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Methanol to Olefin (MTO) Value Chain Management

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Abstract
The global methanol market size was USD 27.95 Billion in 2020 and is projected to grow from USD 28.74 billion in 2021 to USD 39.18 billion in 2028 at a CAGR of 4.5% during the 2021-2028 period. The methanol-to-olefins (MTO) reaction is one of the most important reactions in C1 chemistry, which provides a chance for producing basic petrochemicals from nonoil resources such as coal and natural gas. As olefin-based petrochemicals and relevant downstream processes have been well developed for many years, MTO is believed to be a linkage between coal or natural gas chemical industry and modern petrochemical industry. Many institutions and companies have put great effort to the research of MTO reaction since it was first proposed by Mobil Corporation in 1977. Getting ethylene and propylene from methanol by the MTO process represents a major progress in chemical technology in recent years. This paper deals with the conceptual design of an energy efficient and cost-effective MTO process. Hence, we try to introduce the basic value chain management of Methanol to Olefin Process and hope to give the researcher a holistic approach to develop this research by mathematical modeling, system thinking approaches and so on. The economic evaluation results revealed that the conversion of methanol to olefins is more attractive for investment than the sale of crude methanol. The development of methanol to olefins units is more economical than constructing a new gas to ethylene, polyethylene and propylene unit because of the lower investment costs.
Keywords: Methanol to Olefin (MTO), Value Chain Management (VCM), Natural Gas (NG).

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1. Introduction

Natural gas consists mainly of methane (80 to 95% by volume) and other light alkanes, commonly utilized for industrial electricity/ heating load generation. Based on the anticipated data, the remaining reserve gas is about 6.879 trillion cubic feet. It is projected that the demand for natural gas will increase to 203 trillion cubic feet in 2040. To synthesize relatively pure methane (93 Vol %), natural gas is first dewatered before distribution through pipelines, and after that it is devoid of carbon dioxide, hydrogen sulfide, and higher alkanes. Moreover, based on the report published in a statistical review of world energy markets, Iran has 17.3% of the world's whole natural gas reserves and has been ranked as the second richest country in this regard. So, it can be considered a promising region to investigate and develop propylene and methanol production plants. From technical viewpoint, a significant chunk of natural gas includes methane and other components of natural gas; for instance, ethane can be produced through steam cracking. In addition, other natural gas components such as propane and butane can be used to produce propylene and butadiene, respectively. These olefins are the building blocks of many chemicals, namely, resins, plastics, and adhesives. Reportedly, ethylene generation in 2015 was around 150 million tons, and it is projected that the worldwide demand for olefin will increase steadily at a rate of 1.5–4.1% per year (Syah et al., 2021).

The methanol-to-gasoline process (MTG, as introduced first by Mobil researchers', in 1977), and its companion, methanol-to-olefins (MTO, as introduced first by Union Carbide, in 1981) are 2 seminal and indeed epochal technological breakthroughs in synfuels research, some 50 years after the Fischer–Tropsch process. Initially developed in the United States in response to the energy crisis of the 1970s (oil embargo with the accompanying gasoline price volatility and uncertain supply chain), these 2 technological wonders are now viewed upon as a "synfuels factory", ready to put in place as technological and economic demands warrant. The genesis and evolution of the methanol-to-hydrocarbons (MTH) technology, from its discovery up until successful commercial implementation/practice, has also provided a rich tableau for scientific research and pursuits, filled with research controversies/challenges and advances (Gogate, 2019).

In contrast to olefin production from light naphtha cracking, olefins can also be produced from natural gas condensates. This is the least expensive method of producing olefins in the United States. It must be mentioned that among all the available production processes considered for methanol and propylene generation, utilizing natural gas as a feed is the more environmentally friendly process as it generates lower carbon dioxide. Based on the comprehensive study in, the amount of carbon dioxide released by natural gas-based plants is lower than coal-based plants. Developing natural gas-based plants to generate propylene and methanol will lead the world to less greenhouse gas emissions (Li et al, 2018; Wang et al, 2017; Duan et al, 2021).

