Manufacturing of Methanol Using Natural Gas

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Abstract: - *The world methanol consumption has exceeded million tons per annum and is still growing progressively, indicating an increasing importance of methanol in the chemicals market. At present, methanol is produced in a twostep process: steam reforming of a hydrocarbon feedstock, followed by synthesis gas conversion into methanol. This study includes production of existing plants. The data includes basic production of methanol currently active in the world. This study also includes the recent development in the methanol production and an in-dept study of process currently active in the plants.*

Keyword: - Methanol, Methane, Feedstock, Hydrocarbon, Catalyst

1. Introduction

Methanol is a primary liquid petrochemical made from renewable and non-renewable fossil fuels comprising of carbon and hydrogen. Containing one carbon atom, methanol is the simplest alcohol. It is a colorless, tasteless liquid that boils at 64.96 °C (148.93 °F) and hardens at −93.9 °C (−137 °F) and is commonly known as "wood alcohol".

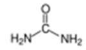
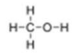
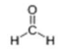
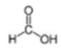
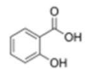
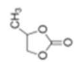
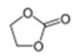
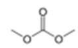
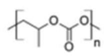
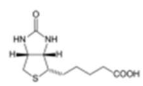
Natural gas is the feedstock used in most of the world's production of methanol.

The current world energy system is still largely based on the use of fossil fuels and, even though the use of renewable energy sources has increased, it will continue in the medium and short term. This immense use of fossil fuels in industry and transport produces large amounts of CO_2 emissions [1] that could reach 35.2 billion metric tons in 2020 [2].

Therefore, it is essential to develop technological approaches to lessen these CO_2 emissions connected with the use of fossil fuels which must include the capture and following reutilization of the CO_2 produced.

Today, the foremost chemical products obtained at the industrial scale using CO_2 as a raw material are urea, methanol, formaldehyde, formic acid, carbamates, polymer-building blocks, and fine chemicals (Table 1) [3]. Among them, the synthesis of urea and methanol are the predominant consumers of CO_2 in industry with an annual consumption of CO_2 of more than 110 Mt/year.

Table 1. Main chemicals products industrially produced from CO_2

Chemical	Molecular Formula	Production (t/year)	CO_2 Consumption (t/year)
Urea		1.5×10^8	1.12×10^8
Methanol		1.0×10^8	2×10^6
Formaldehyde		9.7×10^6	
Formic acid		7.0×10^5	
Salicylic acid		7.0×10^4	3.0×10^4
Cyclic carbamate		8.0×10^4	4.0×10^4
Ethylene carbamate			
Di-methyl carbamate		1.0×10^7	
Copolymers			
Polymer-building blocks			
Fine chemical: for example, biotin			

One of the most fascinating products that can be synthesized from CO_2 is Methanol. Methanol is an industrial product used as a feedstock in several industrial chemicals and fuels products. The main chemical methanol byproducts are formaldehyde, acetic acid, Methyl Tertiary-Butyl Ether (MTBE) and Dimethyl Ether (DME).

2. Production of Methanol

Methanol being a commercial solvent should also have an economical production method. With the growth and demand of methanol and DME as alternate fuel, the conventional wood distillation process was not able to cope up with surging demand. BASF was the first to acquire a patent on production of synthetic methanol via syngas (syngas). The first plant was [4] started in 1923. This started the conventional method for production of methanol and DME which is being followed today. The current production of methanol is largely based on fossil sources with only between 1 to 2% of total methanol being produced from biomass. The carbon footprint of methanol is no better than that of fossil-based transportation fuels. This is because syngas is usually produced from coal or natural gas. The present emphasis is to produce bio methanol because all the benefits of using methanol/DME as fuel will only be realized when they are produced from non-fossil fuels. Presently concentrated research is being carried on biomass gasification. Several plants are operation around the world but only a few are being operating at commercial scale.

China is the largest producer of methanol in Asia and also the largest consumer. China is the leading producer of methanol, approximately 50% of the global production and a total of 43 million tons was produced [5] in 2016. While India consumption is more compared to production. India to meet its demand largely depends on imports. India consumes 1.5 million tons of methanol while its production is only around 0.385 million tons. In coming years, the demand in methanol is only expected to grow and estimated consumption is around 2.5 million tons per year. The major concern for India is feedstock availability. India does have sufficient amount of coal, but the quality of coal is major concern. Hence methanol is mainly produced using steam reforming of syngas in India.

