Proposal for the Production of Propylene from Methanol

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• Introduction

Propylene, which is also referred to as methyl ethylene or simply as propene, is a second member of a hydrocarbons group belonging to homologous series, called alkenes. Alkenes are unsaturated hydrocarbons with at least a double carbon-to-carbon bond within the chain. It has a molecular formula of C$_3$H$_6$\(^{(1)}\). The common shortening for the process is “MTP” which stands for “Methanol To Propylene”. MTP Process is an industrial chemical process that involves the production of the propylene from the methanol as a raw material. The main raw material, which is the methanol, is obtained from the synthesis gas. However, the synthesis gas is obtained from the natural gas or coal. MTP Process can be broken down into two primary processes namely the first step and the second step. The first step involves dehydration of the methanol to compound called dimethyl ether. The dehydration of the menthol requires the presences of the aluminum oxide catalyst as the condition for the reaction. However, propylene is the primary product when the reaction is performed in the presence of the zeolite-based catalyst (Zeolite HMOR (Na8Al8Si40O96.24H2O)). The second step, when the propylene produced is further channeled to a series of purifiers to obtain compound called polymer grade propylene\(^{(2)}\).

Throughout this proposal paper, research has been conducted for the on purpose polymer grade -propylene production form methanol using the methodology of literature review. Many journal articles, research papers, books, industrial statistics, and data bases have been used in conducting this proposal; all of which are presented in each section.
• Importance of the MTP Process

Apart from production of the propylene, another reason this project is worth considering is that it offers a cheaper alternative to producing the propylene. As stated earlier, the main raw material for this process is the methanol. Methanol is cheap because it is also processed from the readily available natural gas or the coal. These cheap raw materials make the process cost effective and sustainable. Another reason this project is worth considering is the fact that it produces other useful products apart from the targeted propylene. Other useful products that this process provides include the gasoline, fuel gas, and Liquid Petroleum Gas (LPG). Therefore, the production of these useful products together with the target product makes this process more profitable (4).

MTP process get our attention also because of the importance of the propylene in the petrochemical industries and also Propylene demand is growing very fast in the world. Moreover that the propylene is involved in many downstream product that can be used in many products.

Another advantage is the new technology that is going to be used in this process, the new technology which is using a new catalyst (Zeolite HMOR (Na8Al8Si40O96.24H2O)) used in MTP reactors to produce propylene with high selectivity and catalytic stability. The new catalyst introduces better stability and reduces the cost of utility consumption while maintain the high quality of the propylene product.
• **Downstream Uses of Propylene**

It is worth noting that propylene is one of the essential chemicals used in the petrochemical industries. It is ranked second after ethylene in regards to their importance as raw materials for manufacturing of the industrial chemicals. Propylene is considering one of the most important row materials for the chemical industry. Propylene has more than one use in chemical industry. Propylene can be used to produce polypropylene, propylene oxide, acrylonitrile, and other uses. From Figure 1, in 2014 64 % of propylene sent to the manufacture of polypropylene, also 7 % sent to manufacture of propylene oxide and the third largest use of propylene sent to manufacture of acrylonitrile (6 %). The remaining percentage sent to other manufacture of chemical such as acrylic acid, cumene, and Oxo alcoholes. Figure 2 to shows more of the downstream uses of Propylene. (8)

![Pie chart showing global propylene demand by application in 2014](image)

- Polypropylene
- Propylene oxide
- Acrylonitrile
- Others

Figure 1: Global Propylene Demand by Application in 2014
Figure 2: Downstream use of Propylene and examples
- Prices of Propylene and Historical Trends

![Propylene World Demand](image)

Figure (3): Propylene World Demand

As I mentioned before that the propylene demand is growing very fast in the world. Shown in figure (1) of demand, there are 5.5 percent average annual growth from 1995 to 2000 which is 37.2 million tons demand grow in 1995 and 52 million tons in 2005. Also, 4.6 percent average annual growth from 2000 to 2006 and roughly 5 percent average annual growth from 2007 to 2015 \(^{(9)}\).
As you can see from the pie chart (Figure 5) that China is the major propylene market. The propylene price is changing in the world. For instance in Asia the propylene price went up due to higher upstream crude oil and the Naphtha value. In United States the propylene price went down because of weak buying sentiments amid sufficient product availability. In the Europe also the price decreased because of bearish upstream energy value amid ample product availability in the region. \(^{(8)}\)
Historically, the prices of the propylene have been constantly fluctuating; the fluctuations that have been experienced are due to some of the factors. Examples of such factors include the fluctuations of the prices of the raw materials, and also the strict environmental rules and regulations that governs the pollutions that are caused by the production of the propylene.