Methanol is primarily produced from surplus coal and natural gas and used to produce methyl tertiary butyl ether (MTBE), acetic acid, and formaldehyde. It has many general solvent and antifreeze applications and can be used to fuel internal combustion engines, although it is usually blended with gasoline. Formaldehyde is used in pressed wood products, disinfectants and adhesives. It is also used to make chemicals for construction, automotive, healthcare and consumer products and applications. The Asia-Pacific region accounts for more than 60% of global consumption of formaldehyde and the construction industry is the largest global consumer by sector. Market growth is propelled by growing demand for fuel applications and Methanol-to-Olefins (MTO) technology, but hampered by fluctuating methanol prices. Methanol to olefins (MTO) reaction as an important non-oil route to produce light olefins has been industrialized, and received over 80% ethylene plus propylene selectivity. However, to achieve high single ethylene or propylene selectivity towards the fluctuated market demand is still full of challenge.

2. Methanol Production

Methanol (CH_3OH, conventionally indicated as MeOH) is today one of the most important building blocks in the chemical and pharmaceutical industry and in the production of synthetic hydrocarbons. The worldwide methanol production is about 90 Mt/yr.: most of it (about 65 %) comes from natural gas by means of steam methane reforming, while the remainder (35 %) comes from coal through gasification processes (Sollai et al, 2023).

The production of high-demand chemical commodities such as ethylene and propylene (methanol-to-olefins), hydrocarbons (methanol-to-hydrocarbons), gasoline (methanol-to-gasoline) and aromatics (methanol-to-aromatics) from methanol obtainable from alternative feedstock, such as carbon dioxide, biomass, waste or natural gas through the intermediate formation of synthesis gas has been central to research in both academia and industry. Methanol can be produced from several carbon-containing feedstock's, such as Natural Gas (NG), coal, biomass, and CO2. For each of them, the reactions and technologies involved are examined in detail.in this paper we focused on Methanol production from Natural Gas.

The fabrication of methanol from natural gas as a feedstock is a simple manner and the preferred purity of methanol can be attained. Furthermore, the utilization of natural gas as a feedstock is safer compared to gasoline fuels which have a high risk of flammability. Methanol derived from natural gas has an efficiency of around 55-65% which is expected to grow the methanol market size in the forecasting period. The coal sub-segment is expected to have lucrative growth in the forecasting years as there is an increase in the usage of coal to obtain methyl alcohol in the territories abundant with coal reserves. The natural gas sub-segment accounted for the highest market share in 2021 whereas the coal sub-segment is estimated to show the fastest growth during the forecast period.