The steam reforming method is traditional method of preparation of methanol. The methanol production can be summarized as

Carbon source + Oxygen (air) → Syngas (CO+ Hydrogen) → Methanol → DME+ Water

Methanol production from syngas preparation requires three major steps:

- Syngas preparation
- Methanol Synthesis
- Methanol purification/distillation

2.1 Syngas Preparation

Syngas preparation can be done using various methods depending upon feedstock. There are two types of feed stock for syngas:

Hydrogen deficient: Coal, Coke, biomass, or residual hydrocarbon.

Hydrogen Rich: Methane (Natural Gas) or Naphtha.

When coal is used as feedstock, partial oxidation is used for syngas preparation. When hydrogen rich feedstock is used, steam reforming is the process. Syngas conversion to methanol as intermediate for other chemicals is well established technology.

Syngas preparation is very similar to Fisher -Tropsch (FT) gas to liquid (GTL) process, but major difference is the scale at which syngas is produced. For A natural gas feedstock with little heavy hydrocarbon and sulfur impurity in in it, a steam reforming-based plant is considered most cost effective. With better reliability and higher energy efficiency. POX based units are generally more suited for syngas preparation from heavy – hydrocarbon feedstock (e.g., fuel oil). A POX based unit for natural gas feed requires a larger air separation plant and typically produces sub stoichiometric syngas, which requires additional processing for methanol synthesis.

2.2 Steam Reforming of Natural Gas

Natural gas is one of the most important sources of syngas production, due to its low cost and lower GHG emission compared to coal, and the ease of conversion either to hydrogen or to syngas. Natural gas and lower hydrocarbons such as ethane, naphtha or biogas are easily converted to syngas following pathway.

$CH_4+H_2O \rightarrow CO + 3H_2$ $\Delta H = +206 KJ/mol$

This reaction is known as steam reforming reaction. This reaction is highly endothermic and hence external energy needs to be supplied to the process. The hydrogen to carbon monoxide ratio is 3 which is not suitable for the process. The required ratio is about 2. However, steam reforming is suitable when hydrogen production is objective. For hydrogen production, the carbon monoxide in the steam reformate is used to generate hydrogen by shift reaction. This carbon dioxide is separated by pressure swing absorption to recover pure hydrogen.

$CO+H_2O \rightarrow CO_2 + H_2$ $\Delta H = -41 KJ/mol$

Steam reforming is carried out using nickel catalyst at 700 to 1000ºC. A pre reformer is used to convert higher liquid hydrocarbons to lighter hydrocarbons in presence of hydrogen before entering methane reformer. The reaction temperature of pre reformer is about 400 to 500ºC.

Catalyst used in pre reforming is also based on nickel, but to prevent coke formation some noble metals such as Rhodium is deposited. Steam reforming is a simple but an energy intensive process.

$2CH_4 + 4H_2O \rightarrow 2CO_2 + 8H_2$ (Steam Reforming)

2.3 Methanol Synthesis

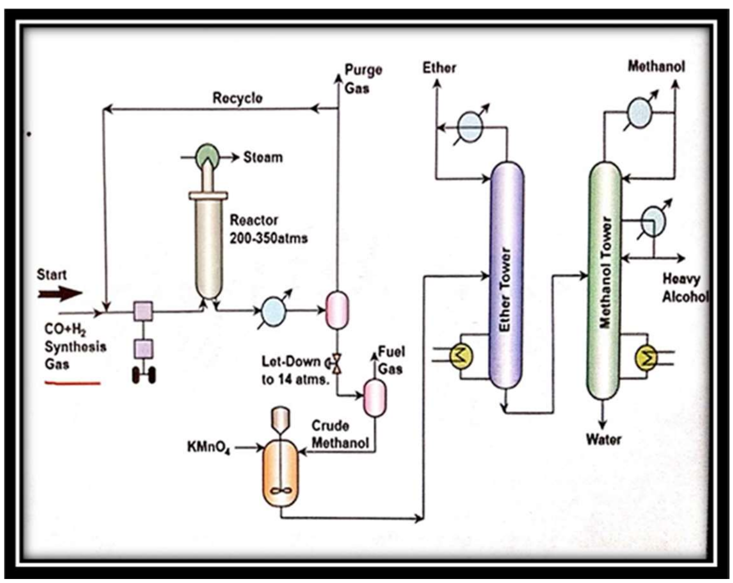


Figure 1. Process of Methanol Synthesis

Once the synthesis gas of correct composition is manufactured, methanol is produced by high pressure reaction over catalyst in fixed bed. The natural gas reforming results in considerable hydrogen surplus in syngas. If external source of CO_2 is available, the excess hydrogen can be converted to additional methanol.

