operating temperatures and pressures in comparison to other technologies. Nevertheless, expensive catalyst tubing and a large heat recovery section make an SMR plant a costly investment that can only be justified for very large-scale production. The large size of the reformer and the potential risk of local overheating leads to a complicated heat management system with a slow response, furthermore, external heating results in relatively high atmospheric emissions from the combustion process. The presence of catalyst imposes other problems: care should be taken to avoid sulfurization and carbon deposition, also the catalyst should be regularly refilled due to its deterioration. These prevent the use of heavy hydrocarbons as a feedstock in the SMR process.

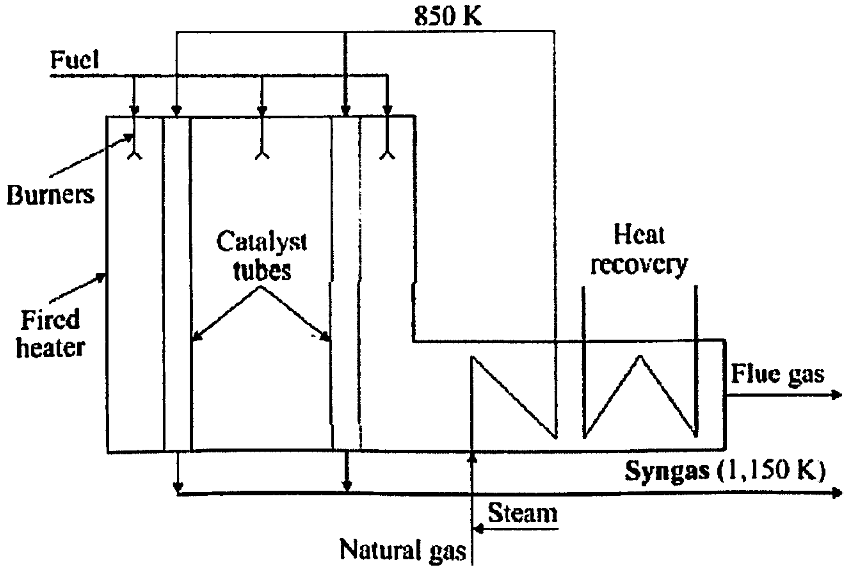


Fig 2.6 Typical SMR process scheme

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Economic aspects:-

The large size of an SMR plant results in a higher capital cost than other technologies due to its high-alloy tubes, catalyst, and bulky heat recovery section. Chauvel and Lefebvre indicated that an SMR plant of 2 mln Nm^3/day syngas capacity would cost 80 mln USD (data for France, situation in 1986). For each 1000 m^3 of syngas (H_2/CO ratio of 2) about 14 GJ of natural gas will be required. In addition, 7 GJ of fuel, 45 kWh of electricity, and 85 m^3 of cooling water will be consumed as utilities. A study by SINTEF gave a figure of 145 mln USD (battery limits) for an 8 mln Nm^3/day syngas plant. Thus, these sources indicate a range of specific investment costs for an SMR-based syngas plant between 20 and 40 USD per Nm^3/day (40–80 USD per kg per day). Unlike other syngas processes, the SMR process does not need oxygen, it is therefore usually the preferable choice when oxygen is expensive. Tindall and Crews indicated that an oxygen price of 30 USD or more per ton makes the SMR a more attractive investment.

Development status:-

Of the syngas production technologies, steam methane reforming is the most developed and commercialized. Lurgi, for example, has built more than 100 plants to date (Lurgi, 1999). Many engineering companies design and build SMR plants, among them M.W. Kellogg, Haldor Topsoe, ICI, Howe-Baker, KTI, Foster Wheeler, and Kvaerner.

Partial oxidation (POX)

Background:-

In the partial oxidation reaction, which proceeds exothermically according to

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2, \ \Delta H = -44 \text{ kJ/mol}, \qquad (3)$$

complete conversion of methane is obtained above 750°C, resulting in a H_2/CO ratio of 2. Since the reaction is exothermic, no fuel is required. When applied to heavy hydrocarbons, coal, or vacuum residue this process is commonly referred to as gasification.

First papers on this conversion route appeared in the 1930s. In the early experiments by Padovani in 1933 and by Prettre et al in 1946 a nickel catalyst was used. Temperatures of the reaction varied between 750 and 900°C and the pressure was slightly above atmospheric. From 1946 to 1954 Texaco Laboratory in Montebello performed a series of experiments on their pilot plant to provide syngas by partial oxidation for the Fisher-Tropsch process. In the late 1970's interest in the partial oxidation of methane was resumed. Nowadays, pressures up to 75 bar and temperatures up to 1400°C are employed. In addition to the non-catalytic oxidation, a lower-temperature catalytic process has been developed. The catalytic partial oxidation (CPO) has a higher flexibility and is less susceptible to soot formation.

Process description:-

A refractory-lined pressure vessel is fed with natural gas and oxygen at a typical pressure of 40 bar (Fig. 2.7). Both natural gas and oxygen are preheated before entering the vessel and mixed in a burner. Partial oxidation reaction occurs immediately in a combustion zone below the burner. To avoid carbon deposition the reactants should be thoroughly mixed and the reaction temperature should not be lower than 1200°C. Sometimes steam is added to the mixture to suppress carbon formation. In the case of catalytic partial oxidation steam is not required and the temperature can be below 1000°C.

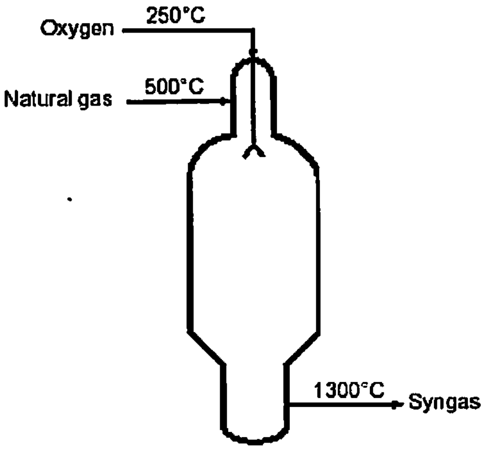


Fig.2.7 *Partial oxidation reactor.*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

The syngas produced leaves the reactor at temperatures of 1300–1500°C. Since the natural gas is usually supplied from a network at high pressure and oxygen is delivered in the liquid form, the costs of upstream compression are almost negligible. In this manner, compression work is saved in the downstream synthesis process. In practice, syngas from the POX process has a H_2/CO ratio between 1.6 and 1.8, so a shift converter or steam injection should be employed to increase this ratio, for instance, for methanol synthesis.

The non-catalytic process allows the use of a broad range of hydrocarbon fuels from natural gas to coal and oil residue and remains the only viable technology for heavy hydrocarbons. Almost 100% conversion is obtained in the POX reaction, and this is the reason why a POX reactor is used in combined reforming to complete conversion of methane coming from a steam methane reformer. At high temperatures carbon particles are burned completely, so that no steam is required, this simplifies the process operation. However, the need for oxygen results in high operating costs, and also provisions should be made to minimise the risk of explosion.

The catalytic process has a reduced size and consumes less oxygen, but runs the risk of catalyst destruction by local thermal stress.

Economic aspects:-

According to the SINTEF study, the investment costs for a POX-based syngas plant constitute 80% of the reference SMR plant, while a CPO plant would require an investment of just 55% of the reference. Another source indicated that the syngas production costs from a POX plant are 60 to 70% of those of SMR.

The SINTEF report cites an investment of 116 mln USD for a POX-based syngas plant with an output of 5.5 Nm^3/day, resulting in specific costs of 21 USD per Nm^3/day. Institut Français du Petrole (IFP) gives a figure of 80 mln USD for a smaller plant of 2 mln Nm^3/day, i.e. 40 USD per Nm^3/day. The oxygen costs can constitute 50% of operational costs of the syngas production at the POX plant.

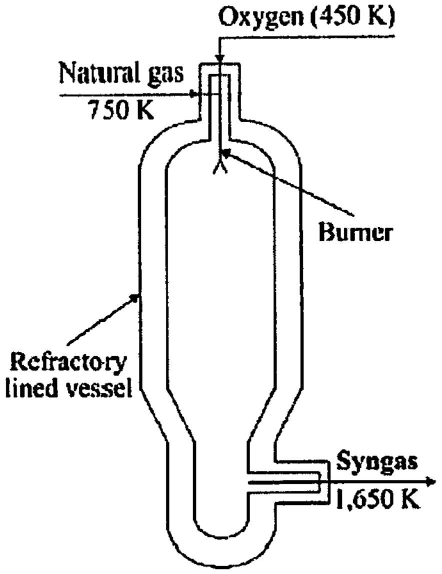


Fig. 2.8 Typical POX reactor

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Development status:-

Syngas production via the POX route is an established technology. Texaco and Shell technologies have been employed for many years for partial oxidation of petroleum cuts and other heavy hydrocarbons. In the field of coal gasification, along with Texaco and Shell, other companies are active in this field such as Lurgi, Koppers, Foster Wheeler, British Gas, Starchem. In 1992, Texaco had more than 100 licensed commercial POX plants on their reference list, of which 28 were using gaseous and 62 were using liquid feedstock.

The POX technology is used at the Shell Middle Distillate plant in Bintulu, Malaysia, where a natural-gas feedstock is processed via Fischer-Tropsch synthesis to produce synthetic fuels and waxes at a scale of 12 000 barrels per day.

Exxon has developed a fluid bed in which partial oxidation and steam reforming reactions are carried out simultaneously in a single large reactor containing a bed of catalyst particles. Between 1990 and 1992 test runs were performed at the demonstration unit in Baton Rouge, Louisiana.

Autothermal reforming (ATR)

Background:-

This process combines partial oxidation and steam reforming in one vessel, where the hydrocarbon conversion is driven by heat released in the POX reaction. Developed in the late 1950's by Haldor Topsoe and Société Belge de l'Azote, the process is used for methanol and ammonia production. Both light and heavy hydrocarbon feed stocks can be converted. In the latter case, an adiabatic pre-reformer is required.

Process description:-

The process represented in figure 2.10 consists of a natural gas preheat section, a reactor and heat recovery section and a gas separation unit. A desulphurization unit is also present. The steam reforming of natural gas takes place in the autothermal reformer. A mixture of natural gas-steam and oxygen is fed to the reactor. Partial oxidation reactions occur in a combustion zone and then the products pass through a catalyst bed, where reforming reactions occur. The ATR reactor consists of a refractory lined pressure vessel with a burner, a combustion chamber and a catalyst bed. It has a design similar to that of the POX reactor shown in figure 2.7, but contains also a catalyst bed in the last part. The produced syngas temperature is about 1,300 K as compared to 1,650 K for the POX reactor. This reduction in the syngas temperature is required by the presence of the catalyst which does not support higher temperature values. The outlet

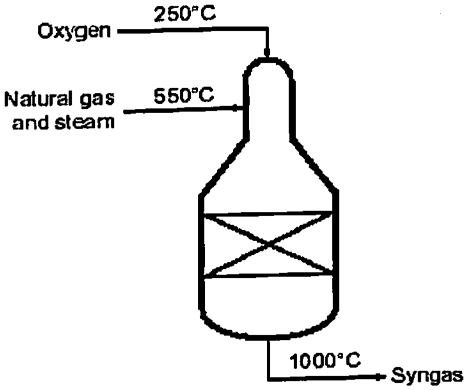


Fig. 2. 9 *Autothermal reforming*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Temperature of the catalyst bed is between 850 and 1050°C. The main advantages of ATR are a favourable H_2/CO ratio (1.6 to 2.6), reduction of emissions due to internal heat supply, a high methane conversion, and the possibility to adjust the syngas composition by changing the temperature of the reaction. However, it requires an oxygen source.

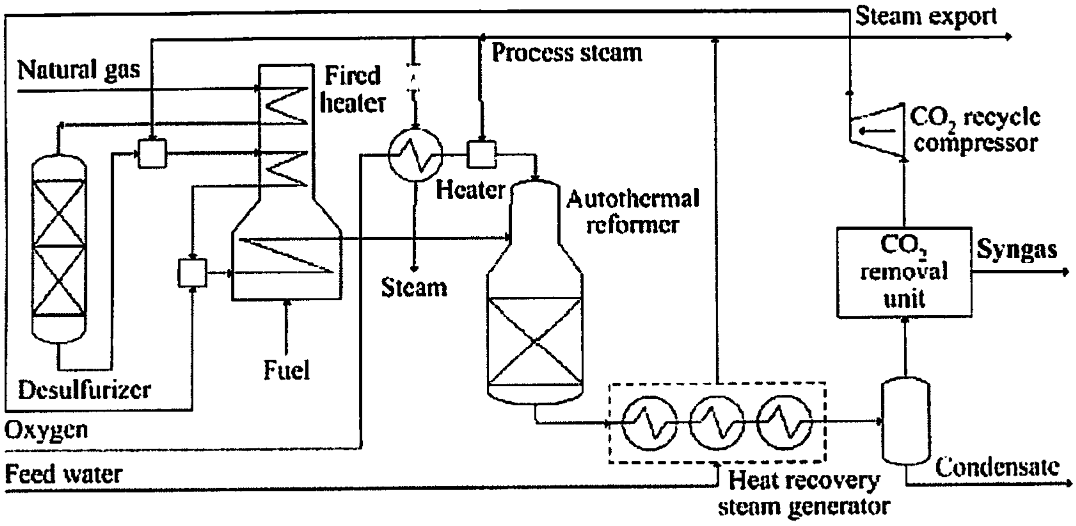


Fig 2.10 Typical ATR process scheme

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Economic aspects:-

The capital costs for autothermal reforming are lower than those of the SMR plant by 25%, as reported by Haldor Topsoe. Operational costs, however, are the same or even higher due to the need to produce oxygen. The SINTEF study reported a capital-cost reduction of 35%, but an 8%-increase in operational costs for the ATR technology in comparison to the SMR process.

Development status:-

ATR technology is commercially available, but still has limited commercial experience. The main licensors are Haldor Topsoe, Lurgi, ICI, Foster Wheeler.

Combined Reforming

Background:-

Since less than 100% of methane is converted in the SMR reaction, a secondary reformer behind the SMR unit can be installed to provide complete methane conversion and the possibility to adjust H_2/CO ratio. In addition, the size of the costly SMR plant can be reduced by shifting part of its load to the secondary, oxygen-fired reactor. This is why this process is also called two-step reforming, or oxygen-enhanced reforming.

Process description:-

As the schematic of the process shows (Fig.2.11), it consists of a primary SMR unit and a secondary ATR or POX reformer with oxygen supply.

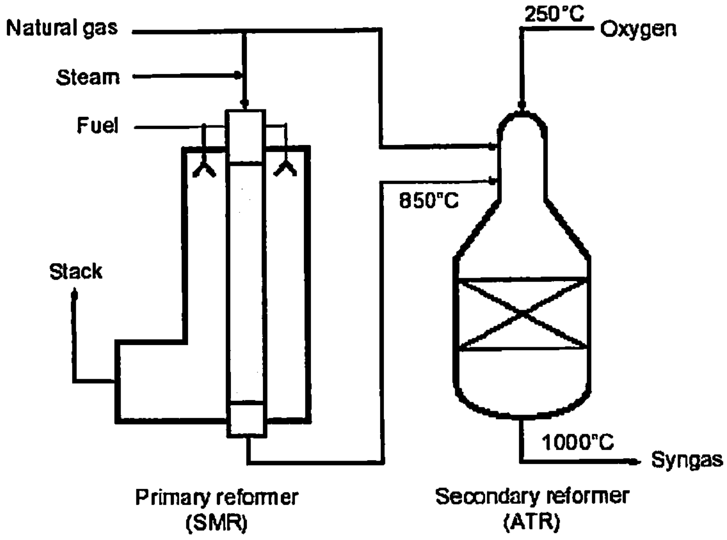


Fig 2.11 *Combined reforming*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

A pre-reformer is often installed before the main reformer (Fig. 2.12). Pre-reforming, which proceeds at low temperatures, is usually adiabatic. The pre-reformer widens the range of hydrocarbons suitable for reforming. It also takes over some duty from the primary reformer, in order that it can operate under less severe conditions. This, in turn, allows for less costly materials and a smaller heat transfer surface, which results in reduced costs of the equipment. However, the need for an oxygen plant might overweigh this advantage. Outlet temperatures of up to 1050°C are common. Methane conversion of above 99.6% can be obtained.

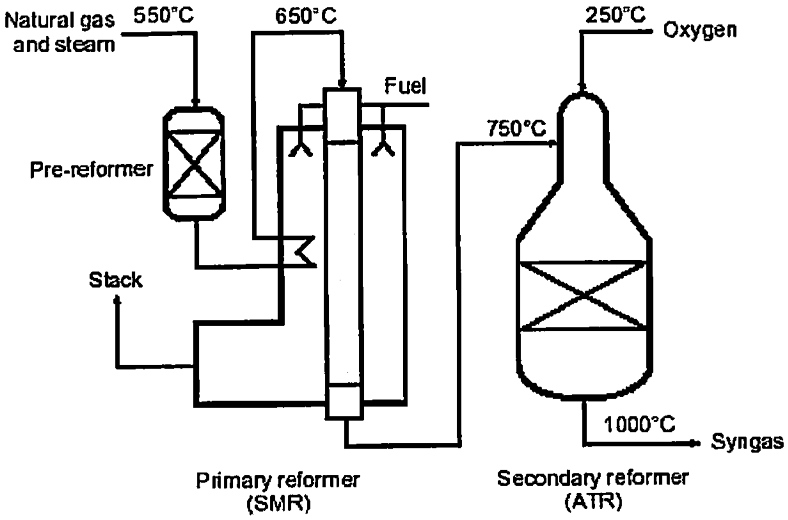


Fig 2.12 *Combined reforming with prereforming*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

Economic aspects:-

Schneider and LeBlanc reported that a combined reforming plant would consume about 3% less energy than an SMR plant. Sogge et al confirm this figure giving a 1-6% decrease in operational costs. The capital costs, however, are lower: these constitute 72–76% of those by SMR. A study undertaken by Haldor Topsoe indicated that the required investment for the combined reforming scheme would be 15% lower, mainly due to the savings in the reformer section.

Development status:-

This is a technology based on two established processes. Its advancement is directly related to the developments of these processes. Combined reforming technology is being offered by the main contractors in the process industry (Haldor Topsoe, M.W. Kellogg, etc).