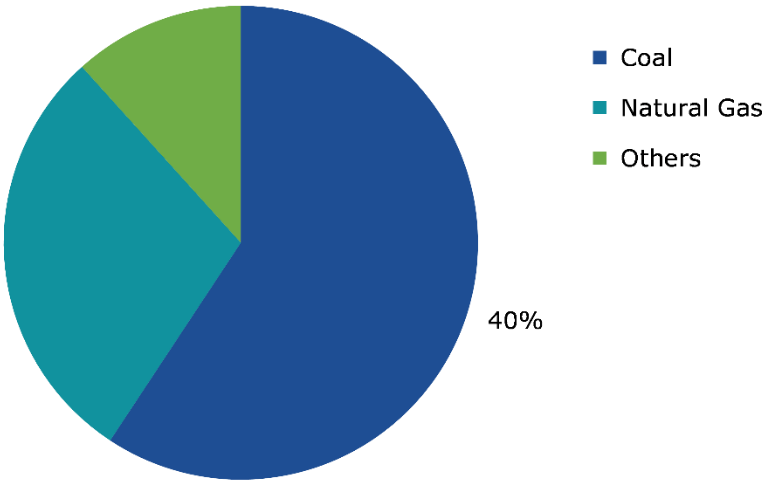

Figure 1. Global Methanol Market Size, By Feedstock

The natural gas sub-type is anticipated to have a dominant market share and generate a revenue of $23,522.9 million by 2030, growing from $14,951.2 million in 2021. The production of methanol from natural gas is a simple process that involves simple processes such as synthesis gas production, syngas conversion into crude methanol, and crude methanol distillation to achieve the desired purity. The methanol produced using this process is water soluble, clear liquid, and readily biodegradable. The use of methanol as a feedstock offers several advantages such as energy security owing to low dependence on gasoline-based fuel, lower production cost, and others. The use of natural gas as a feedstock is safe compared to gasoline-based fuels owing to low risk of flammability. In addition, the efficiency of methanol production from natural gas is as high as 50-60%and it depends on degree of waste heat recovery.

Figure 2. Methanol Market Share, By Region

Asia Pacific region happens to be the major contributor for the growth of this market. As an expansion of the automotive and construction industries in China and India the market is expected to grow. China is a major manufacturer and consumer of derivatives and this happens to be an important factor in the growth of the market. The North American region is also seeing a good growth in the methanol market as there is a demand for fueling applications like production of green fuels and fuel blending. The increasing petrochemical industry is also supporting the market's progress. A growing preference for sustainable products and increased demand for automotive in the European region will lead to a growth of the market in this region. The Middle East, Africa and Latin America are also expected to see a growth due to industrialization and rising construction activities. The Indian government is consistently pushing the utilization of methanol in the automobiles and the use of methanol in cooking fuel. These steps will help in promoting sustainable development as it is an ecofriendly option. A capital investment of U.S. dollar to 46 million was made in order to convert around 3,600,000 tons of waste into green methanol by the Netherlands. This initiative is expected to provide growth opportunities for the methanol market across the European region.

3. Methanol Form Natural Gas

The reserves of natural gas increased 18.2% between 2007 and 2017 worldwide, reaching 193.4 Trillion Cubic Meters [TCM] according to the following distribution: 40.9% in the Middle East, 30.6% in the Commonwealth of Independent States (CIS), 10.0% in Asia Pacific, 7.1% in Africa, 5.6% in North America, 4.2% in South and 1.6% in Central America and Europe. The production of natural gas between 2007 and 2017 raised 25.12% worldwide, ranging from 2.94 to 3.68 [TCM], allocated as follows: North America 25.9%, CIS 22.2%, Middle East 17.9%, Asia Pacific 16.5%, Europe 6.6%, and Africa 6.1%, South and Central America 4.9% [3]. In contrast, world consumption between 2007 and 2017 increased by 24.08%, from 2.96 to 3.67 [TCM]. The reported share of energy consumption was: North America 25.7%, Asia Pacific 21.0%, CIS 15.7%, the Middle East 14.6%, Europe 14.5%, South and Central America 4.7%

and Africa 3.9% (Becerra-Fernandez et al, 2020). Natural gas is one of the important energy resources and recently its worldwide consumption is rapidly increasing because of the growing demand for clean energy and environmental concerns. It is predicted that the natural gas demand increases at an average rate of 2.4 percent annually until 2030 in the world (Mohammadi, 2022).