$CO + 2H_2 \rightarrow CH_3OH$ [Δ H= -90.84 KJ/mol]

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ [Δ H=-49.43 KJ/mol]

The overall reaction for mixture of CO and CO_2 could be written as:

$CO + CO_2 + 5H_2 \rightarrow 2CH_3OH + H_2O$

The synthesis gas mixture is compressed to 200-350 atms. Recycle gas is also mixed and sent to compressor. This reaction mixture is fed to reactor. Steam is circulated in heating tubes to maintain a temperature of 300-375ºC. In the reactor several undesired reactions also take place which are further needed to be separated. After reaction the exit gases are need to be cooled. The mixture is cooled and sent to a phase separator where gases are separated.in this phase separation operation methanol and other high molecular weight compounds enter the liquid phase and unreacted feed is produced in gas phase. The gas phase stream is purged to remove inert components and most of the gas stream is sent as a recycle to the reactor.

The liquid stream is further depressurized to about 14 atms to enter a second phase separator that produces fuel gas. The gaseous product and the liquid stream bereft of the fuel gas components is rich of the methanol component. The liquid stream then enters a mixer fed with $KMNO_4$, this removes impurities and other aldehydes and ketones formed. The liquid then enters distillation column that separates dimethyl ether as top product and further methanol being more volatile obtained as top product and other heavy alcohols as midcut and bottom as water.

Synthesis of methanol is highly exothermic, taking place over a bed of catalyst at moderate temperature. Most plant design use this extra energy to generate electricity needed in process control.

The catalyst used in industrial low-pressure synthesis is based on copper oxide- zinc oxide alumina developed by ICI of England. This catalyst is extremely active and highly selective. Catalyst is prepared in tablet form. Catalyst is activated in site by passing H_2/N_2 (1mol% H2) over catalyst bed. This must be carefully controlled at low temperature to preserve crystalline structure and physical integrity. The catalyst is sensitive to chlorine and sulfur, sulfur level below 0.0125 ppmv and chlorine level below 0.0125 ppmv, the catalyst life of two to four years can be expected.

3. Economics

The size of a huge-scale single-teach methanol plant turned into 2000 to 2500 metric lots in line with day. However, economies of scale and marketplace circumstances are driving the trend towards constructing large-sized plant life with capacities greater than 3,000 [8] thousand lots in step with day. The economics of methanol are very dependent on the fee of manufacturing and the selling charge of methanol. The principal components of the production price of methanol are fuel fee and the investment fee of the plant. The economics of methanol are very reliant on on the cost of production and the selling price of methanol. The market for methanol is unstable and competitive with large swings in the price. The main apparatuses of the production cost of methanol are gas price.

e and the investment cost of the plant. Several literature sources [6] [7] present the investment costs for steam-reforming-based methanol plants. The investment costs for large-scale methanol plants based on progressive syngas generation technologies are expected to be lower. A producer in a remote position must also consider shipping costs for conveying the methanol product to the market.

4. Methanol Demand

4.1 Globally:

In 2020, China accounted for 40 percent of the world's methanol demand, while the rest of Asia accounted for an additional 46 percent of the worldwide demand, becoming the region where the demand for methanol was the maximum by far. Next were North America and Europe, each on behalf of around five percent of the global methanol demand that year. In 2021, some 11.7 million metric tons of methanol were used for gasoline blending and combustion [7].