Combined Autothermal Reforming (CAR)

Background:-

The CAR system combines steam reforming and partial oxidation processes in one single pressure vessel. In a way, this is a logical development of the Gas Heated Reforming concept. Uhde GmbH began developing its process in 1982. And while ICI saw difficulties in putting both reactors within one shell, Uhde succeeded in engineering and building a demonstration unit based on the single-vessel principle.

Process description:-

As depicted in Fig. 2.13, a mixture of steam and primary feed is reformed first in the primary, SMR-type section, utilizing heat produced in the following partial oxidation reaction. The POX reaction proceeds in the lower part of the vessel between the unconverted feedstock and oxygen at a temperature of 1200–1300°C. The temperature and the degree of conversion can be adjusted by controlling the amount of oxygen.

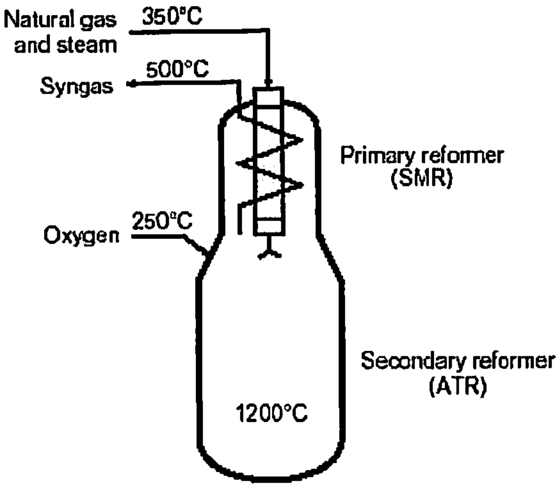


Fig 2.13 *Combined Autothermal Reforming*

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

The following are the process data of a demonstration CAR reactor

H_2/CO	2.8	POX zone temperature	1290°C
CO_2	7.2%	CAR outlet temperature	500°C
CH_4	0.5%	Pressure	17 bar

Economic aspects:-

The CAR unit reduces consumption of oxygen by 35% and consumption of natural gas by 15% in comparison to an existing POX unit. However, an economic evaluation by SINTEF showed that operational costs of the CAR –based plant are 10% higher than those of POX, while the difference in investment costs are in favour of the CAR concept (about 20% less).

Development status:-

Uhde built and operated a pilot plant at UK-Wesseling, Germany in 1987-88. A larger demonstration unit has been in operation since 1991 at Strazke Refinery in Slovakia. Up until March 1994, the demonstration reactor logged about 17 000 hours of operation. It showed a high operating flexibility without problems at loads from 30% to 100%.

Comparison of SMR, ATR and POX

Typical operating conditions and H_2/CO molar ratio for synthesis gas production methods discussed above are given in table 2.2

Table 2.2 Characteristics of syngas production methods.

Method	Operating conditions		H_2/CO
	Temperature (°C)	Pressure (bar)	
SMR	750 – 900	15 – 40	3 – 5
ATR	850 – 1,000	20 – 40	1.6 – 2.65
POX	1,200 – 1,500	20 – 150	1.6 – 1.8

Source: "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment

The comparison of SMR, ATR and POX technologies for syngas production from natural gas leads to the following conclusions. In contrast to POX and ATR, SMR has a bulky installation, due to the large SMR furnace with catalyst tubes and large flue gas heat recovery section. However, this method is preferred for the production of hydrogen, as a result of the high H_2/CO molar ratio (see table 2.2). When compared with ATR, POX has a smaller CO_2 removal system (for full CO_2 recycle) and does not use a catalyst. This makes POX more compact and with a higher power density than ATR. On the other hand, ATR has a less expensive reactor and heat recovery section than POX, due to lower temperatures and produces no soot. In addition, ATR is a more flexible process than POX in view of the H_2/CO molar ratio of syngas produced (see table 2.2). It follows that an optimal process of syngas manufacture from natural gas with a H_2/CO molar ratio below 2 would combine the compactness and power density of POX, the soot free operation of ATR and a high efficiency, compact heat recovery system.

2.4 METHANOL SYNTHESIS

Methanol is produced by the catalytic reactions of carbon monoxide and hydrogen (synthesis gas).Because the ratio of CO: H_2 in synthesis gas from natural gas is approximately 1:3, and the stoichiometric ratio required for methanol synthesis is 1:2, carbon dioxide is added to reduce the surplus hydrogen. The conversion of carbon oxides to methanol is an exothermic process which takes place at high pressures and low temperatures. The synthesis unit operates at 40 - 110 bar and around 200 to 300 °C.

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The aim is to achieve a relatively high carbon efficiency (refer to fig 2.14,2.15,2.16) so as to minimize the amount of synthesis gas to be processed and thus the amount of feed to the syngas generation section.

" The percentage of carbon oxides in the syngas converted to crude methanol is defined as carbon efficiency."

The efficiency increases

- As the synthesis pressure increases
- As the content of inerts in the syngas decreases
- As the molar CO:CO_2 ratio in the syngas increases
- As the conversion rate (concentration of methanol ex catalyst) decreases.

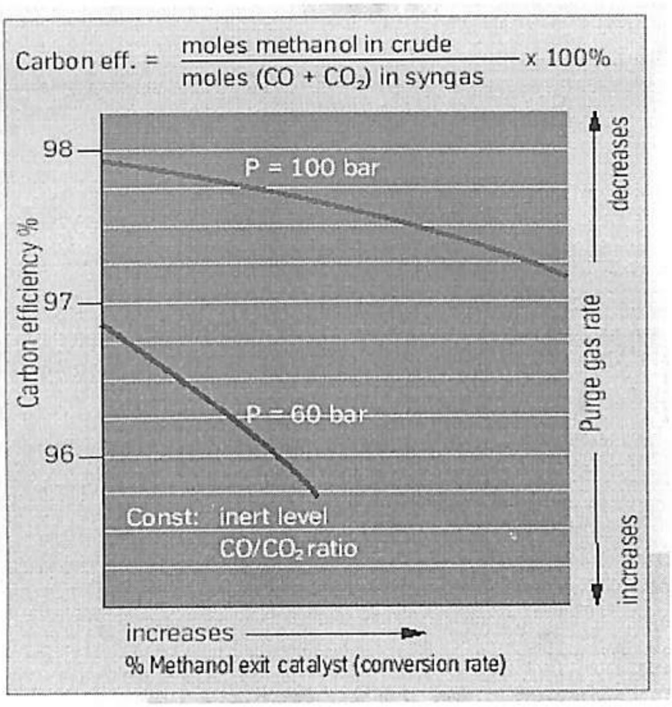


Fig 2.14 Carbon efficiency Vs. Pressure and Conversion rate
Source: www.thyssenkrupp.com/uhde

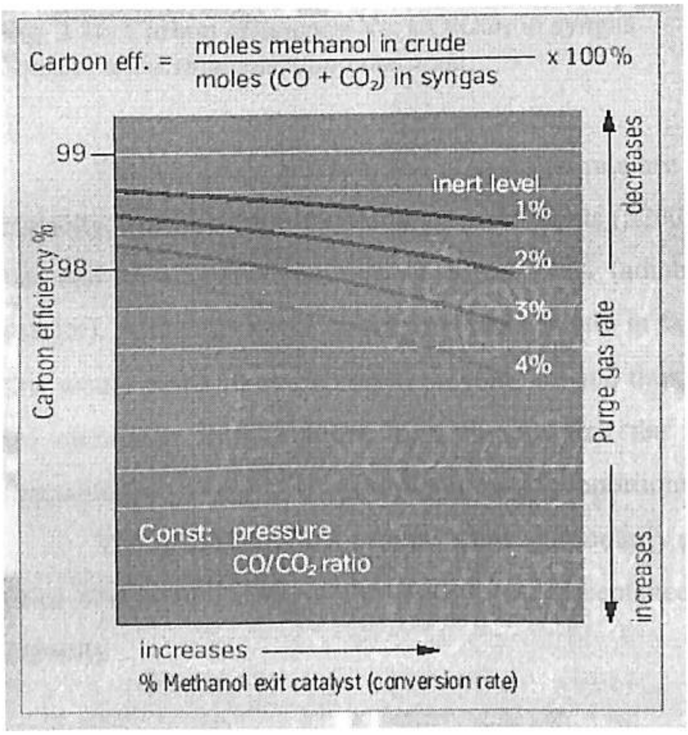


Fig 2.15 Carbon efficiency Vs. Inert level and Conversion rate
Source: www.thyssenkrupp.com/uhde

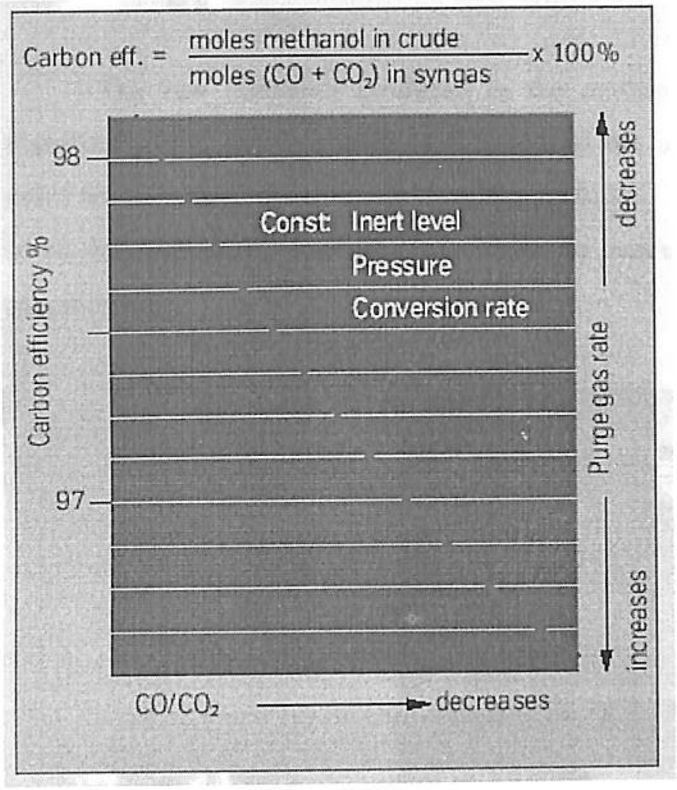


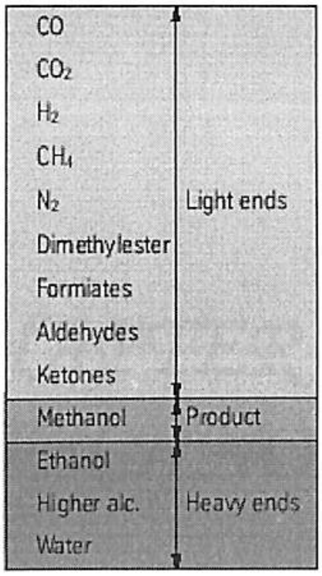
Fig 2.16 Carbon efficiency Vs. CO/CO_2 in syngas
Source: www.thyssenkrupp.com/uhde

The synthesis pressure and conversion rate are optimized for the particular plant capacity. For instance, typical large scale plants (5000 mtpd of methanol) operate at 80 bar and at a conversion rate of approx. 6% (adiabatic reactor) or 8% (isothermal reactor). Although lower conversion rates would in fact increase the carbon efficiency, this would result in an increased recycle rate and thus in a higher compression duty for the circulator. Further more it is obvious that the ideal syngas should contain the reactants CO, CO_2 and H_2 in stoichiometric proportions.

The selection of the process steps, particularly syngas generation, depends on the price and composition of the natural gas, acceptance of energy export and the plant capacity.

2.5 METHANOL PURIFICATION

The raw methanol produced in the methanol synthesis unit contains water, dissolved gases, and a quantity Of undesired but unavoidable by-products that have either lower or higher boiling points than methanol. The purpose of the distillation unit is to remove those impurities in order to achieve the desired methanol purity specification.



CO	Light ends
CO_2	
H_2	
CH_4	
N_2	
Dimethylester	
Formiates	
Aldehydes	
Ketones	
Methanol	Product
Ethanol	Heavy ends
Higher alc.	
Water	

Fig. 2.17 Components in raw methanol

Source: www.thyssenkrupp.com/uhde

Components in raw methanol the components present in raw methanol are shown in Figure 7-1. The distillation unit consists of a topping and a refining section. The light ends are removed in the topping column. The stabilised raw methanol, consisting of methanol, water and minor amounts of higher alcohols, is fractionated in the refining section to produce pure methanol.

The design of the methanol distillation unit primarily depends on the energy situation in the front end. The two-collumn distillation unit represents the low-cost unit and the three-column distillation unit is the low-energy system.

CHAPTER-3
MAJOR TECHNOLOGIES

3.1 LURGI MEGAMETHANOL® TECHNOLOGY

HISTORY:-

One of Lurgi's core process technologies, synthesis of methanol an important chemical raw material-has become established all over the world, known as the Lurgi Low Pressure Methanol Process. Basically, the methanol process consists of synthesis gas generation, methanol synthesis, and methanol distillation. Gas may be generated starting from various different feed stocks (such as natural gas, naphtha, heavy residues, and coal).

Methanol production on an industrial scale was introduced in 1923 when BASF Ludwigshafen commissioned a methanol synthesis plant on the basis of a chromium/zinc catalyst. Since this type of catalyst was not highly active, it was necessary to apply operating pressures of between 300 and 400 bar and operating temperatures of between 350 and 400°C. Based on this type of high-pressure methanol catalyst, Lurgi has built six plants in various countries that use synthesis gas produced from natural gas or steam reforming of light naphtha or by partial oxidation of heavy residual oil, the total capacity amounting to 181,000 metric tons per annum (MTA).

In order to improve the process economics, in the 1960s, Lurgi initiated the development of a process that allows processing of methanol at low pressures and temperatures. Development work at Lurgi's research and development (R&D) center focused on a suitable catalyst. The first LP methanol tests were run in 1969. Since Lurgi itself is not a catalyst manufacturer, it started a cooperation with Sud-Chemie AG in 1970 for fabrication of the catalyst. In the same year, Lurgi built a semi commercial demonstration unit with a 100-tube methanol reactor. The design and technology of the methanol reactor were based on a water-cooled reactor, already service-proven in Lurgi's Fisher-Tropsch synthesis. In the demonstration plant, extensive research and experimental work was conducted for virtually all types of synthesis gas, irrespective of origin, i.e., produced by steam re-forming of natural gas or naphtha or by partial oxidation of heavy residue oils. The influence of harmful components on the methanol catalyst also was investigated indepth in the demonstration unit. The operating results of the demonstration unit convinced Lurgi's clients so much that the first three contracts for Lurgi LP Methanol Process plants were signed in that same year, representing a total capacity of more than 300,000 MTA. Given that each of these plants was based on a different feedstock-heavy residue of a refinery, natural gas, feed range from natural gas to naphtha-Lurgi was able to prove that the new LP Methanol Process technology can cope with all those feed stocks. Thanks to the know-how and experience gained with the demonstration unit, all three plants went on-stream without problems in early 1973.

Meanwhile, the methanol catalyst has been improved significantly in terms of selectivity, conversion rates, and durability through intense joint research efforts of Lurgi and Sud-Chemie AG. Today, Lurgi has highly active and stable catalysts available for varying process conditions so as to largely suppress the formation of by-products.

The economics of the process also have been improved continuously with respect to equipment, feedstock requirements, and capacity. Lurgi has so far built (or is building) 41 LP Methanol Process plants with a total capacity of 20.1 million MTA. This represents about a third of the world installed capacity.

Vast natural gas and oil-associated gas reserves are available in remote areas at low and stable cost. Combining low-cost feedstock with large single-train synthesis technology will be the strategy of the next decades in order to achieve a remarkable production cost reduction.

Lurgi has developed its MegaMethanol technology on the basis of the syngas technologies available in the 1990s, i.e., conventional steam reforming and combined reforming together with a new synthesis concept. Lurgi's MegaMethanol process is an advanced technology for converting natural gas to methanol at low cost in large quantities. It permits the construction of highly efficient single-train plants of at least double the capacity of those built to date. This paves the way for new downstream industries that can use methanol as a competitive feedstock.

MegaMethanol Technology

Lurgi's MegaMethanol technology has been developed for world-scale methanol plants with capacities larger than I MMTA. To achieve such a capacity in a single train, a special process design is needed, incorporating advanced but proven and reliable technology, cost optimized energy efficiency, low environmental impact, and low investment cost.

The main process features to achieve these targets are

- Oxygen-blown natural gas re-forming, either in combination with steam methane reforming or as pure autothermal reforming.
- Two-step methanol synthesis in water- and gas-cooled reactors operating along the optimal reaction route.
- Adjustment of syngas composition by hydrogen recycle.

The configuration of the reforming process autothermal or combined reforming - mainly depends on the feedstock composition, which may vary from light natural gas (nearly 100 percent methane content) to oil-associated gases. The aim is to generate an optimal synthesis gas, characterized by the stoichiometric number given below:

$$SN = (H_2 - CO_2) / (CO + CO_2) = 2.0 - 2.1$$

The Lurgi MegaMethanol process, based on re-forming of gaseous hydrocarbons, especially natural gas, consists of the following essential process steps:

- Desulfurization
- Pre-re-forming (optional)
- Saturation
- Pure autothermal or combined re-forming
- Methanol synthesis
- Methanol distillation

The syngas generation section of a MegaMethanol plant using combined re-forming is shown in Fig. 3.1.