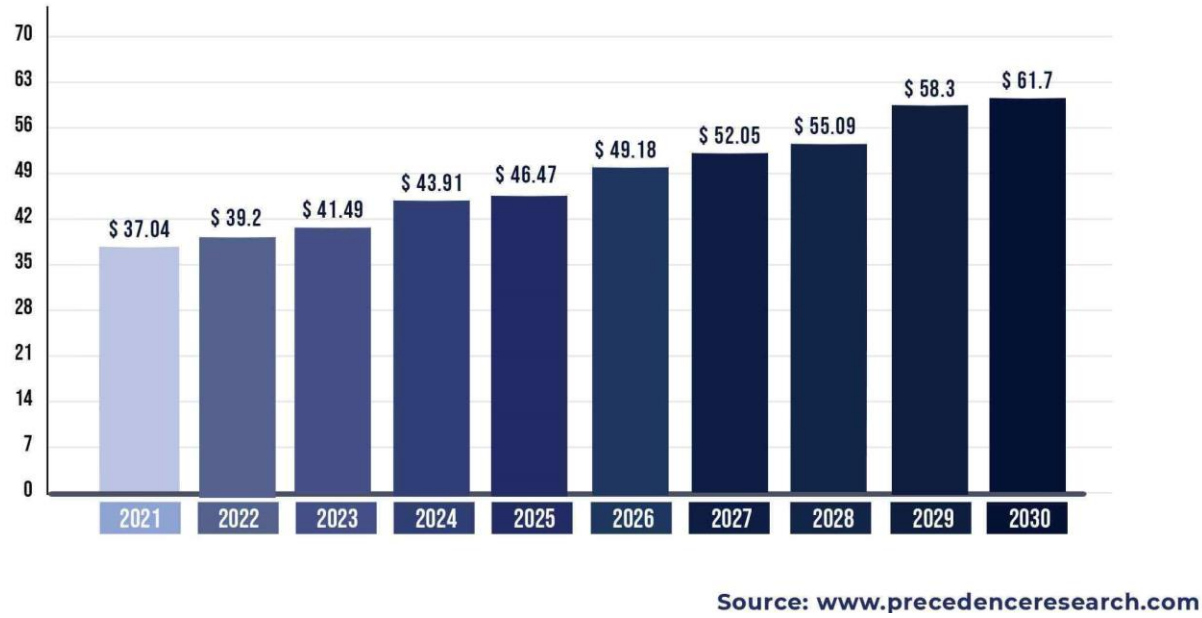

Figure 3. Methanol market size, 2021 to 2030 (USD BILLION)

A search into a viable method for natural gas conversion to methanol becomes imperative not only to save the soul of the ever-changing climate but also to bring an end to wastage of valuable resources by converting hitherto wasted natural gas to wealth. Currently the technologies of conversion of natural gas to methanol could be categorized into the conventional and the innovative technologies. The conventional technology is sub-divided into the indirect method also called the Fischer-Tropsch Synthesis (FTS) method and the direct method. The major commercial technology currently in use for production of methanol from methane is the FTS method which involves basically two steps which are the steam reforming and the syngas hydrogenation steps. The FTS method is highly energy intensive and this is a factor responsible for its low energetic efficiency. The direct conversion of methane to methanol is a one-step partial oxidation and lower temperature method having higher energetic efficiency advantage over the FTS method (Salahudeen et al, 2022).

The current structure of the production and consumption of methanol is reviewed. The main processes of methanol processing and catalysts for their implementation are highlighted: the production of formaldehyde, hydrocarbons (MTH), olefins (MTO), and the production of hydrogen from methanol by means of steam reforming, partial oxidation, auto thermal reforming, and decomposition.

Currently, about 90% of methanol is produced from natural gas. The process route for the production of the simplest alcohol is relatively straightforward, involving the three following basic steps:

1) Production of Synthesis Gas.
2) Conversion of the syngas into crude methanol;
3) Distillation of the reactor effluent (crude methanol) to achieve the desired purity.