The most up to date prices are for propylene is 1016 dollar per ton, and the methanol is 427 $/ton. From Saudi Aramco, liquefied petroleum gas (LPG) prices for September 2014 are 20-45$ /ton. This is the first increase since last June. The price of the methanol is 1177 $/ton. (6)
• **Environmental Considerations:**

Methanol’s properties and toxicity are well understood in the industry. Human exposure to methanol can occur via the inhalation, ingestion, or dermal contact pathways. Identified human illnesses associated with methanol exposure include organic solvent poisoning and systemic acidosis. Methanol’s occupational Threshold Limit Value (TLV) is 200 ppm where gasoline is 300 ppm which is slightly lower.

Inhalation of methanol vapors is the most frequent type of exposure that affect human. Moreover, inhalation exposure is the most common route of entrance into the body. Methanol storages tanks that are located underground might affect the environment in the case of leaking.

Propene has low acute toxicity from inhalation. Inhalation of the gas can cause anesthetic effects and at very high concentrations, unconsciousness. However, the asphyxiation limit for humans is about 10 times higher than the lower flammability level

• **Health and Safety Consideration**

Safety procedures should be considered very seriously in the industry. All employees should be well educated regarding to health and safety concerns. Personal protective equipment should be provided for all works in the industry. Plant managers should consider safety as first priority by scheduling weekly safety meeting. Safety meetings present incidents and educate works regarding to avoiding incidents and following the safe procedures during work.
**Plant Design Safety:**

There is several safety factors should be taken to the consideration in the location of the plant. Since there is gases presented in the process of producing propylene, gas detectors should be distributed roughly everywhere in the plant. In addition to that, it was mentioned in the environmental consideration that all products and reactants are flammable therefore; fire prevention equipment and fire fighting equipment should be provided. Final, workers in the plant should be educated enough to deal with emergency situations.

**Site Location:**

The plant will be located in the Kingdom of Saudi Arabia. Saudi Arabia is more than quarter of the world’s proven oil reserves. More than 95% of the basic petrochemicals are derived from methane and natural gas feedstock. The Kingdom has the 6th largest natural gas reserves in the world and is the 9th largest producer. The Kingdom is working on diversifying its income sources and satisfying the local demand of propylene and other petrochemical derivatives as well as producing the downstream products of various petrochemicals. Saudi Arabia is planning to expand its natural gas infrastructure and that will improve the competitive in the petrochemical market. Last that might be useful to choose Saudi Arabia is that there is no Cooperate Tax. The source of our feed methanol is from neighboring plant which is Sipchem (Saudi Arabia’s leading methanol manufacturer). Our products will be also sold to neighboring plants for Sabic Company and Sadara Company.
**Reaction Chemistry**

The main reactions occurring in the process are the following:\(^{(13)}\):

1. DME Reaction: \(2CH_3OH \rightarrow CH_3OCH_3 + H_2O\)
2. DME to Ethylene: \(CH_3OCH_3 \rightarrow C_2H_4 + H_2O\)
3. DME to Propylene: \(3CH_3OCH_3 \rightarrow 2C_3H_6 + 3H_2O\)

Reaction 1 is the formation of dimethyl ether from the dehydration of methanol; this reaction is going to occur in the dimethyl ether reactor, DME reactor. Reactions 2 is the formation of Ethylene from DME in the methanol to propylene reactors, MTP reactors. Reaction 3 is the formation of propylene, also from DME, and this reaction occurs in the MTP reactors as well.