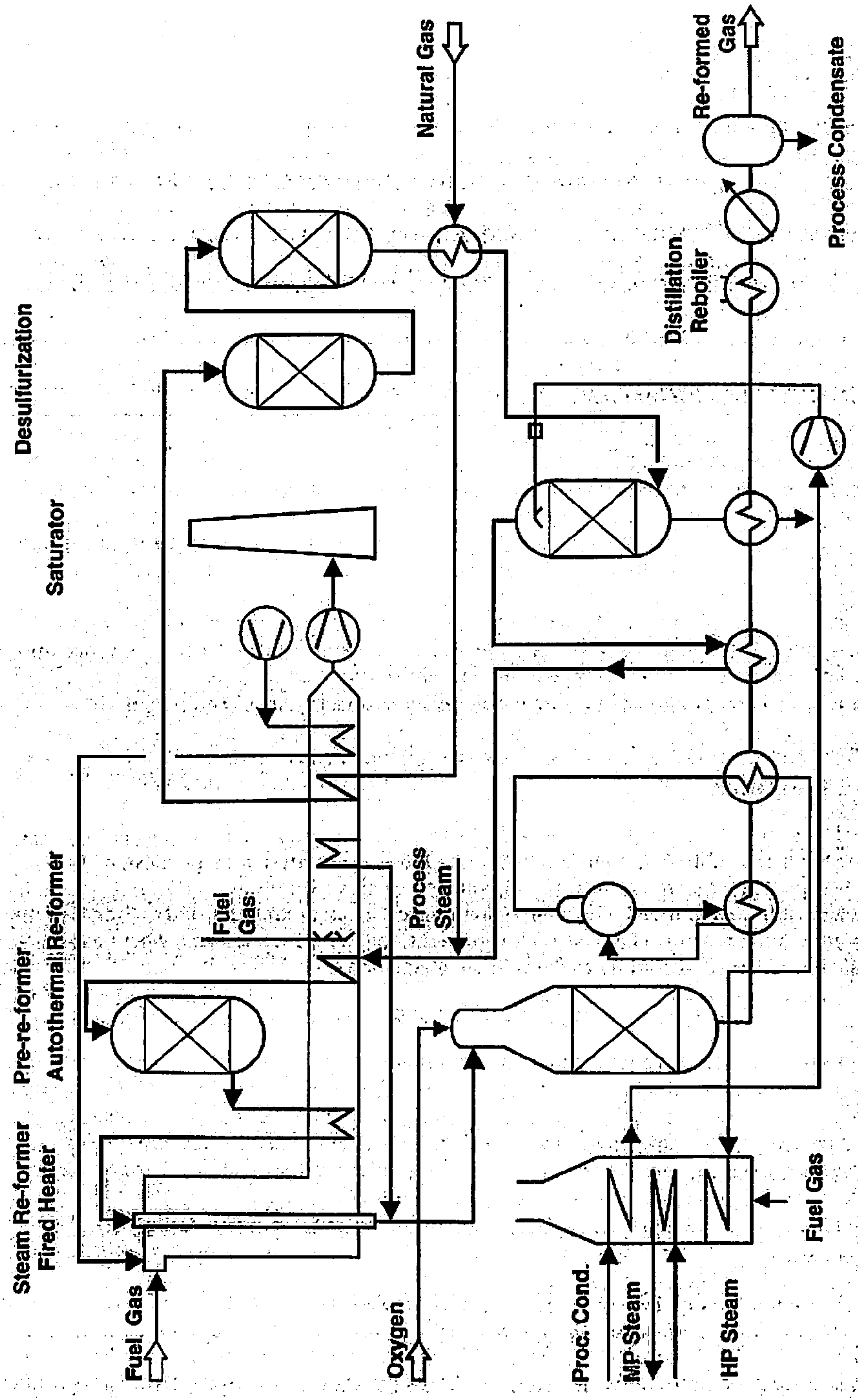


FIGURE .1 Syngas generation using combined re-forming for the MegaMethanol process.

Source: Handbook of Modern Refining Process , Robert E.Meyers

PROCESS DESCRIPTION

The synthesis gas production section of a conventional methanol plant accounts for more than 50 percent of the capital cost of the entire plant. Thus, optimizing this section yields a significant cost benefit. Conventional steam methane re-forming is economically applied in small and medium-sized methanol plants only, with the maximum single-train capacity being limited to about 3000 metric tons per day (MTD). Oxygen-blown natural gas reforming, either in combination with steam re-forming or as pure autothermal reforming, is today considered to be the best-suited technology for large syngas plants. The reason for this appraisal is that the syngas generated through oxygen-blown technology becomes available in stoichiometric composition and under very high pressure. Hence very high quantities can he produced in a single train using reasonably small equipment.

Desulfurization:-

Catalyst activity is seriously affected even by traces of catalyst poisons in the gas feedstock. Among others, sulfur compounds in particular lower the catalyst activity considerably.

In order to protect the re-former and synthesis catalysts from sulfur poisoning, the feedstock must be desulfurized. Desulfurization operates at approximately 350 to 380°C in the desulfurization reactor. The feedstock is routed through zinc oxide beds, where hydrogen sulfide is adsorbed according to the following equation:

$$H_2S + ZnO \leftrightarrow ZnS + H_2O$$

If the feedstock contains organic sulfur compounds such as mercaptans or thiophenes, hydrogenation is required prior to desulfurization. This is often accomplished in a separate reactor, where the feedstock, after adding a small amount of hydrogen-rich methanol synthesis purge gas, is hydrogenated over cobalt-molybdenum catalysts. A residual sulfur content of less than 0.1 ppm is obtainable and can be tolerated for the downstream processes.

Saturation:-

After desulfurization, the natural gas feed gas is cooled and then enters the top of a saturator for saturation, with water supplying a major part of the H_2O required for the reforming reactions. After makeup with process condensate and process water from distillation, hot circulation water is fed to the top section of the saturator. Circulation water is withdrawn from the bottom of the saturator by a recirculation pump and then is heated by a circulation water heater in the re-formed gas cooling train before it is refed to the saturator.

Pre-re-forming (Optional):-

If the feedstock contains fractions of higher hydrocarbons, the steam re-former catalyst can be affected by carbon deposits owing to cracking reactions when operated at low steam carbon ratios. This should be avoided by pre-re-forming the feedstock in a pre-reformer. The conversion of higher hydrocarbons in an adiabatic reactor produces a gas rich in methane and hydrogen that is perfectly suitable for further steam re-forming. The fixed bed type pre-re-former is arranged between the process feed super heater and the steam reformer. The desulfurised feedstock, with process steam added, is routed through the catalyst bed, where almost all higher hydrocarbons and a small percentage of the methane are re-formed with steam according to the following equations:

Steam reforming of higher hydrocarbons:

$$C_nH_m + n\,H_2O \leftrightarrow nCO + (m/2 + n)\,H_2$$

Methanation

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O$$

Water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Pre-re-formed gas is produced at about 380 to 480°C, the overall heat balance being slightly endothermic or exothermic depending on the content of higher HCs in the feedstock. The pre-reformed gas only contains a few parts per million of hydrocarbons higher than methane and allows reduction of the steam-to-carbon ratio for the steam re-former to 1.8. A low steam to carbon ratio and superheating of the pre-re-formed gas upstream of the steam re-former inlet reduces the size of the steam re-former significantly. Additionally, the amount of waste heat is reduced by saving steam re-former under firing when combined re-forming is used.

Autothermal Re-forming:-

Pure autothermal re-forming can be applied for syngas production in MegaMethanol plants whenever light natural gas is available as feedstock to the process. The desulfurized and optionally pre-reformed feedstock is reformed with steam to synthesis gas at about 40 bar using oxygen as the re-forming agent. The process offers great operating flexibility over a wide range to meet specific requirements. Reformer outlet temperatures are typically in the range of 950 to 1050°C. The synthesis gas is compressed to the pressure required for methanol synthesis in a single-casing synthesis gas compressor with integrated recycle stage.

With the help of a proprietary and proven three-dimensional computational fluid dynamics (CFD) model (Fig. 3.2), gas flows and temperature profiles are simulated with the objective of designing burner and reactor as an integrated unit. Autothermal processes produce the heat required for gasification through partial combustion of the feedgas to be converted in the reactor. Oxygen is usually added for this purpose. Suitable feed stocks for autothermal catalytic reforming are light natural gases or steam reformed gases with high residual methane content.

The principal chemical reactions involved in the process are those of complete combustion of methane

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$$

partial oxidation of methane

$$CH_4 + O_2 \leftrightarrow CO + H_2 + H_2O$$

as well as methane and higher hydrocarbon re-forming and a CO shift reaction, as described under "Steam Re-forming."

The combustion (partial oxidation) is highly exothermic, the re-forming reaction being endothermic. In order to attain the desired product gas quality, the outlet temperature of the reactor is selected and controlled by metering in the required amount of oxygen to maintain the heat balance between exothermic and endothermic reactions.

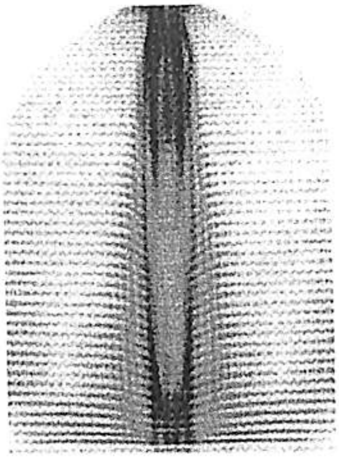


FIGURE 3.2 Autothermal reactor simulation, performance by 3D CFD model.

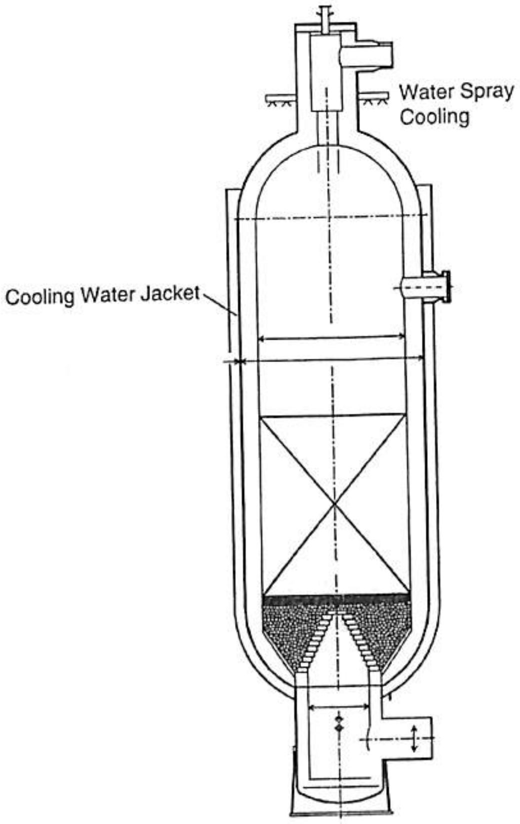


FIGURE 3.3 Autothermal re-former.

Source: Handbook of Modern Refining Process , Robert E.Meyers

The autothermal re-former (ATR) is a refractory-lined pressure vessel. A cross section of an ATR is illustrated in Fig. 3.3. The lower, cylindrical part of the ATR contains reforming catalyst. The entire ATR shell is protected by high-temperature-resistant brick lining. A mixer in the ATR top section provides fast and uniform mixing of the gas-steam mix with preheated oxygen. The combustion and prereaction zone is located above the catalyst bed. The catalyst employed is a steam re-forming catalyst. Because of the operating conditions, establishing a stable flame contour is essential to protecting the reactor walls and catalyst from excessive temperatures. Even when using pure methane as feedstock for autothermal re-forming, it is necessary to condition the synthesis gas because its stoichiometric number is below 2.0. The most economical way to achieve the required gas composition is to add hydrogen, withdrawn from the methanol synthesis purge stream by a membrane unit or a pressure swing adsorption (PSA) unit.

Compared with its competitors, Lurgi has the most references and experience for this re-forming technology. This process has been implemented in Lurgi plants since the 1950s.

Combined Re-forming:-

The combination of oxygen-blown autothermal re-forming and conventional steam methane reforming, the so-called combined reforming process, has an advantage in that it yields synthesis gas of optimal composition and at a high pressure. A cross section of Lurgi steam reformer is shown in Fig. 3.4. In a steam re-forming process, hydrocarbons and steam are catalytically converted into hydrogen and carbon oxides. The composition of the product gas is reached according to the following equilibrium reactions:

$$C_nH_m + n\,H_2O \leftrightarrow nCO + (m/2 + n)\,H_2$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The overall reaction is highly endothermic, so reaction heat has to be provided externally. The synthesis gas is characterized by a relatively low pressure and a surplus of hydrogen. By adding carbon dioxide, the composition of the synthesis gas can be adjusted to be more favorable for methanol production.

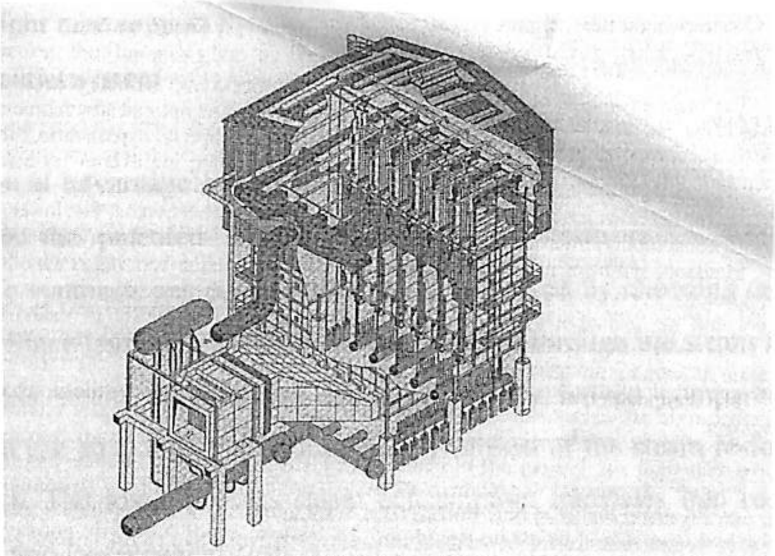


FIGURE 3.4 Cross section of a Lurgi Reformer.

Source: Handbook of Modern Refining Process , Robert E.Meyers

The tubular steam reformer is the most expensive single item of a methanol plant when combined reforming is used.

Against this background, Lurgi has developed the Lurgi Reformer^{TM} that allows for the construction of' very large reformers of up to 1000 catalyst tubes in a single cell. The largest Lurgi Reformer implemented so far contains 720 tubes.

The Lurgi Reformer is a top-fired reformer, and as such, it exhibits all the advantages of this typical design:

- Multiple-tube rows, resulting in a lower number of burners and lower heat loss
- Almost uniform wall temperature over the entire heated tube length
- Easier burner adjustment and reduced burner maintenance because of the reduced number of burners
- Less NO_x formation by more accurate fuel and combustion air equipartition of the burners
- Easier noise abatement

The features of this re-former design are

- Advanced inlet pigtail design

- Internal insulation at the top of the re-former catalyst tube
- Counterweight tube support System
- Flexi tube outlet system

The main advantage of the combined re-forming process over similar process alternatives is the patented feedgas bypass of the steam re-former. The optimal stoichiometric synthesis gas composition can be achieved by choosing the appropriate bypass ratio. Since less than half the feed gas is routed through the steam re-former, the overall process steam requirements are also roughly halved compared with other processes that use an autothermal reformer downstream of the steam re-former without such a bypass. The lower process steam consumption translates into reduced energy requirements and lower capital costs.

Methanol synthesis gas generation by means of combined re-forming is a well-proven technology. For natural gases or oil-associated gases with methane content above 80 percent and for methanol syntheses with capacities above 1500 MTD of methanol, this process route offers potential capital investment savings compared with the conventional steam re-forming process.

The composition of the generated synthesis gas is characterized by the stoichiometric number

$$\mathbf{SN = (H_2 - CO_2) / (CO + CO_2)}$$

In the steam methane reforming process, the given C : H ratio of the natural gas and the hydrogen added by steam decomposition leads to a stoichiometric number that is higher than optimal for methanol production. The surplus of hydrogen would have to be compressed and behaves as an inert gas in the synthesis loop. It increases the size of the equipment and has to be discharged with the purge gas. Thus it can only be used as fuel gas for firing. In autothermal reforming, the heat required for reforming is generated by partially combusting feedgas. Since the ATR is a pressure vessel with an inner lining, its limitations with regard to pressure and temperature are much less stringent than those of a steam reformer tube. The temperature is only limited by the thermal stability of the catalyst and of the interior lining. On the other hand, if autothermal reforming were to be applied alone, the heat required for reforming largely would be generated by free oxygen, and the resulting synthesis gas would exhibit a substoichiometric ratio.

Therefore, Lurgi combined the two processes in such a way that only the amount of natural gas is routed through the steam reformer that is required to generate a final synthesis gas with the desired stoichiometric number of about 2.05. Thus the synthesis gas demand per ton of methanol is reduced by approximately 25 percent compared with steam methane reforming. Depending on the composition of the natural gas, only about 30 percent of the hydrocarbons are converted in the steam methane reformer, and hence the steam methane reformer in the combined reforming is only about one quarter of the size of a reformer in the conventional steam methane reforming process. This means considerable savings in cost and energy. Owing to the higher pressure in the reforming section, the compression energy is reduced, and compression to synthesis pressure is possible in a single-stage compressor.

The cost saved in comparison with conventional steam methane reforming is higher than the investment for the air separation unit. Further energy savings of about 8 percent are achieved by combined reforming.

An important secondary effect is that instrument air, plant air, and nitrogen required in the plant are obtained as byproducts from the air separation unit so that no separate utility units are to be considered.

Waste Heat Recovery:-

Flue-Gas Cooling Section:-

When combined re-forming is used for the syngas production, the flue gases leaving the steam re-former tubes are routed through a duct to the flue gas waste heat recovery section.

In order to use the sensible heat of the flue gas, several heat exchanger tube banks are arranged in series. The feed preheater, which appropriately serves to heat the natural gas/process steam mixture, is arranged at the outlet of the re-former. Subsequently, superheating of high and medium pressure steam is achieved. Before the flue gases are exhausted, further cooling is obtained by simultaneously preheating combustion air. The draft necessary for reformer firing and transport of the flue gases through the waste-heat section is provided by a flue gas fan that delivers the flue gas to the stack.

Re-formed Gas Cooling Section:-

The reformed gas leaving the base of the ATR at approximately 950 to 1050°C represents a considerable source of heat with a potential for energy recovery. Directly at the outlet of the ATR the gas enters the waste heat boiler to generate saturated high pressure steam. The waste heat boiler is a horizontally arranged cooler with fixed tube sheet. It is connected to the high pressure steam drum by risers and down comers using a natural circulation system. The reformed gas leaving the waste heat boiler is cooled in the natural gas preheater while simultaneously preheating the natural gas. Reformed gas leaving the natural gas preheater is then routed to the circulation water heater, where the circulating water for the saturator is preheated. Further cooling is performed in the distillation section where the reformed gas heat is utilized for reboiler duties. Final cooling to syngas compressor suction temperature is achieved in the final cooler. During the cooling process, the gas temperature drops below the water dew point. Separation of the process condensates is achieved subsequently and the saturated reformed gas is routed to the methanol synthesis unit.

Methanol Synthesis:-

In the Lurgi MegaMethanol process methanol is synthesized from hydrogen, carbon monoxide, and carbon dioxide in the presence of a highly selective copper based catalyst. The principal synthesis reactions are as follows:

$$CO + 2H_2 \leftrightarrow CH_3OH$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

These reactions are highly exothermic, and the heat of reaction must be removed promptly from its source. This is accomplished most effectively in the Lurgi methanol reactors described below.