The mixture of syngas (H2, CO, and CO2) is mainly produced by steam reforming (SR) and Auto Thermal Reforming (ATR) of natural gas, as shown in Equations (1), (2):
Steam Reforming:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (1)$$

Auto Thermal Reforming:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (2)$$

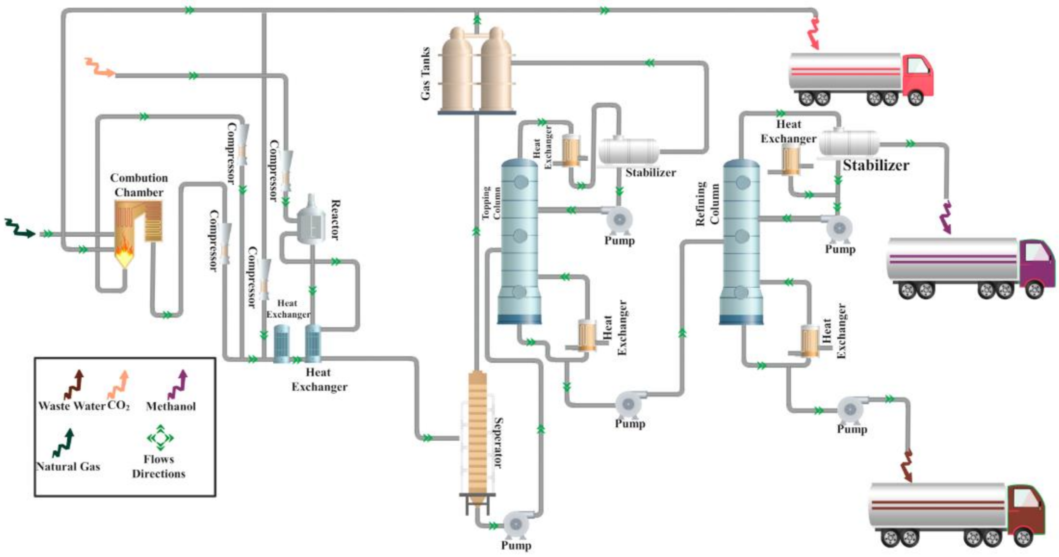

Figure 4. Methanol generation loop via natural gas reforming based on Lurgi Technology

4. Methanol to Dimethyl Ether (DME)

Due to a plenty of advantages, dimethyl ether (DME) is currently receiving a great deal of attention. Efficient ignition, non-toxic emissions, high heating value, easy and safe transportation, and the capability of converting to a variety of products are the major advantages of DME. Despite diverse technologies for DME manufacturing, methanol dehydration is currently the well-developed route (Bakhtyari & Rahimpour, 2018). A major part of DME is consumed in the production of dimethyl sulfate through the reaction with sulfur trioxide. Besides, it could be efficiently converted to acetic acid through carboxylation reaction (Muller & Hubsch, 2005). DME is a key building block for the production of downstream chemicals such as ethanol, light olefins, methyl acetate, and aromatics. Due to the environmentally friendly nature of DME, it is suggested as an aerosol and refrigerant in cooling facilities. In fact, DME makes zero ozone defects and thus does not intensify global warming issues. Therefore, in competition with the conventional refrigerants such as Freon, CFCs (i.e., chlorofluorocarbon), and R-134, DME is acquiring popularity (Azizi et al, 2014; Zhou et al, 2016; Park et al, 2016).
Dimethyl ether (DME) is a promising multisource and multipurpose clean fuel and value-added chemical synthesized from syngas. This process can be either performed in a single stage (direct process) using a dual catalysis system or a two stage (indirect process) where syngas is first converted into methanol and then dehydrated to produce DME. While the dehydration reaction has been studied extensively over multiple decades, to date no review has been conducted on the catalysts involved in the methanol dehydration reaction (Bateni & Able, 2019).

5. Methanol to Olefin (MTO)

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The production of olefins via the catalytic conversion of methanol on zeolites and zeotypes is of great interest to both the scientific community and specialists in related areas of the national economy. Due to the gradual industrial implementation of the above process, the focus of attention is gradually shifting from scientific research devoted to the synthesis and modification of zeolites and zeotypes of different structures; to studies of pilot and industrial installations; to determining the main economic and environmental indicators, both existing and planned; and to the construction of production facilities. In 2019 alone, China licensed the construction of 26 production sites with a capacity of 14 million T/Yr for ethylene and propylene, and commissioned 14 enterprises with a total capacity of 7.67 million T/Yr for ethylene and propylene. The established production facilities include a full cycle of coal processing that consists of coal gasification units for the production of synthesis gas; units for the production and purification of methanol and olefins; and units for the production of polyethylene and polypropylene. The total productivity of the commissioned plants is more than 21 million T/Yr for ethylene and propylene (Brovko et al., 2022).