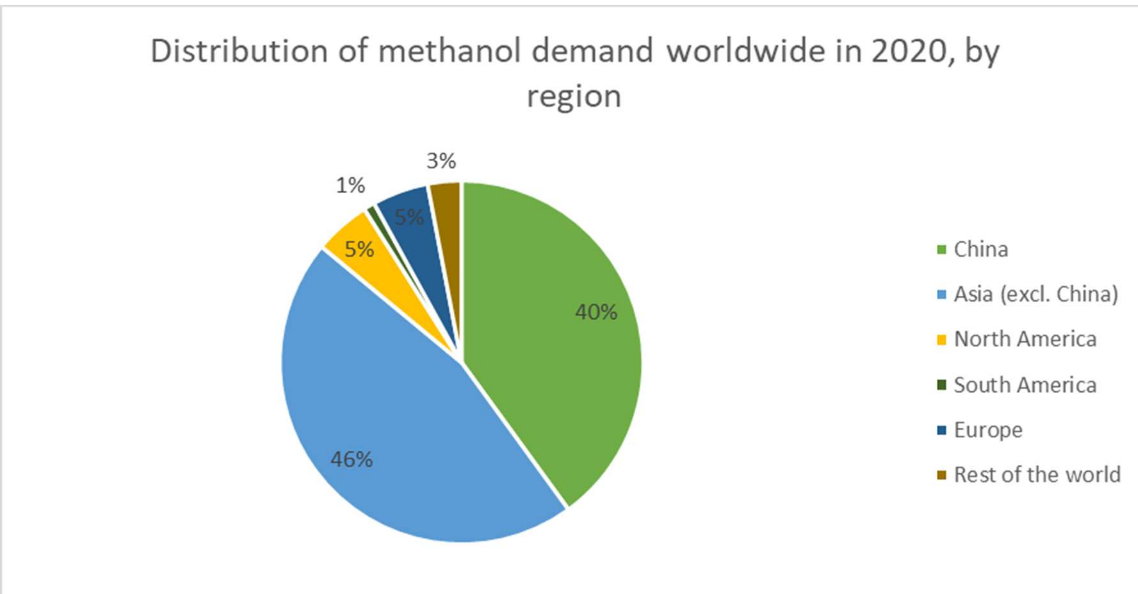


Figure 2. Methanol Demand Worldwide

The methanol marketplace is projected to sign up a CAGR of over 4.87% during the estimate period 2022-2027. The COVID-19 pandemic depressingly impacted the worldwide economic system, making it hard to forecast the marketplace's future because of the uncertainties surrounding the pandemic. The petrochemical enterprise plays a key part in production numerous merchandises, together with methanol. But, due to the cessation of these industries, the methanol marketplace changed into quite impacted. Methanol is favored over conventional gas for decreasing carbon monoxide, nitrogen oxides, and hydrocarbon emissions. Consequently, methanol is used as an alternate to standard gasoline in North the United States and Europe. Asia-Pacific conquered the market worldwide with the most important intake in China and India [9].

4.2 India:

The modern-day consumption of methanol in India is by and large for the manufacture of chemical compounds together with acetic acid. Use as gasoline or gasoline additives is not commonplace. Presently, India imports a huge quantity of methanol. The Indian authorities is pushing methanol usage as a gas in motors and cooking to sell sustainable improvement with less environmental harm. Beneath the Methanol economic system software by way of NITI Aayog, methanol manufacturing capability is anticipated to increase by means of up to twenty ton annually [10] by 2025, the use of Indian high ash coal, stranded gasoline, and biomass. GNFC is the biggest producer of methanol in India. . Maximum of the methanol flora in India produce Syngas from natural gas, but the current focus is to replace to coal, as is well-known in China . There was an offer to installation a 1500 TPD [11] methanol and 14 mil Cu ft./Day pipe fuel consistent with day from Ranigunj coal.

5. Uses of Methanol

Mixing of 15% methanol in gas can result in at least 15% reduction inside the import of crude oil. Further, this will deliver down greenhouse gases emissions [12] by using 20% in phrases of particulate count number, NOx, and SOx, thereby enhancing the urban air high-quality.

On 5th October 2018, assam petrochemicals released Asia's first canister-primarily based methanol cooking gasoline [13] program. This initiative is an extension of our hon'ble high minister's imaginative and prescient of decreasing the import of crude oil and striving closer to the availability of a smooth, fee-effective, and pollutants-free cooking medium. Methanol fuel cells : methanol critical in fuel cells as an environmentally friendly hydrogen provider gas. Two types of methanol cells: direct methanol gas cells (DMFCS) and reformed methanol fuel cells (RMFC) / oblique methanol gasoline cells (IMFCS).

6. Conclusion

Methanol can be produced from diverse feedstock resources such as natural gas, naphtha, coal, and biomass. Majority of methanol production plant nowadays is based on natural gas while coal comes second and small amount of other alternative ways like biomass and oil. The low-pressure catalytic process is used for methanol production from natural gas. The process includes sulphuring, steam reforming, methanol synthesis and distillation Now, coal is converted into methanol through gasification which is cleaner approach than traditional coal-to-liquids technology. Gasification process can convert coal into syngas then goes through some certain process to remove impurities and byproducts. Petroleum naphtha is an intermediate hydrocarbon liquid stream refined from crude oil. The development of viable catalytic technologies for the selective catalytic hydrogenation of CO2 to methanol offers a path advancing into a carbon neutral society reducing the huge CO2 emissions from fossil fuels by altering them into fuels and chemicals. Since the early 1990s, the chemical valorization of CO2 by hydrogenation to methanol has been the emphasis of research and much effort has been spent in the development of catalysts. For the wider implementation of this technology, important advances must be made in both catalysts with the detailed needs of the reaction conditions and process design and with reactors and separators accustomed to plants of small capacity to minimalize the gas recycle volume.

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