Efficient conversion in the methanol synthesis unit is essential to low-cost methanol production. In addition, optimal use of the reaction heat offers cost advantages and energy savings for the overall plant.

Nowadays, two types of catalytic fixed bed reactors are used in industry: steam raising reactors and gas cooled reactors. From the very beginning of the low-pressure technology era, Lurgi has been equipping its methanol plants with a tubular reactor in which the heat of reaction is transferred to boiling water.

The Lurgi Water Cooled Methanol Reactor (WCR) is basically a vertical shell and tube heat exchanger with fixed tube sheets. The catalyst is accommodated in tubes and rests on a bed of inert material. The water steam mixture generated by the heat of reaction is drawn off below the upper tube sheet. Steam pressure control permits an exact control ol'the reaction temperature. The quasi-isothermal reactor achieves very high yields at low recycle ratios and minimizes the production of by-products.

A significant improvement in synthesis technology has been achieved by combining the WCR with a downstream Gas Cooled Reactor (GCR). The so called combined converter synthesis is shown in Fig. 3.5. The excellent heat transfer in the WCR allows this reactor to operate with a high concentration of reaction components in the inlet gas. This highly concentrated gas results from a drastically reduced recycle rate.

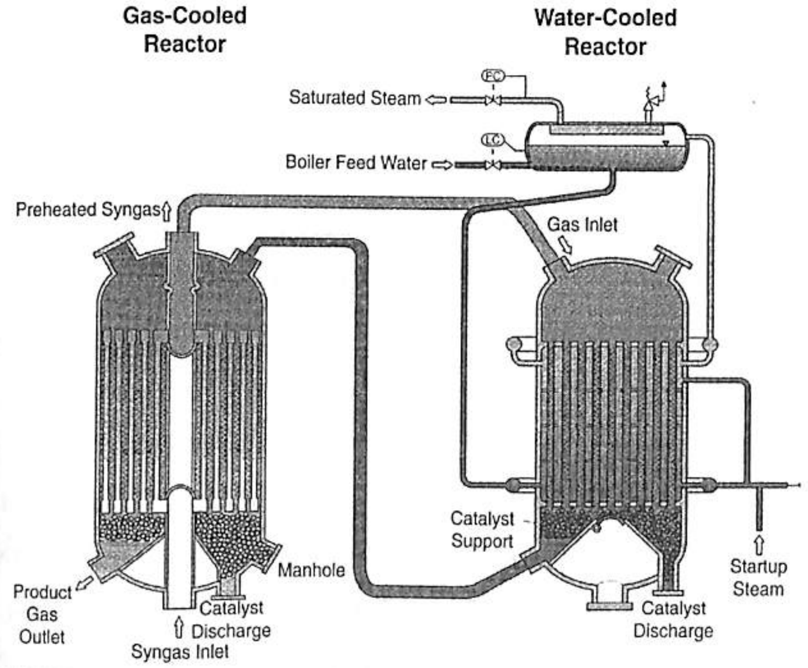


FIGURE 3.5 Combined converter synthesis.

Source: Handbook of Modern Refining Process , Robert E.Meyers

Under these conditions, a very high methanol yield is achieved in the WCR. The methanol containing exit gas of the WCR is fed to the downstream GCR. In the GCR, the reaction is accomplished at continuously reduced temperatures along the optimal reaction route. The optimal temperature profile is achieved by countercurrent preheating in the inlet gas to the WCR. The latest generation of methanol catalysts makes it possible to select an outlet temperature of the GCR of about 220°C.

Methanol Synthesis Loop:-

Since economical conversion of the synthesis gas to methanol cannot be achieved in a single reactor pass, unreacted gases are circulated in a loop, thus increasing the conversion rate. Figure 3.6 shows a typical diagram of the synthesis loop with distillation section. Recycle gas and synthesis gas are mixed and preheated in the trim heater by cooling the reactor outlet gas. Preheated recycle gas and synthesis gas are routed to the GCR. On the tube side of the GCR, the reactor inlet gas is further heated to the inlet temperature of the WCR (approximately 240°C).

Boiler water from the steam drum enters the reactor shell side at the bottom through a distributor and rises up to the outlet at the top due to a thermosyphoning effect. The steam water mixture coming out of the reactor shell side is separated in the steam drum. Saturated middle pressure (MP) steam is discharged front the steam drum via a pressure control valve, and water circulates back to the reactor. The pressure control at the steam drum outlet controls the pressure in the shell side of the reactor and thus the boiling point of water, which in turn controls the reaction temperature.

The "preconverted" gas is routed to the shell side of the GCR, which is filled with catalyst, and the final conversion to methanol is achieved at continuously reduced temperatures along the optimal reaction route. The heat of reaction is used to preheat the reactor inlet gas inside the tubes.

Aside from methanol and water vapor, the reactor outlet gas contains nonreacted H_2 ,CO and CO_2 inerts such as CH_4 and N_2 and some parts per million of reaction byproducts. This gas needs to be cooled from the reactor outlet temperature to about 40°C in order to condense and separate CH_3OH and H_2O from the gases. The hot gas is routed to the MP-BFW preheater, where the heat released is used to preheat MP boiler feed water for the steam drum. The gas stream is further used for preheating the recycle gas and the synthesis gas to the reactor in the trim heater.

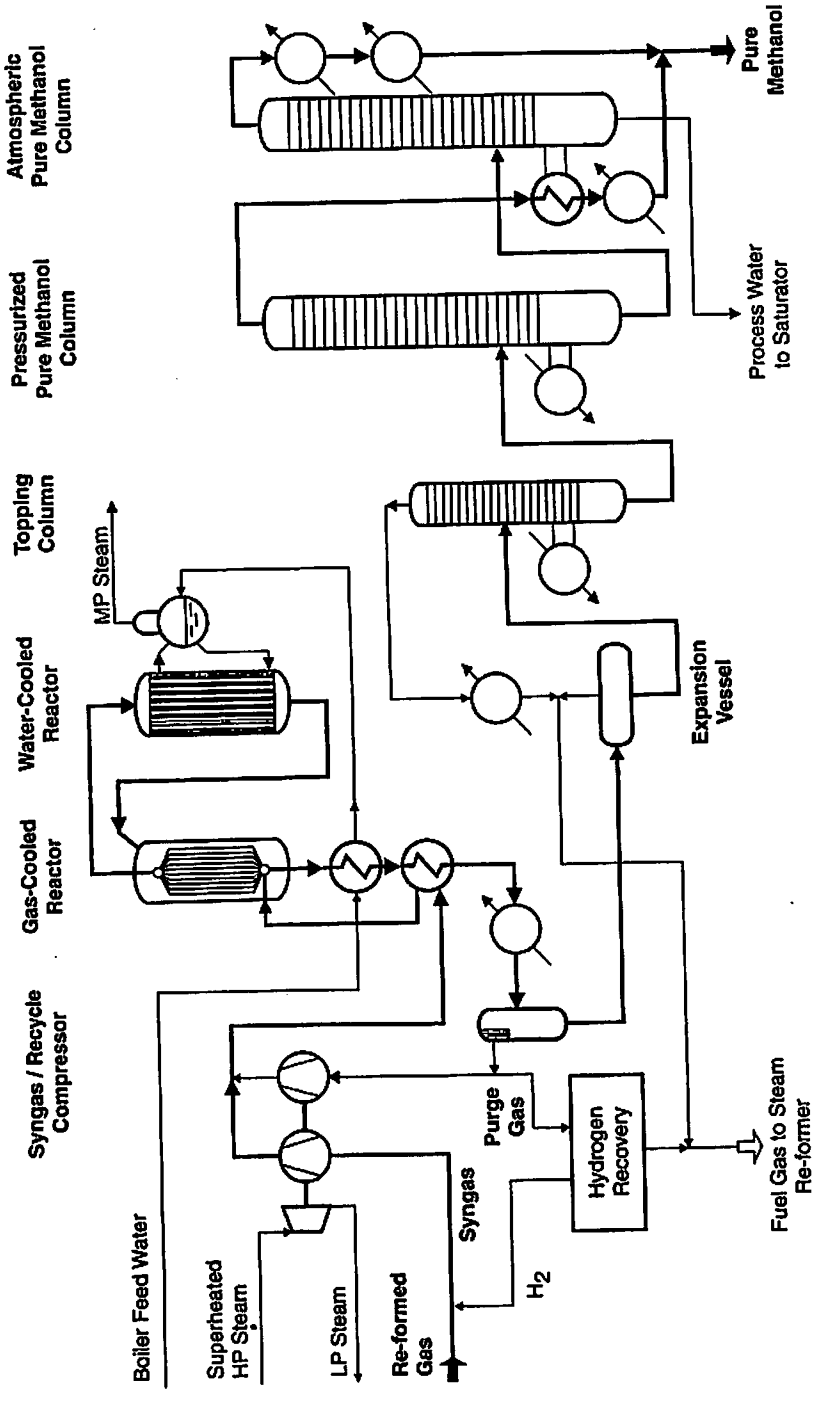


FIGURE 1.6 Methanol synthesis section with distillation.

Source: Handbook of Modern Refining Process, Robert E. Meyers

At last the gas is cooled in the synthesis air cooler and the final cooler by cooling water. Condensed raw methanol contains, apart from methanol and water, dissolved gases and reaction byproducts.

Separation of raw methanol from nonreacted gases takes place in the methanol separator. Raw methanol leaves the vessel on a level control for distillation, where pure methanol is distilled from water and other impurities. The major portion of gas is recycled back to the synthesis reactors via a recycle gas compressor in order to achieve a high overall conversion. A small portion is withdrawn on pressure control as purge gas to avoid excessive accumulation of inerts in the loop.

The major portion of the purge gas is routed to the hydrogen recovery unit, where hydrogen is recovered. The hydrogen product is mixed with the synthesis gas, whereas the remaining gas is recycled as fuel gas. During startup and shutdown, the purge gas is routed to the flare. A small amount of purge gas is used for hydrogenation of the natural gas for desulfurization.

The most important advantages of combined-synthesis converters are

- ***High syngas conversion efficiency:*** At the same conversion efficiency, the recycle ratio is about half the ratio in a single-stage, water-cooled reactor.
- ***High energy efficiency:*** About 0.8 t of 50 to 60 bar steam per ton of methanol can be generated in the reactor. In addition, a substantial part of the sensible heat can be recovered at the gas-cooled reactor outlet.
- ***Low investment cost:*** The reduction in catalyst volume for the water-cooled reactor, the omission of a large feedgas preheater, and savings resulting from other equipment due to the lower recycle ratio translate into specific cost savings of about 40 percent for the synthesis loop.
- ***High single-train capacity:*** The design of two plants has confirmed that single-train plants with capacities of 5000 MTD and above can be built.

Methanol Distillation:-

The raw methanol produced in the methanol synthesis unit contains water, dissolved gases, and a quantity Of undesired but unavoidable by-products that have either lower or higher boiling points than methanol. The purpose of the distillation unit is to remove those impurities in order to achieve the desired methanol purity specification. A three-column methanol distillation is shown in Fig. 3.7

This is accomplished in the following process steps:

- Degassing
- Removal *of* low-boiling by-products
- Removal *of* high-boiling by-products

Dissolved gases are driven out of the raw methanol simply by flashing it at a low pressure into the expansion-gas vessel. Removal of light ends and remaining dissolved gases is carried out in a light ends column. Finally, the methanol is separated from the heavy ends in a pure methanol distillation section consisting of one or two columns. The split *of* the refining column into two columns allows for very high single-train capacities. Methanol purity remains unaffected, whereas the single-train capacity, consumption of steam, and investment cost depend on the distillation concept.

The first pure methanol column operates at elevated pressure and the second column at atmospheric pressure. The overhead vapors of the pressurized column heat the sump of the atmospheric column. Thus about 40 percent of the heating steam and, in turn, about 40 percent of the cooling capacity are saved. The split of the refining column into two allows for very high single train capacities.

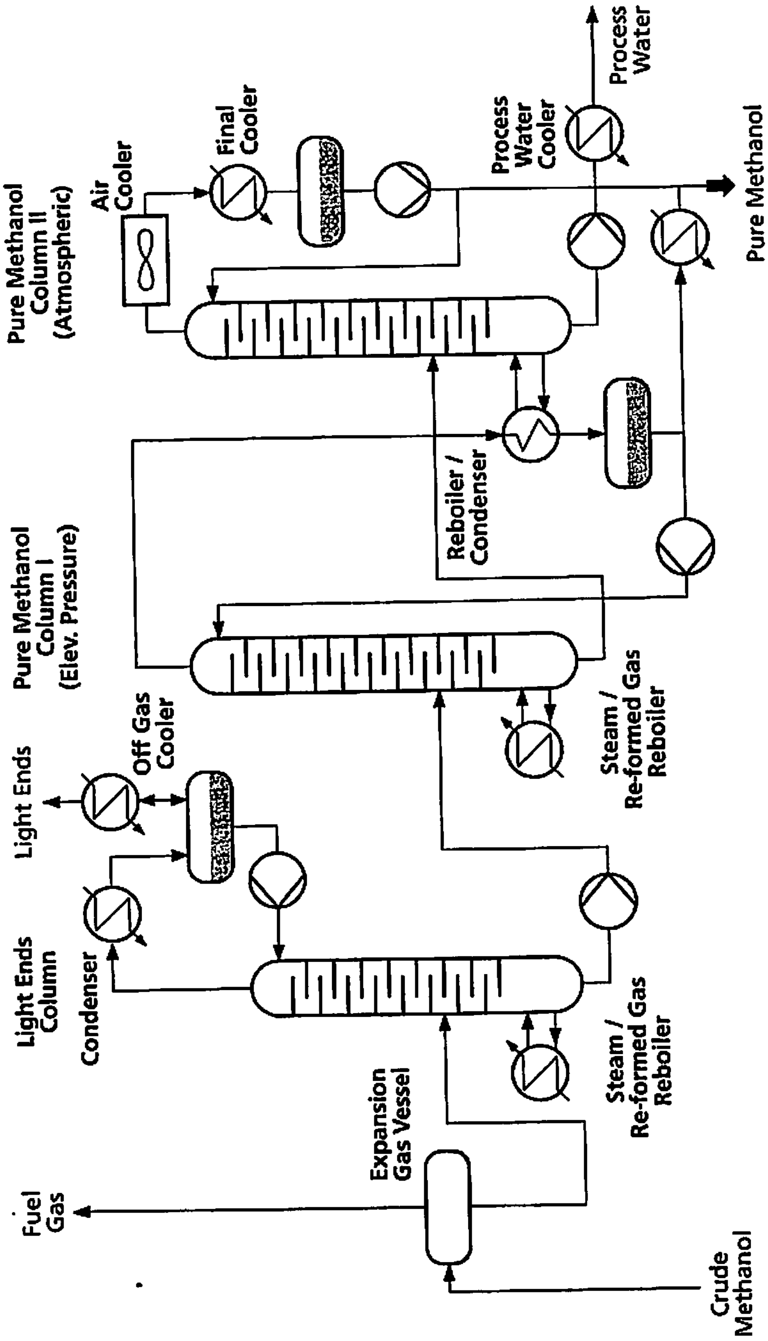


FIGURE .1.7 Three-column methanol distillation.

Source: Handbook of Modern Refining Process , Robert E.Meyers

LURGI METHANOL PROJECTS

1) Methanex, United States,1700 MTD,1992.
2) Statoil, Norway, 2400 MTD,1992.
3) CINOPEC, China, 340 MTD, 1993.
4) KMI, Indonesia, 2000 MTD,1994.
5) NPC, Iran, 2000 MTD, 1995.
6) Sastech, South Africa, 400 MTD, 1996.
7) Titan, Trinidad, 2500 MTD, 1997.
8) PIC, Kuwait, 2000 MTD,1998.
9) YPF, Argentina, 1200 MTD, 1999.
10) Atlas, Trinidad, 5000 MTD, 2000.
11) ZAGROS, Iran, 5000 MTD, 2000.
12) Methanex, Chile, 2400 MTD, 2002.
13) ZAGROS II, Iran, 5000 MTD, 2004.
14) Hainan Methanol, China, 2000 MTD, 2004.
15) QAFAC, Qatar, 6750 MTD, 2004.

3.2 SYNETIX LEADING CONCEPT METHANOL (LCM) PROCESS

This process has been developed around the Synetix Advanced Gas Heated Reformer (AGHR), which is a compact tubular reformer, and Synetix's Low Pressure Methanol process for methanol synthesis. This process is applicable for offshore applications, as it is safe and practicable. The ability to manufacture liquid fuels via synthesis gas offshore on floating facilities has always been restricted by the unsuitability of conventional steam reforming processes. The AGHR coupled with a Secondary Reformer have the following benefits: compact size, resistant to motion, and self-contained. LCM therefore provides an opportunity to monetize stranded gas, add value to marginal oil discoveries, and convert flared gas to marketable liquids.

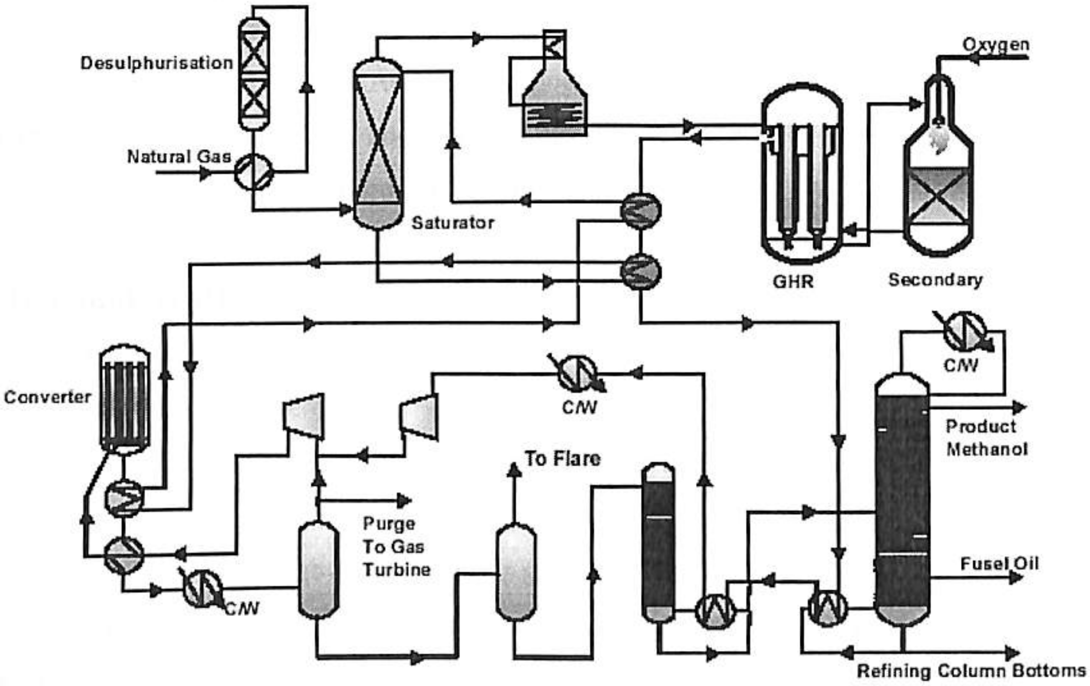


Fig 3.8 Typical lay out of an LCM flow sheet
Source: www.synetix.com

Synthesis Gas Production:-

The feedstock natural gas is desulphurised prior to entering the saturator, where the natural gas is contacted against process water, heated using the reformed gas exit the shell side of the AGHR, the water cooled converter and sometimes the gas turbine duct. The arrangement of the saturator circuit provides the entire process steam requirement thus completely eliminating the need for a steam system.