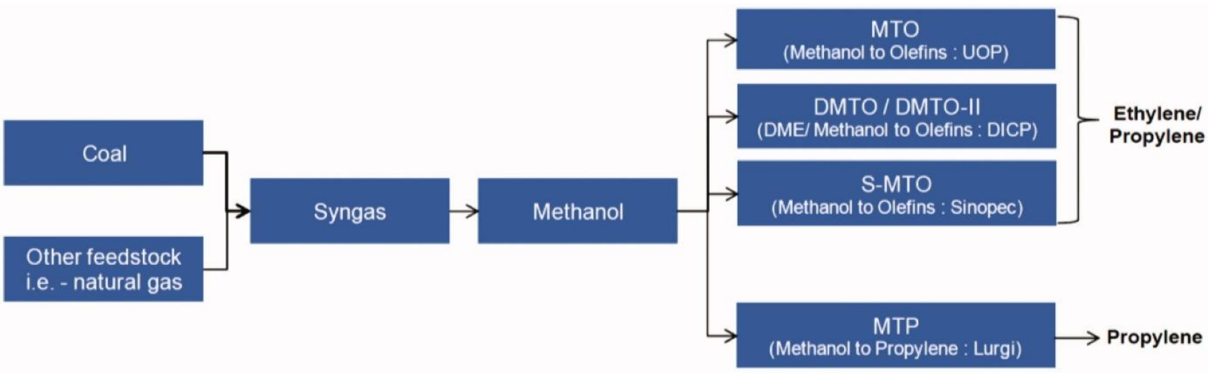

Figure 5. Overview of the methanol-to-olefins process (MTO), with four primary technologies available for commercial installations (Gogan, 2019)

6. Methanol Production Value Chain

Currently, global energy generation largely relies on fossil fuel resources. Coal, oil, and natural gas represent nearly 80% of global energy resource consumption. Petroleum oil is still the most important raw feedstock for the production of numerous key petrochemical building blocks. Nevertheless, it is non-renewable or finite resources and the use of this fuel type releases large amounts of greenhouse gas, causing global warming problems and a public health concern (Olah et al., 2018). Among the petrochemical building blocks, light olefins, such as ethylene (C_2H_4) and propylene (C_3H_6), are the two hydrocarbon intermediates having the largest volume requirements, and they can be used to generate many important derivatives (Arvidsson et al., 2016).

Coal was the driving force behind the Industrial Revolution in the 19th century, and crude oil took over that role in the 20th century. However, due to environmental concerns, the global energy demand has shifted to lower carbon fuels since the late 20th century. Natural gas is considered as a “transition fuel” toward a cleaner, more sustainable, and environmentally-friendly energy supply (Mohammadi, 2022). The availability of low-cost methanol is a requirement for profitable MTO business. However, a supply-chain of higher-value end-products, namely specialty polymers, allows getting profitable margins even with higher methanol cost, as it is the case in IRAN. The starting point for methanol production is syngas (CO and H_2 mixture), in turn available from various sources, as natural gas, biogas, biomass, or coal. The aim of any value chain & network analysis is to understand the systemic factors and conditions through which a value framework and its firms can achieve higher levels of performance. Industry stakeholders commonly benefit from a systemic value network analysis because it identifies key areas in the value network where constraints occur and opportunities for improvements arise. The global oil & gas industry is under considerable pressure to meet the world's demand for affordable and secure energy supply. Environmental concerns have intensified the inter-fuel competition and this battle can be prolonged in favor of optimum utility for the remaining global reserves of oil and gas (Weijermars, 2010).

The production of methanol from natural gas consists of two stages. The first stage is converting the feed gas into synthesis gas by catalytic reforming. The synthesis gas contains carbon monoxide, carbon dioxide, water, and hydrogen. The second stage is the catalytic synthesis of methanol from the synthesis gas. The two stages of methanol production are presented in equations (3) and (4). The produced methanol is considered to be kept at a temperature of 5^0C in the liquid form. The required energy to produce methanol from natural gas is about 22.356 MJ/kg (Al-Breicki & Bicer, 2020).

$$2CH_4 + 3H_2O \rightharpoonup CO + CO_2 + 7H_2 \quad (3)$$

$$CO + CO_2 + 7H_2 \rightharpoonup 2CH_3OH + 2H_2 + H_2O \quad (4)$$

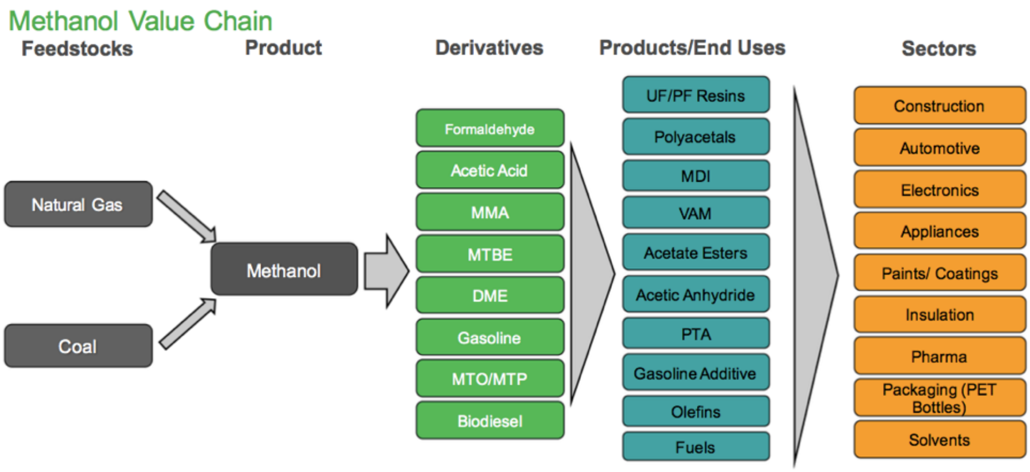

Figure 6. Methanol Value Chain

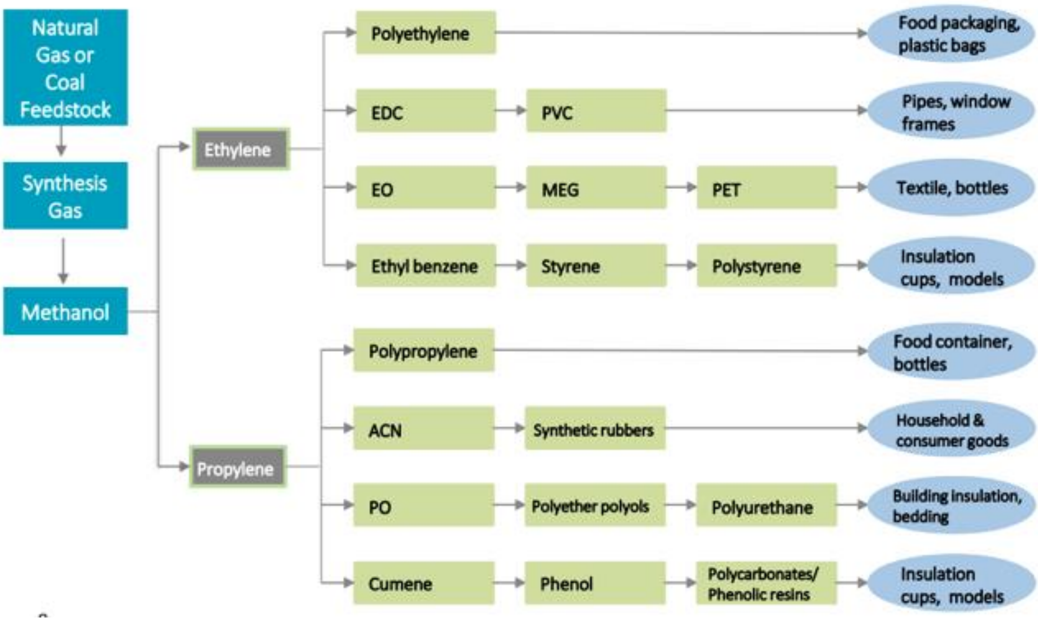

Figure 7. The Matrix of Methanol Derivates Products

7. Conclusions

The rising demand for industries like the construction and the automotive industry we will have an increased consumption of methanol. Methyl alcohol is used for the production of adhesives, textiles, plastics add insulation materials. Plastics play a vital role in automobiles by reducing the weight of the vehicle which helps in increasing the fuel efficiency of the vehicle and appears to be similar to a metal. The use of plastics in the construction industry will propel the growth during the forecast period. The demand for dresses in the furniture and consumer goods industries will support the growth of the market during the forecast period. Increasing consumption of methanol in fuel blending applications is another driving factor. Methanol is a colorless volatile light, flammable liquid which is usually mixed with ethyl alcohol which is useful for many industrial applications. Major opportunities are created for the methanol market as there is a shift of end users towards the sustainable fuels. The nature of this alcohol is versatile and has application in various industries; owing to these factors it shall serve the needs of the growing world.