The mixed natural gas and steam is heated prior to entering the AGHR. Here the gas is interchanged against the effluent of the secondary reformer while passing through a bed of reforming catalyst contained within the tubes of the AGHR. Approximately 25% of the natural gas is converted to carbon oxides by the time it leaves the AGHR. On leaving the AGHR, the gas then passes to oxygen blown secondary reformer where the remainder of the natural gas is reformed over a bed of catalyst. The effluent from the secondary is around 1000°C and contains approximately relatively low levels of unconverted methane. This passes back to the shell side of the AGHR to provide the heat into the mixed natural gas and steam reacting inside the tubes.

The effluent from the AGHR next goes through a series of heat exchangers to maximise heat recovery and cool the gas stream, at the end of which condensate is removed and the dry gas compressed to synthesis pressure of 80 bar.

Methanol Synthesis:-

The synthesis loop comprises of a circulator, converters (a Tube Cooled Converter would preferentially be used for the main converter), feed/effluent interchanger, saturator water-cooled reactor, a crude cooler and knock out pot. To get high conversion, the effluent gas (after the methanol has been knocked out) is circulated back and mixed in with the fresh synthesis gas.

The mixed gas is first preheated in an interchanger before entering the reactor where carbon oxides and hydrogen react to form methanol and water. After the main converter, heat is recovered into the saturator water circuit via the water cooled reactor and then into the converter feed. Finally the effluent passes through a crude cooler which gets the temperature as low as possible before entering the loop catchpot to separate off the crude methanol. Any unconverted gas is either recycled back to the synthesis reactors or purged from the process to keep the inerts to manageable levels within the synthesis loop.

Distillation:-

The crude methanol from the synthesis loop contains both water and low levels of by-products, which must be removed to achieve required product purity. Synetix offer both two and three column designs, which can easily achieve US Federal AA grade purity product. The US Federal AA grade specification is the most commonly accepted specification in world methanol trade. Product grades are outlined in the table below.

In a two-column system, the first column removes light impurities such as the ethers, esters, acetone and lower hydrocarbons and dissolved synthesis gases, and the second column removes the water, higher alcohols and higher hydrocarbons.

Product Specifications :-

There are different specifications set for methanol on the open market. The table below gives an overview of the most important methanol specifications.

Characteristic	Federal Grade		IMPCA	Method[1]
	A	AA		
Acetone[2] (ppm w/w)	30.	20.	30.	ASTM E 346-92
Acidity (ppm w/w as acetic acid)	30.			ASTM D 1613-85
Appearance	Free of opalescence, suspended matter and sediment		Clear and free of suspended matter	Visual
Carbonizable impurities colour, Pt-Co scale, maximum	No. 30			ASTM E 346-92
Colour, Pt-Co scale, maximum	No. 5			ASTM D 1209-84
Distillation range at 760 mm Hg	1°C and shall include 64.6°C±0.1°C			ASTM D 1078-86
Ethanol (ppm w/w)	—	10	50	ASTM E 346-92
Non-volatile matter	10 mg/100 ml		10 mg/kg	ASTM D 1353-90
Odour	Characteristic with no residual			ASTM D 1296-84
Permanganate fading time (mins)	30		60	ASTM D 1363-88
Specific gravity at 20°C /20°C	0.790		0.791 to 0.793	ASTM D 891-86
Water (% w/w)	0.15	0.1	0.1	ASTM E 1064-92 or ASTM E 346-92
Purity (% w/w)	—	—	99.85	IMPCA 001-92
Chloride (ppm w/w)	—	—	0.5	IMPCA 002-92
Sulphur (ppm w/w)	—	—	0.5	ASTM D 3961-89
Hydrocarbons[3]	—	—	pass test	ASTM D 1722-90
Total Iron (ppm w/w)	—	—	0.1	ASTM E 394-91

[1] The references given here are those applicable to the IMPCA spec.

[2] Strictly in the IMPCA spec. this is "carbonilic compounds".

[3] This test is a water-miscibility test and involves mixing 15 ml of methanol with 30 ml of water and observing it for 30 minutes.

Table 3.1 Product methanol specifications , Source: www.synetix.com

Heat Recovery:-

The heat recovery scheme for an LCM plant can be much simpler than for a conventional reforming plant since there is no flue gas duct system and a greatly reduced reformed gas cooling system. The gas turbine duct provides a useful source of heat for preheating the mixed natural gas and steam feed to the AGHR, vaporizing the liquid oxygen feed and topping up the heat into the saturator water circuit if required. Heat is recovered from the reformed gas cooling train into saturator water circuit, into the natural gas feed prior to desulphurisation and into distillation. Loop heat is also recovered into the saturator water circuit and into distillation.

Efficiency and Utilities Consumption:-

Typical process efficiencies and utility consumption derived from other studies based upon similar feedstocks are as shown in the table below for both the Low Pressure Methanol Process (LPM) and the Leading Concept Methanol (LCM) Technology. The total gas usage is indicative of what would be required for the whole plant (including offsites and utilities) although the exact figure will depend upon the precise design adopted.

Typical Consumption Figures

		LPM	LCM
Total gas use	GJ/te	33.5	29.5
Oxygen	te/te	0	0.47
BFW import	te/te	0.63	0.11
Cooling water circulation	te/te	60	60

As you can see the newer process is more efficient and has lower water consumption at the expense of requiring an air separation unit to provide liquid oxygen.

The Tube Cooled Converter:-

Design:-

In this design, circulating synthesis gas enters at the base of the reactor into the manifold system, which distributes gas to the tubes of the internal heat exchanger. Synthesis gas is heated using the heat of reaction developed on the shell side of the converter as it passes up the tubes. The gas then enters the catalyst bed and reaction commences.

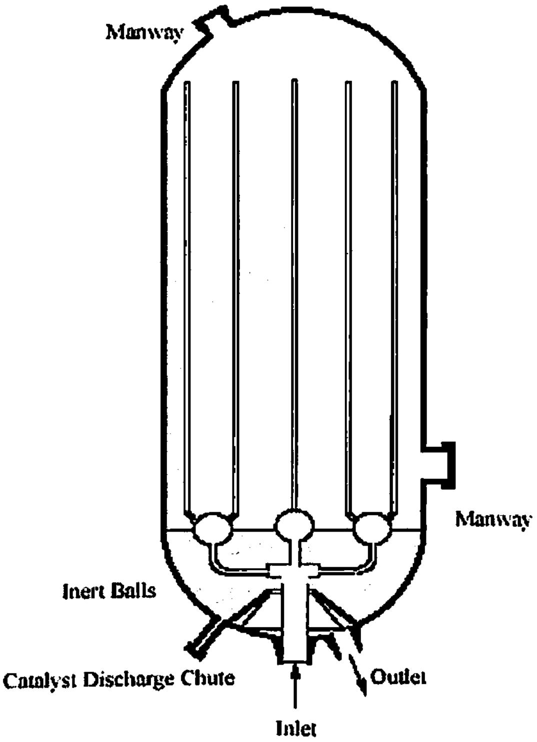


Figure 3.9 - Synetix TCC
Source: www.synetix.com

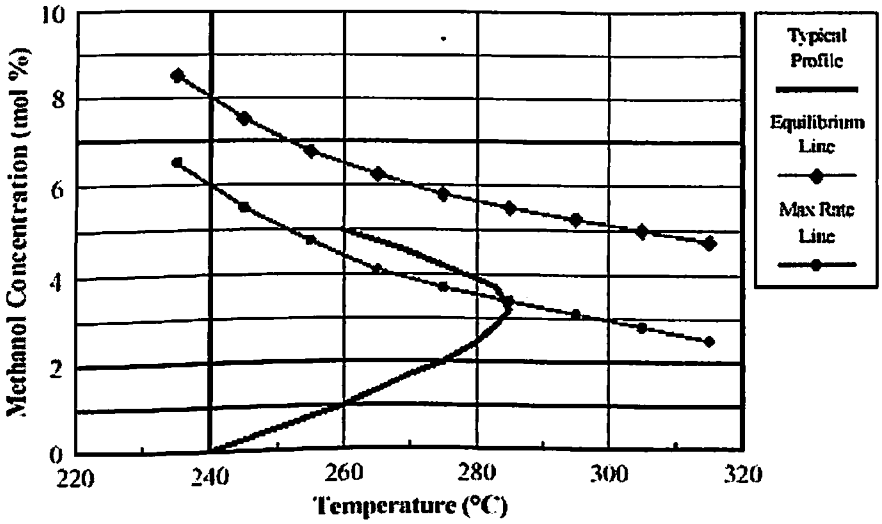


Fig 3.10 TCC: Methanol equilibrium profile
Source: www.synetix.com

Mixing System:-

In order to ensure the best possible temperature uniformity across the bed of catalyst in the TCC, a mixing system has been devised both for new converters and for retrofits. This minimises the hot and cold regions that could otherwise occur within the catalyst bed during operation and which would lead to more rapid catalyst deactivation and high by-product levels.

Features

The Tube Cooled Converter combines the hot loop interchanger within the methanol synthesis reactor bed and so eliminates a pressure shell. As a result this type of loop is cheapest configuration available. As with the original quench converter, catalyst loading and discharge is easy, as the bed is continuous. Tube Cooled Converters are very simple to operate since only the turn temperature has to be controlled.

Synetix Water Cooled Converter:-

Synetix have patented a new synthesis loop configuration comprised of a conventional converter, either a tube cooled converter or a quench reactor in series with a water-cooled converter. When this arrangement is coupled with a saturator circuit, many benefits can be achieved including a lower circulation ratio that requires less power in the circulator compressor, reduced diameter in all of the equipment in the loop and enhanced heat recovery into the saturator water circuit.

CHAPTER-4

PRODUCTION OF OLEFINS FROM METHANOL

Changing natural gas into olefins is a two-step process. The first step, converting natural gas to crude methanol, The second step, transforming the resulting methanol into olefins. The MTO process primarily converts the methanol into ethylene and propylene. Ethylene and propylene are in increasing demand worldwide and have significant financial value in the marketplace.

MTO is part of a two-step process, which converts natural gas to methanol followed by the conversion of methanol to light olefins.4 MTO projects are driven by the desire to monetize stranded gas and the market demands for ethylene and propylene and their derivatives. Stranded natural gas prices are generally independent of crude oil and naphtha market prices so MTO provides another means for olefin derivative producers to diversify the cost structure for their feedstocks. MTO can provide much lower costs of production and higher returns on investment. Methanol to olefins process provides an economical means to convert natural gas to olefins.

4.1 LURGI MTP TECHNOLOGY

PROCESS OVERVIEW:-

Lurgi's new MTP process is based on an efficient combination of the most suitable reactor system and a highly selective and stable zeolite-based catalyst. Sud-Chemie AG manufactures this catalyst commercially; it provides maximum propylene selectivity and has a low coking tendency, a very low propane yield, and also limited by-product formation. This, in turn, leads to a simplified purification scheme that only requires a reduced cold box system as compared with on-spec ethylene-propylene separation.

Based on Fig. 4.1 a brief process description reads: The methanol (MeOH) feed from the MegaMethanol plant is sent to an adiabatic DME prereactor, where methanol is converted to dimethylether (DME) and water. The high-activity, high-selectivity catalyst used nearly achieves thermodynamic equilibrium. The methanol -water-DME stream is routed to the first MTP reactor stage, where steam is added. Methanol and DME are converted by more than 99 wt %, with propylene as the predominant hydrocarbon product. Additional reaction proceeds in the subsequent five MTP stages. Process conditions in the six MTP reactor stages are chosen to guarantee similar reaction conditions and maximum overall propylene yield. The product mixture is then cooled, and the product gas, organic liquid, and water are separated.

The product gas is compressed, and traces of water, CO_2 and DME arc removed by standard techniques. The cleaned gas is then further processed, yielding chemical-grade propylene with a typical purity of more than 97 wt % or, if specified as polymer-grade, 99.6 wt %. Several olefin-containing streams are sent back to the main synthesis loop as an additional propylene source. To avoid accumulation of inert materials in the loop, small purges are required for light ends and the C_4 / C_5 Cut. Gasoline is obtained it's an important by-product.

Water is recycled to steam generation for the process; the excess water resulting from the methanol conversion is purged. This process water can be used as raw-water supplement or for irrigation after appropriate and inexpensive biologic treatment. It can even be processed to potable water where needed.

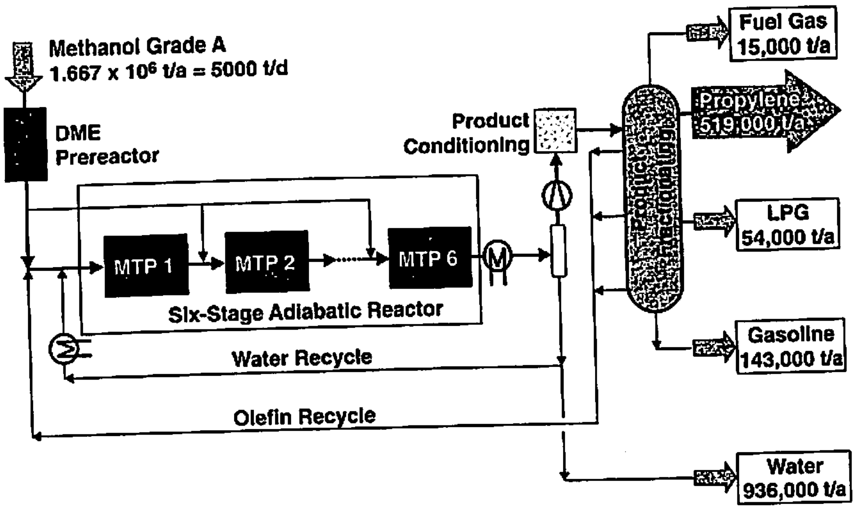


Fig 4.1 Simplified block flow diagram

Source: Handbook of Modern Refining Process, Robert E.Meyers

An overall mass balance is depicted in Fig. 4.1 based on a combined MegaMethanol /MTP plant. At a feed rate of 5000 t of methanol per day (1.667 million tons annually), approximately 519,000 t of propylene is produced per year. By-products include fuel gas and LPG, as well as liquid gasoline and process water.

DETAILED PROCESS DESCRIPTION:-

The detailed process description is related to the block flow diagram of the MTP plant (Fig. 4.2). It describes the process flow of reaction, compression, and product separation, thus giving an overview of the MTP process.

DME Reactor:-

The major part of the methanol feed is vaporized, superheated, and fed into the DME reactor. A smaller part of the feed methanol is used as solvent for purification within the DME removal section.

The DME reactor is a single-stage adiabatic reactor where most of the methanol vapor is dehydrated to dimethylether (DME) on an aluminum oxide catalyst (γ-Al_2O_3) according to the following equation

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

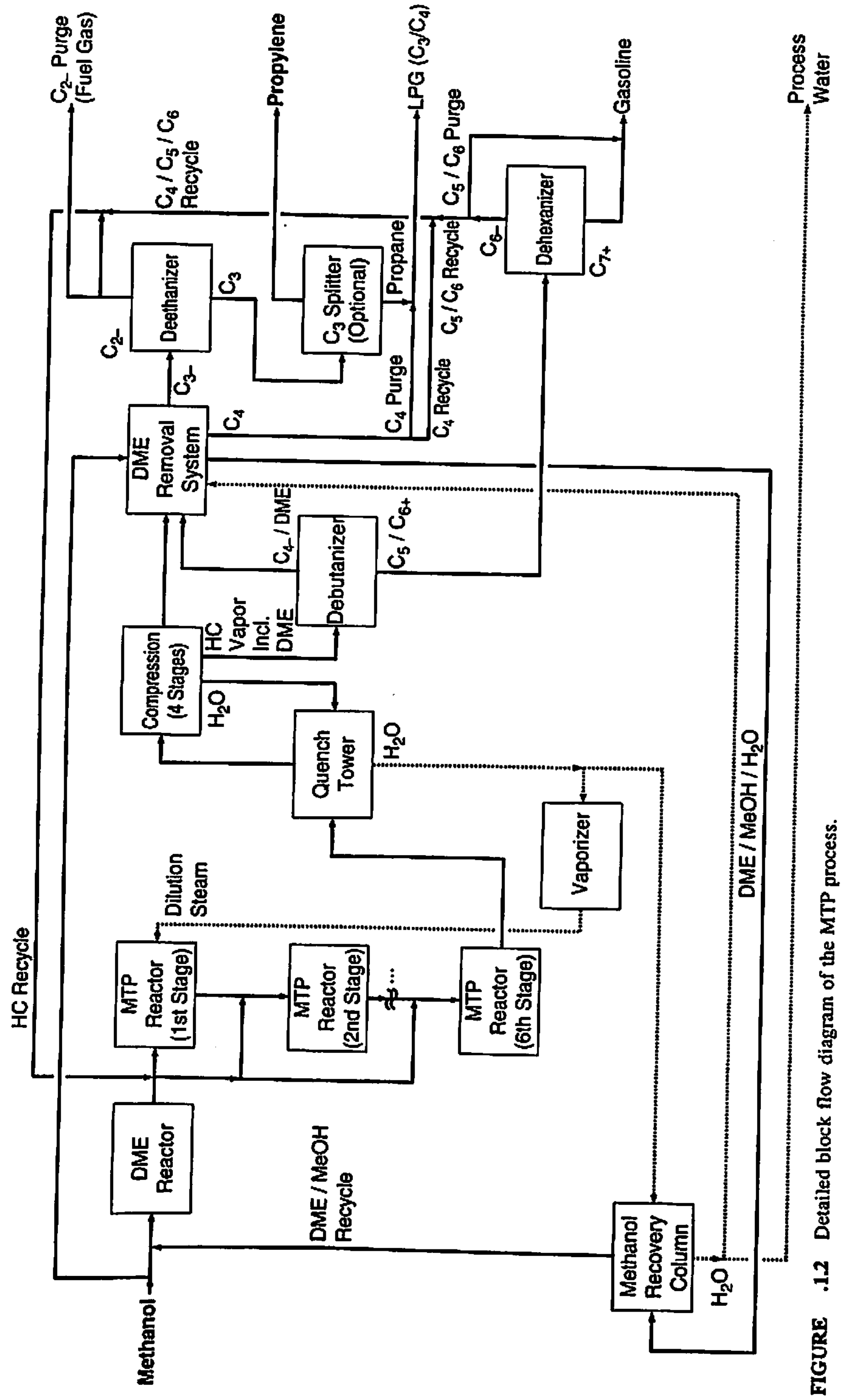


FIGURE .12 Detailed block flow diagram of the MTP process.