Global Methanol demand stood at 84.55 million Tons in 2020 and is forecast to reach 135.60 million Tons by 2030, growing at a healthy CAGR of 4.97% until 2030. Methanol is used in a wide variety of applications in the Construction Industry, Automotive, Electronics, Fuel, Paint and Pharmaceutical Industry. With the onset of Covid-19 in the March 2020, the demand of methanol has shrunk, and the prices are lower in comparison to previous months. The largest manufacturer of methanol, Methanex Corporation has closed its operations and the imports of the methanol from the largest importer of Methanol i.e., China also came to halt due to shutdown of the Methanol producing Industries. But as the impact of Coronavirus on the economy is expected to decrease over the coming months, the demand of methanol is also expected to gain stability.

Olefins are essential building blocks for the organic synthesis. Today the olefins are manufactured almost exclusively from fossil oil and gas resources. Modern technologies, as methanol-to-olefin (MTO) and methanol-to-propylene (MTP), are available by employing renewable raw materials, namely biogas and biomass, as well as coal, which in this way becomes a clean resource for chemical industries. Today methanol is emerging as the most important building block for sustainable chemical industries. Light olefins (ethane and propene) are vital platform chemicals for the petrochemical industry. In recent years, the global energy crisis has driven the development of novel technologies for seeking alternative energy resources and diversifying the supply of petrochemical products. The catalytic conversion of methanol to hydrocarbons (MTH) over acidic zeolites, as a viable nonpetroleum route for preparation of light olefins and gasoline, has received widespread concern since it was discovered in the late 1970s. Several MTH processes including DMTO, UOP/ Hydro MTO, and Air Liquide's MTP have been successfully developed. In such a way that the nominal production capacity of methanol in the country is about 9 million tons per year; According to investment plans in this industry until 1408, this number will arrive to 26 million tons yearly. Due to the attractive economic market of these products inside and outside of Iran, almost no significant investment has been considered to increase this capacity. High production capacity of methanol in the country and the development of domestic markets for products with propylene and ethylene base materials, provided new opportunities to create units for the conversion of methanol to olefins (propylene and ethylene) in the country.

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