Source: Handbook of Modern Refining Process, Robert E. Meyers

The catalyst features high activity and high selectivity, achieving almost thermodynamic equilibrium. The reaction is exothermic, and the reaction equilibrium is nearly independent of the operating pressure. The process is designed for a high conversion rate at moderate operating conditions.

Besides fresh methanol vapor, a recycle stream also consisting of methanol, DME, and some water is fed to the DME reactor. This stream is the overhead product of the methanol recovery column, which recovers methanol and DME from aqueous phases.

MTP Reactor:-

For a better approach to isothermal conditions, the MTP reactor was designed with six stages including six catalyst beds. The product of the DME reactor is divided into six streams, each feeding one of six stages of the MTP reactor. The feed to the first MTP reaction stage is mixed with a hydrocarbon recycle stream and some recycle steam. The mixture is further heated and then introduced into the MTP reactor.

In the MTP reactor, the DME-MeOH mixture is converted to olefins on a Zeolite-based catalyst according to the following summary reaction:

$$\mathbf{nCH_3OCH_3 \rightarrow 2\,C_nH_{2n} + n\,H_2O} \quad n = 2, \ldots, 8$$

The MTP catalyst converts nearly all the DME-MeOH mixture with a high selectivity toward low-molecular-weight olefins. About 85 wt % of the carbon from the fresh feed (DME or MeOH) reacts to olefins in the range of C_2 to C_8 with the peak for propylene.

The quantity of fresh DME-MeOH fed to each catalyst bed is adjusted in such a way that the adiabatic temperature rise caused by the heat of the exothermic reaction is the same for each bed. This guarantees similar reaction conditions, resulting in maximum overall yield of low-molecular-weight olefins.

The above-mentioned high selectivity toward olefins requires relatively high operating temperature over the catalyst beds and low operating pressures.

The intermediate reaction products from stages 1 to 5 are cooled and mixed with additional fresh DME-MeOH feed before entering the next reaction stage. During operation, small amounts of heavy hydrocarbons are formed that partly block the active sites of the catalyst. In order to minimize the carbonization process, steam is added to the feed of the first MTP reaction stage. The steam also serves as a heat sink for the exothermic reaction and thus supports control of the temperature rise over the catalyst.

The hydrocarbon recycle to the first MTP reaction stage increases the propylene yield by conversion of olefins with a carbon number lower or higher than 3 (propylene). In addition, the hydrocarbons serve as a heat sink for the exothermic reaction, again supporting temperature control over the catalyst.

The MTP reactor catalyst has to be regenerated when the overall conversion of the DME-MeOH feed falls below the economical limit. The regeneration is done *in situ* by controlled combustion of coke with an air-nitrogen mixture. In order to ensure continuous operation of the plant, the design consists of three MTP reactor trains. Two trains are in operation while one train is in regeneration or in standby mode.

A simplified reaction model for the methanol conversion is shown in Fig. 4.3. It is assumed that a so-called reactive pool exists on the zeolite surface that contains CH_2 fragments. It is very unlikely that isolated CH_2, species are actually formed, but for illustrative purposes, it can be assumed that this pscudospecies is formed by dehydration of methanol (or DME) and serves as a building block for all olefinic products in the MTP reaction. In addition, almost all reaction products can be converted on the catalyst, so this reactive pool is filled from several sources, with methanol-DME being the most prominent one.

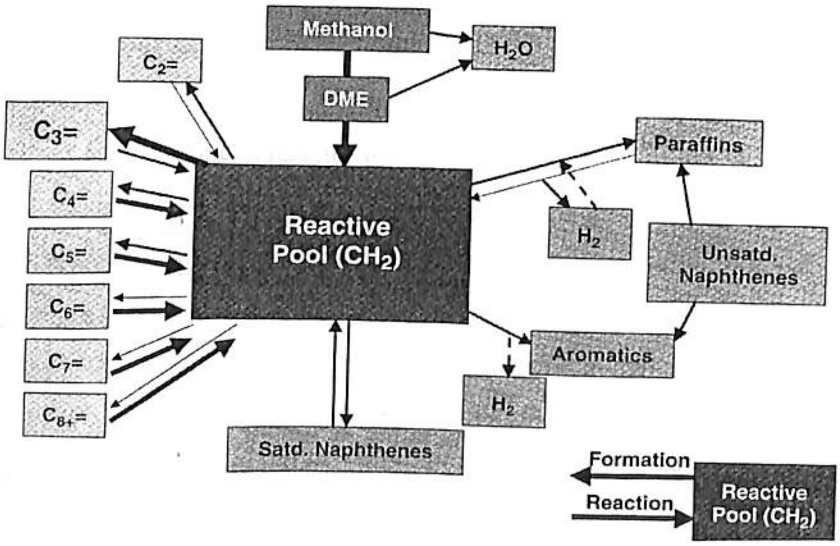


Fig 4.3 Simplified reaction model

Source: Handbook of Modern Refining Process , Robert E.Meyers

The actual selectivities of the MTP reaction and the overall product distribution, i.e., the relative reaction rates from the reactive pool to each single product species, are an inherent feature of the specific catalyst used and depend on its pore and atomic Structure. The catalyst used in the MTP process was optimized for maximum propylene yield and maximum total olefin selectivities.

Similar reactive pools are widely described in the literature for hydrocarbon reactions on zeolites, and their existence has been proven by isotope-exchange experiments.

Quench Tower and Water Stripper:-

The product leaving the reactor contains naphthenes, paraffins, aromatic components, and light ends, as well as olefins and process and reaction water. The hydrocarbon yield based on converted fresh DME-MeOH feed is 85 wt % olefins, about 9 wt % paraffins, less than 3 wt % aromatic compounds, and less than 2 wt % naphthenes, as well as light components (H_2, CO, CO_2). The reaction product is cooled in heat exchangers and finally in the quench tower, where the hydrocarbon product is separated from most of the water. The hydrocarbons leave the quench tower as overhead vapor, whereas the water is condensed and sent to the methanol recovery column.

The reactor product leaves the MTP reactor at a low pressure and has to be sent to the first compressor stage with a very small pressure drop. The use of an additional cooler and separator instead of the quench tower, with its virtually negligible pressure loss, therefore would cause problems with the maximum permissible pressure drop.

In addition to the components mentioned earlier, the reaction over the zeolite-based catalyst forms small amounts of organic acids such as acetic acid and propionic acid. Prior to withdrawal, process water, having a pH in the range of 3 to 4, is neutralized by adding caustic solution to the quench tower sump. The smaller portion of the water condensate is vaporized and recycled as dilution steam to the first MTP reaction stage, whereas the major portion of process water is routed to the methanol recovery column for recovery of methanol and DME. The stripped water containing about 3500 wt ppm of methanol is routed to battery limits as process water. It can be biotreated easily to supplement raw water or for use as irrigation water. A smaller portion of the process water from the methanol recovery column is recycled into the process for use as a solvent in the DME removal system.

Compression:-

The hydrocarbon vapor product from the quench tower is compressed by a multiple-stage turbo compressor. Between the compression stages, the product is cooled, and residual water, as well as hydrocarbon liquid, is separated from the vapor phase, which is compressed further. Residual water is recycled to the quench tower, whereas hydrocarbon liquid and hydrocarbon vapor are sent to a dryer each, which is not shown in the block flow diagram of the MTP plant. The dryer removes the remaining water by adsorption on mole sieves.

Separation:-

The dried hydrocarbon liquid is fed to the debutanizer column, whereas the dried hydrocarbon vapor is further processed in the DME removal system. The debutanizer distillation column separates light-boiling components C_{4-} and DME from C_{5+} hydrocarbons. The C_{5+} bottoms product is fed to a dehexanizer distillation column, where light naphtha components in the range of C_5 and, C_6 are separated from a heavier gasoline fraction that contains C_{7+} hydrocarbons (paraffins, olefins, naphthenes) and the alcylated benzene derivatives toluene, xylene, and trimethylbenzene.

The C_5 / C_6 overhead product (paraffins, olefins, naphthenes) is mainly recycled to the first MTP reaction stage for further conversion of higher olefins to propylene; a smaller portion is purged out the reaction loop. The C_5 / C_6 purge stream is usually added to the C_{7+} fraction, forming the gasoline by-product.

The compressed and dried hydrocarbon vapor-including light olefins and DME and the C_{4-} / DME overhead product from the debutanizer are both feed of the DME removal system. There, C_{3-} hydrocarbons are separated from C_4 hydrocarbons. In addition, DME is removed from the hydrocarbons. The overhead product C_{3-} is free of DME (< 1wt ppm) or any other oxygenate component. It is fed to the deethanizer distillation column.

The aqueous phase leaving the unit contains methanol and DME and is recycled to the methanol recovery column. The C_4 hydrocarbon fraction, now purified from most oxygenate components, is recycled to the MTP reaction system for further conversion of butenes to propylene. A smaller portion is purged out the reaction loop, forming a C_4 LPG by-product.

In the deethaniser distillation column, the C_{3-} hydrocarbon fraction is split into C_{2-} (Containing ethylene, ethane and some light-ends methane, hydrogen, CO, and CO_2) and the C_3 product containing propylene (about 97 wt %) and propane (about 3 wt %) but no unsaturated components such as methylacetylene or propadiene (the analyzed concentration of these is less than 1wt ppm). Alternatively, depending on the propylene specification requirement, the MTP process produces chemical grade propylene as deethanizer bottoms product or polymer-grade propylene by use of an additional C_3 splitter distillation column that separates pure propylene (99.6 wt %) from the by-product propane. Usually the by-products propane and C_4 LPG are mixed to form a C_{3-} and C_{4-}

containing LPG product.

The C_{2-} product from the deethanizer overhead consists of two streams of different composition. At first, the overhead vapors of the deethanizer are compressed in a single stage compressor from the column operating pressure to an elevated pressure. Then the overhead product is partially condensed by means of propylene refrigerant. In the reflux drum the noncondensable vapor stream is separated from the liquid. The noncondensable vapor stream is withdrawn as first overhead product of the deethanizer. The condensed liquid is used in part as reflux to the column, whereas the remaining portion is taken off the column, forming the second overhead product of the deethanizer. The noncondensable vapor product is richer in light-end components (methane, hydrogen, CO, and CO_2). Therefore, it is purged off the reaction loop and used internally as fuel gas. The liquid overhead product is richer in ethylene. It is vaporized, routed to an adsorber filled with mole sieves for CO_2 removal (not shown in the block flow diagram of the MTP plant), and then recycled to the MTP reaction system for further conversion of ethylene to propylene. CO_2 is separated from the C_{2-} recycle stream to reduce the buildup of this component.

Products, Byproducts, Wastes & Emissions

The products, byproducts, wastes and emissions listed below refer to a feed rate of 5000 t/d of methanol (fig 4.1).

Product

Propylene : 64,875 kg/h

Polymer grade : 99.6 wt

By-products

Gasoline: 17,875 kg/h

Composition:

- Olefins: about 20 wt%
- Paraffins: about 50 wt%
- Aromatics (methylated benzene derivatives): about 30 wt%
- No benzene
- No sulfur

An analysis of gasoline was made by Statoil refinery laboratory in Norway. The analyzed gasoline was received from the demo unit at Tjeldbergodden, Norway. The values were stated as approximately "unlead3d premium", which defines a typical gasoline with a research octane number (RON) of 95 and a motor research number (MON) of 85.

LPG: 6750 kg/h

Process water: 117,000 kg/h

for use as raw-water supplement or as irrigation water after biotreating; the fuel gas is used internally.

Wastes

The catalyst of the DME reactor is an aluminum oxide catalyst (y-AI,O,) with an expected lifetime of 10 years, whereas the catalyst of the MTP reactor is a zeolite-based catalyst with a life of more than 1year. Both catalysts are easily disposable as landfill after use.

Emissions

The only emissions of note are the "standard" flue gases from gas-fired heaters and boilers and the catalyst regeneration gas, which basically consists of nitrogen-diluted air with a somewhat elevated CO_2 content.

TECHNICAL AND COMMERCIAL STATUS

The technological status of MTP in the areas of process and catalyst can be summarized as follows: The basic process design data were derived from more than 9000 operating hours of a pilot plant at Lurgi's Research and Development Center. Besides optimization of reaction conditions, several simulated recycles also have been analyzed.

Parallel to this, Lurgi has opted to build a larger-scale demonstration unit to test the new process in the framework of a world-scale methanol plant with continuous 24/7 operation using methanol feedstock from an existing plant. The main purpose of the test was to demonstrate that the catalyst lifetime meets or exceeds the commercial target of 8000 hours on stream. After a cooperative agreement with Statoil ASA was signed in January 2001, the demo unit was assembled in Germany and then transported to the Statoil methanol plant at Tjeldbergodden, Norway, in November 2001 .Later in 2002, Borealis joined the cooperation.

The demo unit was started up in January 2002, and the plant has been operated almost continuously since then. By April 2004 the on-stream time of the first catalyst batch had reached 8000 hours, and 3000 hours more had been used for tests with a new batch.

Cycle lengths between regenerations have been longer than expected. Deactivation rates of the methanol conversion reaction decreased with operation time. Propylene selectivity and yields were in the expected range for this unit, with only a partial recycle. To verify the full recycle of all light and heavier olefins, a bench-scale unit with a complete purification section will be installed at Lurgi's R&D center. This also will prove again the polymer-grade quality of the product, i.e., the absence of polymerization poisons. This was first demonstrated by producing polypropylene cups from a batch of MTP propylene that was distilled offline at the R&D center and then polymerized in Borealis' labs.

The gasoline product of the demo unit was analyzed in a Statoil refinery lab that reported the sample to have "premium gasoline quality." The catalyst development is completed, and the supplier commercially manufactures the catalyst, which is already used in a similar application.

Integrating all these favorable results and conditions allowed Lurgi to prepare commercial designs for middle- and large-scale MTP plants. These designs were the basis for thorough in-house costing and benchmarking. Client feasibility studies for large polypropylene complexes have been concluded. With that, Lurgi today offers MTP on commercial terms. By July 2004 negotiations for the first commercial size MTP plant were in the final stage.

PROCESS ECONOMICS

Since propylene itself is more an intermediate than an end product, an economics estimate was performed for a methanol-propylene-polypropylene complex. This just needs the addition of a block polypropylene synthesis to Fig. 4.1.

Thus the economic assessment included the MTP route with a polypropylene unit for the production of a more salable, higher-value end product. The case presented here is based on a feasibility study for a complex in the Middle East/Arabian Gulf region. It takes into account contingencies for the newly developed route. With that, the investment cost estimate is fairly high, and still an attractive return can be expected, as shown in Tables 4.1. and 4.1. The price basis for the investment cost estimate is the third quarter of 2002.

The remarkable facts here are the low production costs for the "intermediates" methanol and propylene and for the end product polypropylene. These leave room for healthy profit margins and for new applications such as MtPower (the direct use of methanol or DME in power generation) and MtSynfuels, the MTP-based route to diesel fuel and gasoline.

Given the fact that MegaMethanol plants are built for around US$300 to US$320 million in investment cost and that contingencies may be outweighed by additional integration savings or may not be needed in full, this route is seen as the most promising and most economical natural gas utilization.

TABLE 4.1 Production Cost: Integrated MegaMethanol-MTP-PP Complex

	Methanol	MTP	PP
Capacity, TPY	1,700,000	520,000	520,000
Investment cost EPC, million US$	350	215	165
Owner's cost, incl. capitalized interest, million US$	70	43	33
Feed cost, US$	Natural gas $0.5/MMBtu	Methanol $43/t	Propylene $174/t
Production cost, US$/t	42.9	210.1	261
Raw materials, US$/t	14.4	150.3	212.8
Utilities, US$/t	1.6	5.6	6.8
Operation and maintenance, US$/t	5.6	11.3	8.6
Plant OVHD and insurance, US$/t	6.0	12.1	9.2
Depreciation, US$/t	15.3	30.8	23.6
Credit for by-product naphtha, US$/t	—	−35.7	—
Cost of product at ROI = 0, US$/t	43	174	261

Source: Handbook of Modern Refining Process, Robert E. Meyers

TABLE 4.2 ROI: Integrated MegaMethanol-MTP-PP Complex

	Methanol-MTP-PP
Investment cost EPC, million US$	730
Owner's cost incl. capitalized interest, million US$	146
Feed stock cost, US$	Natural gas $0.5/MMBtu
Production cost, million US$	154.3
Raw materials, million US$	49.7
Utilities, million US$	9.1
Operation and maintenance, million US$	19.9
Plant OVHD and insurance, million US$	21.2
Depreciation, million US$	54.4
Revenues, million US$	356.6
Naphtha (US$130/t), million US$	18.6
Polypropylene (US$650/t), million US$	338
Return on investment (ROI, %)	23.1

Source: Handbook of Modern Refining Process, Robert E. Meyers

4.2 UOP/HYDRO MTO PROCESS

INTRODUCTION:-

The conversion of natural gas into syngas is the first step in utilizing natural gas for methanol and for the conversion of gas to liquids hydrocarbon products. Methanol as a base chemical offers limited opportunities for natural gas utilization unless linked to other derivative markets. Gas-to-liquids (GTL) technology using Fischer-Tropsch type of catalysts offers large market Opportunities for natural gas utilization but is challenged by the economics of high capital costs with relatively low transportation fuel product values.

Syngas and methanol production technologies are achieving greater economies of scale. World-scale methanol production facilities have doubled in size compared to just a few years ago, and when combined with remote natural gas prices, these facilities offer substantially lower costs of production than those in existing plants. However, although methanol can be economically shipped from remote gas areas, the expected growth in demand for methanol for conventional uses does not support the addition of many new plants.

The conversion of methanol to fuel components was accomplished commercially in the Mobil MTG (methanol-to-gasoline) process at a plant located near New Plymouth in New Zealand, but that plant has since been shut down on account of the relatively poor economics of gasoline production. However, Mobil did demonstrate that over a ZSM-5 (MFI) type zeolitic catalyst, methanol could be converted to a largely aromatic product, up to durene, but also with a significant proportion of olefins, principally propylene. Lurgi has recently developed a modified version of this process that minimizes the production of the gasoline fraction and maximizes production of propylene at about 70 percent; this process is known as MTP for methanol -to-propylene.

Methanol can also be converted to ethylene and propylene via the UOP/Hydro MTO process, thus opening new opportunities for methanol utilization. Ethylene and propylene can then be used to satisfy the growing market demand for polyolefins or can be used in the production of other olefin derivatives. Remote gas strategies for MTO generally consider either the shipping of methanol from remote locations to countries with strong olefin demand or shipping of polymer pellets from fully integrated gas-to-polyolefin (GTP) facilities in remote locations.

Figure 4.4 illustrates various alternatives for the utilization of natural gas in the production of either liquid fuels or petrochemical derivatives. There is at present renewed interest and considerable activity in the planning and construction of large-scale GTL facilities. GTL technology is attractive because it offers great potential for the valorization of stranded gas by taking advantage of the large markets for fuel products. The implementation of GTL and other large-scale gas conversion projects is challenging because investments are high, technologies are often not well proven at the actual scale, there is competition with crude-oil-based products, and plant location is often in remote areas. One way to enhance the economics of GTL projects is to produce products with higher added value. This can include the recovery of normal paraffins for linear alkyl benzene (LAB) production, specialty lube oils, methanol, olefins, and polyolefins. The markets for some of these products can limit the opportunities for production in GTL facilities. The olefin and polyolefin markets, however, are exceptionally large, and these products offer very high added value. Both GTL and GTP facilities incorporate sizable front-end syngas units for the processing of natural gas, as illustrated in Fig. 4.4. These units are the major contributors to the

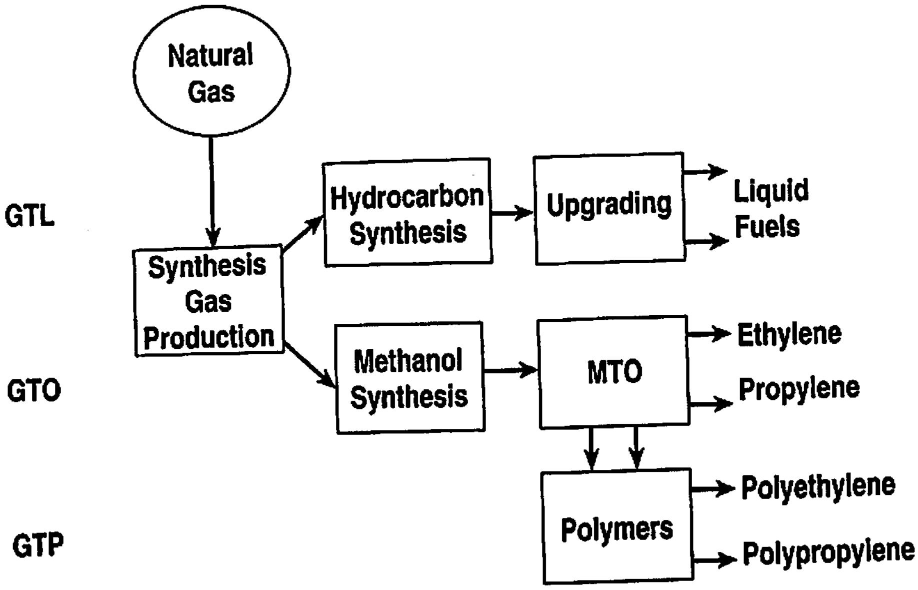


Fig 4.4 Conversion steps for natural gas to liquids and polyolefins
Source: Handbook of Modern Refining Process , Robert E.Meyers

relatively high investments required for these complexes. It follows that the integration of these facilities could offer substantial synergistic savings. Potential savings for integrated GTL/GTP complexes may derive from

- Shared syngas plant
- Shared utility systems with by-products utilization
- Shared wastewater treatment facilities
- Shared administration, laboratory, and maintenance facilities
- Minimal intermediate-product storage facilities needed

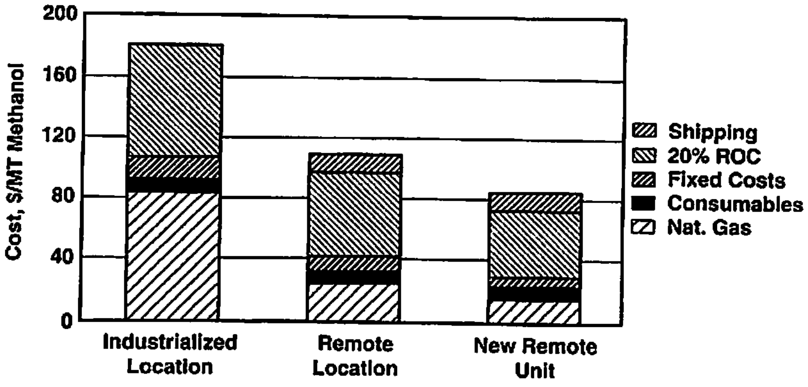
There are other advantages for integrated facilities, such as advantages of back integration for polyolefin production:

- Lower cash costs of production
- Elimination of costs for intermediate-products shipping and handling
- Consistency and better control over feedstock quality.

When one is considering an integrated facility to convert natural gas to polyolefins (GTP), there are three main process technologies involved. These technologies must fit together at world-scale capacities for an ideal integration.

Syngas/methanol process technology is available from several well-known licensors. Until recently, world-scale capacity for methanol production was considered 2500 to 3000 metric tons per day (MT/D). Now there are a number of projects underway with capacities of 5000 MT/D, and licensors of syngas/methanol technologies are discussing capacities as high as 10,000 MT/D. Most of the new capacity that has recently come, or will soon be coming, on-stream reflects a growing trend in which methanol production has been shifting from heavily industrialized countries to locations with access to lower-priced natural gas.

The combination of large-scale production facilities with low-priced natural gas feedstock substantially reduces the fundamental costs of methanol production, as shown in Fig. 4.5.



- "Industrialized Location" is based on 1500 MT/D capacity with $2.50/million Btu gas
- "Remote Location" is based on 3000 MT/D capacity with $0.75/million Btu gas
- "New Remote Unit" is based on 6000 MT/D capacity with $0.50/million Btu gas

Fig 4.5 Examples of methanol production costs
Source: Handbook of Modern Refining Process, Robert E. Meyers

Many smaller plants exist today in industrialized locations. The cash cost of production for these plants is typically more than $100/MT of methanol, due primarily to the cost of natural gas. If capital charges are added to provide, say, a 20 percent return on capital (ROC), then the delivered price of methanol is almost $ 180/MT. Large-scale plants in remote locations experience a considerable advantage due to low cash costs and economies of scale, even after accounting for the costs of shipping to distant markets. For these remote units the cash costs of production can be less than $50/MT. These units can deliver methanol at about $110/MT, even after adding capital charges and costs for shipping. New mega-scale projects enjoy an even greater advantage and can achieve attractive project economics with methanol delivered at prices less than $90/MT. This enables new applications for methanol such as fuel cells or conversion to olefins and offers large market growth potential.

Polyolefins are widely produced using technologies available from several licensors and may include flexibility to produce several grades of homopolymer and copolymer products. World-scale capacity for polyethylene processes is generally considered in the range of 300 to 350 kilometric tons per annum (kMTA). World-scale capacity for polypropylene processes is generally considered in the range of 250 to 300 kMTA.

MTO TECHNOLOGY:-

The remaining technology piece of the integrated GTP plant is an MTO unit capable of converting methanol to light olefins: ethylene and propylene. The UOP/Hydro MTO process provides the key link between natural gas and polyolefin production. It provides more profitable means to valorize remote gas and offers new opportunities for natural gas utilization. The MTO process is an innovative route for the production of olefins from natural gas. It offers yield flexibility that can deliver propylene as well as ethylene and satisfy the propylene demand that cannot be met by conventional ethylene plants alone.

The conversion of methanol to olefins requires a selective catalyst that operates at moderate to high temperatures. The reaction is exothermic so heat can be recovered from the reaction. Methanol first goes through a dimethylether (DME) intermediate, and the reaction proceeds with further dehydration to yield ethylene and propylene. A limited amount of butenes and higher olefins is produced as well. Depending on the design and operation of the MTO unit, the overall yields of ethylene plus propylene can be almost 80 or 90 percent, based on the carbon content of the methanol feed.

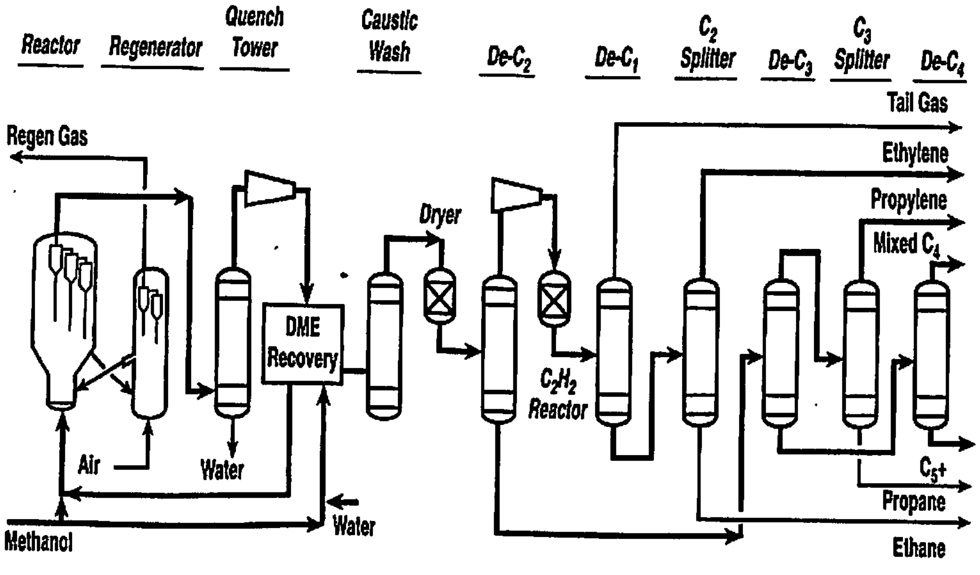
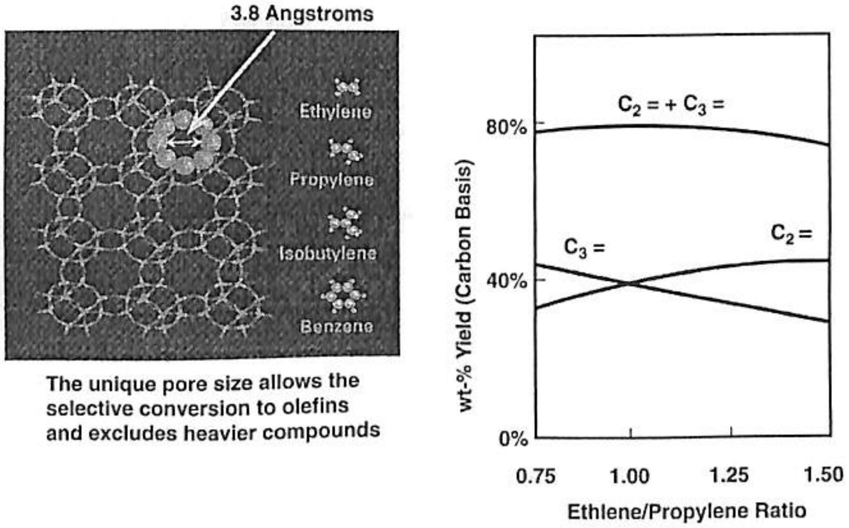


Fig 4.6 MTO process flow scheme

Source: Handbook of Modern Refining Process , Robert E.Meyers

Carbon or coke accumulates on the catalyst and requires removal to maintain catalyst activity. The coke is removed by combustion with air in a catalyst regenerator system. A fluidized-bed reactor and regenerator system is ideally suited for the MTO process. The reactor operates in the vapor phase at temperatures between 350 and 550°C and pressures between 1 and 3 bar gage. A slipstream of catalyst is circulated to the fluidized-bed regenerator to maintain high activity. The UOP/Hydro MTO process can be operated on "crude" or undistilled methanol as well as on pure methanol. The choice of feedstock quality generally depends on project-specific situations because there can be advantages in either case. Figure 4.6 llustrates a simple flow diagram for the UOP/Hydro MTO process. After the oxygenate recovery section, the effluent is further processed in the fractionation and purification section to separate the key products from the by-product components. Ethylene and propylene are produced as polymer-grade products and sent to storage.

The highly selective MTO-100 catalyst is based on SAPO-34, a template-based, silico-aluminophosphate molecular sieve with a chabazite structure and a unique pore size of about 3.8°A (Fig. 4.7).The pore size controls the size of the olefins that emerge from the catalyst pores. Larger olefins diffuse out at a slower rate. Smaller olefins pre-dominate in the reactor product. If, on the contrary, the reaction were conducted over an MFI zeolite with a pore size of about 5.1 to 5.6 °A, the product would comprise much larger molecules, all the way to aromatics.



The unique pore size allows the selective conversion to olefins and excludes heavier compounds

Fig 4.7 SAPO-34 structure and MTO light olefin yields

Source: Handbook of Modern Refining Process , Robert E.Meyers

In a typical operation, up to 80 percent of the methanol feed (on a percent carbon basis) is converted to ethylene and propylene, with approximately 10 percent going to butenes. The overall carbon yield of light olefins can be increased to almost 90 percent by converting the C_4 + co-products, mostly to propylene.

The UOP/Hydro MTO process offers a wide range of flexibility for altering the relative amounts of ethylene and propylene products by adjusting the operating severity in the reactor. The MTO process can he designed for an ethylene-to-propylene product ratio between 0.75 and 1.5.The overall yield of light olefins (ethylene and propylene) changes slightly over this range with the highest yields achieved with about equal amounts of ethylene and propylene, roughly in the 0.8 to 1.25 range. This envelope provides the lowest methanol requirements, but the ratio can be adjusted to reflect the relative market demand and pricing for ethylene and propylene.

An example material balance is shown in Table 4.3. for the production of 600,000 MTA of light olefins with equal amounts of ethylene and propylene. Approximately 3 tons of methanol is required per ton of light olefins. This represents a carbon-based yield of almost 80 percent.

Table 4.3 MTO mass balance
600,000 MTA light olefins (ethylene + propylene)

	Feedstocks, MT/D	Products, MT/D
Methanol*	5204	
Ethylene		882
Propylene		882
Mixed butanes		272
C_5+ hydrocarbons		100
Fuel gas		88
Other (water, CO_x, coke, etc.)		2980
Total	5204	5204

*5204 MT/D of methanol requires about 155 million SCF/day (4.2 million N· m^3/day) of natural gas, assuming MTO by-products are used as fuel.

Source: Handbook of Modern Refining Process , Robert E.Meyers

Because of the high olefin yields and low light-ends make, the MTO process does not require an ethylene refrigeration system. Although it is not yet commercialized, additional projected cost savings have been achieved by optimizing the reactor design and performing value engineering and pinch analysis. Several design packages have been prepared to determine the design requirements and costs for MTO projects. These studies have included design and cost requirements for off-sites and utility systems associated with stand-alone MTO as well as integrated GTP projects.

ECONOMIC BASIS

To arrive at a meaningful economic comparison, we have made a number of pricing assumptions. Investment costs were adjusted to reflect a remote location. Allowances for the costs for off-sites and utilities were assumed to be equivalent to 35 percent of the inside-battery-limits (ISBL) estimated erected costs. This is expected to be a reasonable approximation for integrated facilities.

Product prices were estimated to roughly correspond to a crude oil price of \$18/bbl (1 bbl ~ 0.159 m^3). The natural gas price was assumed at \$0.50/million Btu (1 million Btu ~*1.055* GJ), reflecting a price for remote gas utilization. GTL liquid products were assumed to have an aggregate value equivalent to \$5/bbl above the crude oil price, and gas products were valued at the equivalent to the local fuel value.

Polyolefin yields were assumed at 98 wt % of the monoolefin feed rate. Polyolefin product prices were based on averages of historical spot and contract prices for Western Europe roughly corresponding to crude oil at \$18/bbl.

Shipping costs were assumed to estimate net-back revenues after marine transportation from a remote location to industrialized markets such as western Europe or the United States. These costs can vary significantly depending on project and market locations as well as fuel costs. Handling fees and import duties can also impact the net-back revenues.

Fixed costs of production were based on an allowance of 5 percent of the inside-battery limits estimated erected cost (ISBL EEC) to cover the costs of labor and supervision, overhead, maintenance, taxes and insurance, and interest on working capital. Please refer to Table 4.4 for details.

Item	Cost
ISBL erected cost	Remote location basis
Off-sites and utilities	35% of ISBL assumed
Other costs*	Included
On-stream factor	340 days/yr
Project life	20 yr (17 operating)
Crude oil (corresponding)	$18/bbl
Natural gas feed	$0.50/million Btu
GTL products	$23/bbl
Polyethylene	$800/MT
Polypropylene	$705/MT
Methanol	$120 and $85/MT
Shipping	$12/MT liquids $40/MT polyolefins
Fixed operating costs	5% of ISBL (erected)

*Other costs include catalysts, license fees, and allowances for other miscellaneous owner's costs.

Table 4.4 GTL GTP Economic basis

Source: Handbook of Modern Refining Process, Robert E.Meyers

INVESTMENT ESTIMATES:-

Investment costs were estimated based on scaling the estimated erected costs for the process units. These costs were determined by comparing cost information shown in various papers and publications as well as UOP in-house information. The basis and assumptions used in developing these costs are further explained in the paragraphs that follow.The estimated costs for the options considered in this chapter are compared in Fig. 4.8.

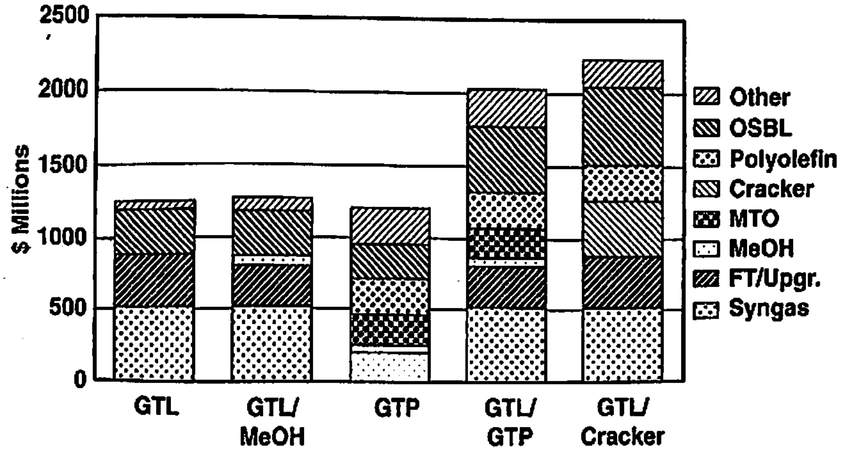


Fig 4.8 Capital investment comparison

Source: Handbook of Modern Refining Process, Robert E.Meyers

The investment costs for GTL and GTL integrated with methanol production are similar at about $1.2 billion. GTP also requires a similar investment. The addition/integration of olefin and polyolefin production facilities increases the investment cost to about $2.0 billion.

GTL Investment:-. A GTL complex for the production of 50,000 BPSD requires the conversion of about 450 million SCF/day of natural gas and has an estimated capital cost of about $1.25 billion. This cost assumes an all-inclusive plant cost in a remote location of $25,000/BPSD. The syngas facilities are assumed to account for about 60 percent of the ISBL costs for a GTL complex.

GTL/Methanol Investment:- The methanol synthesis and purification sections account for about 28% of the ISBL cost of a conventional methanol plant.' A world-scale methanol plant has a capacity of about 5000 MT/D (~1.7 million MTA). By scaling up the costs of the methanol synthesis and purification facilities to the world-scale capacity, it is estimated that the capital costs of these sections would be approximately $80 million. Integrating these facilities with the same syngas facilities used in the 50,000-BPSD GTL case described above would require about 38% of the syngas for methanol Production. Such a complex would produce 5300 MT/D of high-purity methanol plus 31,000 BPSD of GTL liquid products. The size and cost of the Fischer-Tropsch (FT) synthesis and product upgrading facilities would be reduced for the lower GTL capacity. After adding the costs for outside-battery-limits (OSBL) allowance, catalysts, license fees, and other costs, the overall plant costs for the GTL/methanol facility would be only slightly higher than those for the GTL facility.

GTP Investment:- The size of a world-scale GTP complex is mainly set by the capacity of the methanol and polyolefin units. World-scale polyolefin units have capacities of about 300,000 MTA. If equal amounts of polyethylene and polypropylene were desired, the MTO unit would require about 1.8 million MTA of methanol to support 600,000 MTA of polyolefin production. The methanol purification section can be greatly simplified for an integrated GTP complex because crude methanol can be used for feedstock to the MTO unit. This results in significant savings in the methanol plant, and the amount of intermediate-product storage is minimized for an integrated facility. The estimated cost for such a GTP complex is $1.21 billion. This includes the costs for OSBL allowance, catalysts, license fees, and other costs and is based on a remote location with an assumed location factor of 15 percent above the cost for a U.S. Gulf Coast location.

GTL/GTP Investment:- The addition of an MTO unit and polyolefin units allows the methanol to be converted to olefins and then polyolefins. The conversion to polyolefins is necessary because it would be very costly to ship olefins from remote locations. Polyolefins are economically shipped over long distances. The estimated cost for the integrated GTL/GTP facility is about $2 billion. This includes the costs for OSBL allowance, catalysts, license fees, and other costs and is based on a remote location with an assumed location factor of 15 percent above the cost for a U.S. Gulf Coast location.

GTL/Cracker/Polyolefin Investment:-. The most common route to polyethylene and polypropylene production today is through steam cracking of naphtha. The GTL liquid products include naphtha boiling-range product. This naphtha is attractive for steam cracking applications because of its high concentration of normal paraffin components. This offers high ethylene yields for naphtha cracking. The naphtha can be shipped from remote sites to industrialized locations with naphtha crackers, and this is the most commonly envisioned outlet for the GTL naphtha product. Since this chapter discusses the potential advantages of integrating polyolefin production with GTL, it is appropriate to include the integration through conventional cracking. The naphtha portion of GTL products can vary considerably depending on the catalyst and operating conditions in the Fischer-Tropsch unit. For the purposes of this chapter it was assumed the naphtha cut accounts for 28 vol % of the total FT liquids. This would provide 14,000 BPSD of naphtha, but this amount by itself is too small to Support a world-scale naphtha cracker. The resulting economics would be poor for such a project, so a larger cut of the FT liquids would be necessary.

We assumed that 56 percent of the FT liquids would be used as cracker feedstock. We estimate that this 28,000 BPD of feedstock, rich in normal paraffins, could support the production of 442,000 MTA of polyethylene and 166,600 MTA of polypropylene. This ethylene yield is significantly higher than cracker yields based on conventional feed stocks. The estimated erected cost of the ISBL facilities for such a cracker is \$380 million, and the corresponding cost for the polyolefin ISBL facilities is \$360 million. The total investment for this complex is estimated at slightly above \$2.2 billion. This includes the costs for OSBL allowance, catalysts, license fees, and other costs and is based on a remote location with an assumed location factor of 15% above the cost for a U.S. Gulf Coast location.

ECONOMIC COMPARISONS:-

The integration of methanol production with GTL offers enhanced economics provided the methanol sales price is at around \$120/MT or more. However, methanol consumption through conventional applications (i.e., formaldehyde, MTBE, chloromethane, acetic acid, etc.) offers limited opportunities for remote gas utilization. Current demand for methanol is around 30 million MTA, and it is forecasted to grow to 37 million MTA in 10 years. This additional methanol demand would support the installation of only two or three world-scale methanol plants and consume about 665 million SCF/day (17.8 million N• m^3/day) of natural gas. New methanol projects are also likely to result in closures of some existing plants with higher production costs, but this provides limited opportunities and does not support higher market prices. Many of the alternative uses for methanol (i.e., fuel cells or conversion to olefins) require lower methanol prices to be competitive in their respective markets. In the economic comparisons below, an alternative methanol price of \$85/MT is used to give an example of the economics of GTL/methanol integration with the methanol directed toward alternative markets such as MTO. In such a case the economics of the GTL and integrated GTL/methanol plants are essentially the same. See Table 4.5.

If methanol is converted to olefins and polyolefins, it further increases the value added for products derived from natural gas. Other papers have compared the economics of remote gas strategies including LNG, GTL, and GTP.GTP offers attractive economics at about the same investment level as GTL because of the higher value of the polyolefin products compared to liquid fuels, even when those fuels command a price premium over conventional fuels. GTP offers gross profits equivalent to \$5.70/ 1000 SCF of gas consumed. This is more than four times the corresponding gross profit offered by GTL. This helps GTP to be economical at a smaller scale than GTL, so it can he utilized in moderate- as well as large-sized gas fields.

TABLE 4.5 Economic Comparison of GTL Integrated with Methanol Production

	GTL	GTL/MeOH at $120/MT	GTL/MeOH at $85/MT
Investment, million $	1250	1264	1264
Gas consumed, million SCF/day	450	450	450
GTL products, BPSD	50,000	31,000	31,000
Methanol product, MT/D		5309	5309
Gas cost, million $/yr	80	80	80
Operating cost, million $/yr	78	78	78
Total cash cost, million $/yr	158	158	158
Product revenue, million $/yr	391	459	396
Transportation costs	−27	−38	−38
Net revenue, million $/yr	364	421	357
Gross profit, million $/yr	206	263	200
Gross profit, $/million SCF of gas	1.34	1.72	1.31
Gross profit, $/kN · m^3 of gas	50.0	64.2	48.9
Simple ROI	16.5%	20.7%	15.7%
IRR (pretax)	12.8%	16.6%	12.1%

Source: Handbook of Modern Refining Process , Robert E.Meyers

GTL offers huge potential for gas utilization because it links natural gas to markets historically supplied by products derived from crude oil. This is of strategic importance to many, because the world's gas reserve base is greater than the oil reserve base and gas discovery rates exceed oil discovery rates. When crude oil prices are high, GTL can offer attractive economics, but the potential for lower oil prices raises concerns about economic risks for GTL. One way to help mitigate such risks is to produce products with greater value margins. This is evidenced by the GTL/GTP example shown in Table 4.6.

In the example for GTL/GTP, 38 percent of the syngas was used for methanol production and subsequently converted to primarily ethylene and propylene and then converted to polyethylene and polypropylene. The remaining 62 percent of the syngas was converted to FT liquids. Although this requires a substantially greater investment, it doubles the gross profits per thousand standard cubic feet of natural gas consumed and increases the project IRR from about 13 percent for GTL to almost 17 percent for the integrated GTL/GTP project. In this example the MTO C_4+ by-products were used as fuel. This minimizes the amount of byproducts from the complex but only provides the minimum value for this material. If these by-products are either shipped separately or blended into the Fr liquid product streams, they can provide a significantly higher value and thereby further increase the IRR of the project.

TABLE 4.6 Economic Comparison of GTL Integrated with Polyolefin Production

	GTL	GTP	GTL/GTP	GTL/cracker/ polyolefin
Investment, million $	1250	1210	2030	2230
Gas consumed, million SCF/day	450	155	434	450
GTL products, BPSD	50,000	—	31,000	22,000
Polyethylene, MT/D	—	882	882	1300
Polypropylene, MT/D	—	882	882	490
Other by-products, MT/D	—	—	—	1491
Gas cost, million $/yr	80	27	77	80
Operating cost, million $/yr	78	99	150	176
Total cash cost, million $/yr	158	126	227	256
Product revenue, million $/yr	391	452	694	708
Transportation costs	−27	−24	−41	−42
Net revenue, million $/yr	364	428	653	666
Gross profit, million $/yr	206	301	426	410
Gross profit, $/million SCF of gas	1.34	5.72	2.89	2.68
Gross profit, $/kN · m^3 of gas	50.0	213.5	107.9	100.0
Simple ROI	16.5%	24.9%	21.0%	18.4%
IRR (pretax)	12.8%	20.0%	16.9%	14.6%

Source: Handbook of Modern Refining Process , Robert E.Meyers

Also shown in Table 4.6 are the economics of integrating a conventional steam cracker and polyolefin plants with GTL. There is less synergy in this integration because all the syngas must first be converted to FT liquids. In this example, 22,000 BPSD of FT liquids would remain for shipping in addition to more than 350,000 MTA of cracker liquid by-products. These by-products would consist of crude C_4s (~33 percent), pyrolysis gas (~59 percent), and fuel oil (~8 percent). With a substantially higher investment, additional facilities could be installed to recover butadiene, benzene, toluene, and xylenes from these streams. This would also require additional product storage for these extra products.

The GTL/cracker integration option offers slightly better economics compared to GTL, but it requires the largest investment, produces the largest number of products to be shipped from the remote location, and is less economical than the GTL/GTP integration.

The demand for additional ethylene and propylene capacity is expected to require about 60 million MTA of additional ethylene production and 30 million MTA of additional propylene production by the year 2015. If we assume that about 3 million BPSD of GTL capacity comes on-stream during this same period, then approximately 840,000 BPSD of FT-derived naphtha would be produced and 27 billion SCF/day (723 million Nm^3) of natural gas would be consumed. If this naphtha were cracked to produce ethylene and propylene, then about 14 million MTA of ethylene and 5 million MTA of propylene would be produced. This leaves over 75 percent of the additional ethylene production and over 80 percent of the additional propylene production to be supplied by other sources.

If this same amount of natural gas were consumed in an integrated GTL/GTP facility, about 1.86 million BPSD of GTL liquids or 521,000 MTA of FT-derived naphtha would be produced. In addition, about 18.4 million MTA of ethylene and 18.4 million MTA of propylene would be produced by the MTO process. Assuming the naphtha is shipped to other locations to be cracked to light olefins, this would bring the total ethylene production to 27.1 million MTA (18.4 + 8.7) and the total propylene production to 21.5 million MTA (3.1 + 18.4). This still leaves about 55 percent of additional ethylene and almost 30 percent of additional propylene demand remaining for supply by other routes.

ECONOMIC SENSITIVITY:-

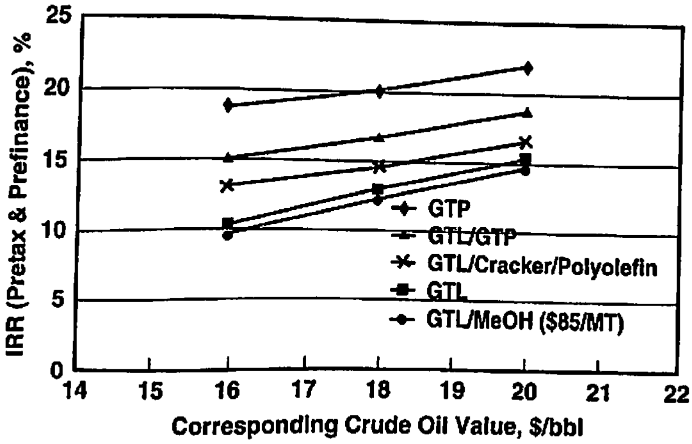


Fig 4.9 Economic sensitivity to corresponding crude oil prices

Source: Handbook of Modern Refining Process, Robert E. Meyers

The economic impact of various corresponding crude oil prices is shown in Fig. 4.9. In general, polyolefin prices tend to trend along with crude oil prices, but there can be a lot of scatter in the prices due to market conditions. However, each of these options achieves better economics as oil prices increase. GTL is slightly more sensitive to crude oil pricing, and it will start to approach GTP economics as crude oil prices reach close to $30/bbl.

Stand-alone GTL projects can look attractive when crude oil prices are about $20/bbl or higher. Integrated GTL/GTP projects can offer similar returns when market prices correspond to Crude oil priced at $16/bbl or higher.

CONCLUSION

The production of chemicals/petrochemicals from natural gas can provide a means of moving natural gas from remote locations with a maximum of marketing flexibility. A range of proven processes are available for both syngas production and synthesis. It is, however, of utmost importance for the economics of an individual project to tailor the syngas production process to that of the synthesis. Out of the several technologies available for production of methanol and olefins from methanol, Lurgi's technology is most promising technology. Lurgi's new Methanol-to-Propylene (MTP®) process presents a simple, cost-effective and highly selective technology.

REFERENCES

1) Handbook of Modern Refining Processes – Robert .E. Meyers
2) Report on Methanol by UHDE, www.thyssenkrupp.com/uhde
3) UOP/HDRO MTO Process , www.uop.com
4) M. Rothaemel and H-D. Holtmann, "MTP, Methanol To Propylene - Lurgi's Way", DGMK-Conference "Creating Value from Light Olefins – Production and Conversion", Hamburg, October 10 – 12, 2001
5) Synetix Leading Concept Methanol (LCM) Process , www.synetix.com
6) Technology Development Trends and Challenges for New Mega GTL Plants, Ola Olsvik, Dag Schanke, Jostein Sogge, Hendrik J.de Bruyn and Roger Hansen, Statoil Research & Technology Centre, Trondheim, N-7005 Norway
7) Journals of Hydrocarbon Asia
8) www.synfuels.com
9) "SOFC AS A GAS SEPARATOR" by M.A. Korobitsyn, F.P.F van Berkel & G.M. Christie. Netherlands Agency for Energy and Environment
10) Synthesis gas processes for synfuel production ,By Christopher Higman

LIST OF TABLES

Table 2.1 World consumption of methanol and forecast demand

Table 2.2 Characteristics of syn gas production methods

Table 3.1 Product methanol specifications

Table 4.1 Production cost: Integrated Megamethanol-MTP-PP complex

Table 4.2 ROI: Integrated Megamethanol-MTP-PP complex

Table 4.3 MTO mass balance

Table 4.4 GTL GTP Economic basis

Table 4.5 Economic comparison of GTL Integrated with methanol production

Table 4.6 Economic comparison of GTL Integrated with Polyolefin production

LIST OF FIGURES

Fig 1.1 Gas processing routes

Fig 1.2 Growth: Chemical sales 1996-2010

Fig 2.1 Methanol applications

Fig 2.2 World Methanol demand by end use – 2001

Fig 2.3 World wide methanol supply and demand

Fig 2.4 Methanol from Natural gas

Fig 2.5 Steam methane reforming

Fig 2.6 Typical SMR process scheme

Fig 2.7 Partial oxidation reactor

Fig 2.8 Typical POX reactor

Fig 2.9 Autothermal reforming

Fig 2.10 Typical ATR process scheme

Fig 2.11 Combined reforming

Fig 2.12 Combined reforming with prereforming

Fig 2.13 Combined Autothermal reforming

Fig 2.14 Graph of Carbon efficiency Vs. Pressure and Conversion rate

Fig 2.15 Graph of Carbon efficiency Vs. Inert level and Conversion rate

Fig 2.16 Graph of Carbon efficiency Vs. CO/CO_2 in syngas

Fig 2.17 Components in raw methanol

Fig 3.1 Syngas generation using combined reforming for the Megamethanol process

Fig 3.2 Autothermal reactor simulation, performance by 3D CFD model

Fig 3.3 Autothermal reformer

Fig 3.4 Cross section of a Lurgi reformer

Fig 3.5 Combined converter synthesis

Fig 3.6 Methanol synthesis section with distillation

Fig 3.7 Three-column methanol distillation

Fig 3.8 Typical lay out of an LCM flow sheet

Fig 3.9 Synetix TCC

Fig 3.10 TCC: Methanol equilibrium profile

Fig 4.1 Simplified block flow diagram

Fig 4.2 Detailed block floe diagram of MTP process

Fig 4.3 Simplified reaction model

Fig 4.4 Conversion steps for natural gas to liquids and polyolefins

Fig 4.5 Examples of methanol production costs

Fig 4.6 MTO process flow scheme

Fig 4.7 SAPO-34 structure and MTO light olefin yields

Fig 4.8 Capital investment comparison

Fig 4.9 Economic sensitivity to corresponding crude oil prices