Of course, there are some side product that are produced in the MTP reactors; the following are the side reactions:\(^{(14)}\):

1. Propylene Formation From Ethylene:
   - **Path 1:**
     - Step 1: \(C_2H_4 + H^+ \rightarrow C_2H_5^+\)
     - Step 2: \(C_2H_5^+ + CH_3OH \rightarrow CH_3CH_2OCH_3\)
     - Step 3: \(CH_3CH_2OCH_3 \rightarrow C_3H_6\)
   - **Path 2:**
     - \(C_2H_5^+ + C_2H_4 \rightarrow C_3H_6\)

2. Butylene/Isobutylene Formation From Propylene:
   - Step 1: \(C_3H_6 + H^+ \rightarrow CH_3CH^+ - CH_3\)
   - Step 2: \(CH_3CH^+ - CH_3 + CH_3OH \rightarrow CH_3CH(OCH_3)CH_3\)
   - Step 3: \(CH_3CH(OCH_3)CH_3 \rightarrow CH_3C(CH_3)CH_2 + H_2O\)
   - Step 4: \(CH_3C(CH_3)CH_2 \rightarrow CH_3CH_2CH = CH_2\)
It can be noticed that the side reaction of ethylene transforming into propylene is a desired reaction that will increase the yield of propylene, the desired product. On the other hand, the formation of butylene from propylene is an undesired reaction, because it consumes the desired product.

The reaction conditions are very important to achieve high propylene yields. The reaction temperatures are from moderate to high with low pressures. The catalyst acidity also plays a great role in the favor of the propylene selectivity.

It is important to note that the production of coke and the regeneration challenges are issues that should be taken into consideration in selecting the reactor system and catalyst. These issues will be tackled further in the next steps of this design.
**Novelty**

The novelty of the process is in a new catalyst. Mordenite, HMOR, is a zeolite catalyst with a composition of Na$_8$Al$_8$Si$_{40}$O$_{96}$.24H$_2$O; which has a silicon to aluminum ratio equal to 5. This promising catalyst has a 99.8 % conversion with 44.2 % selectivity for propylene$^{(15)}$. The following Table 1 shows the MTP reaction and the products selectivity for HMOR and HZSM-5 catalysts. HZSM-5 is the current zeolite catalyst used in the MTP process; it has a silicon oxide to aluminum oxide ratio equal to 80.

**Table 1: MTP Reaction Product Selectivity Comparing HMOR to HZSM-5$^{(15)}$**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Selectivity (C-mol%)</th>
<th>C$_1$-C$_4$$^a$</th>
<th>C$_2$H$_4$</th>
<th>C$_3$H$_6$</th>
<th>C$_4$H$_8$</th>
<th>C$_5^+$ $^b$</th>
<th>Aromatics</th>
</tr>
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<tr>
<td>HZSM-5</td>
<td>99.6</td>
<td>18.5</td>
<td>18.0</td>
<td>22.7</td>
<td>8.25</td>
<td>12.6</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>HMOR</td>
<td>99.8</td>
<td>3.62</td>
<td>6.88</td>
<td>44.2</td>
<td>19.4</td>
<td>23.9</td>
<td>2.60</td>
<td></td>
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$^a$ Saturated Hydrocarbons

$^b$ Excluding Aromatics

From Table 1, it can be noticed that the propylene selectivity is doubled between both catalysts, from 22.7 % to 44.2 %; the selectivity of lighter hydrocarbons, C$_1$-C$_4$, has decreased from 18.5 % to 3.62 % and the ethylene production has also decreased from 18% to 6.88%. However, the butylene production has increased from 8.25% to 19.4 %; and the higher hydrocarbons C$_5^+$ has increased from 12.6% to 23.9%. Finally, aromatics selectivity has decreased from 20% to 2.6%.
It should be noted that the reaction conditions were fixed for both catalysts; the temperature was fixed at 470 °C, a weight hourly space velocity of 1 hr⁻¹, partial pressure of methanol of 0.5 atm and a water to methanol ration of 1:1\(^{(15)}\).

- **Proposed Process Flow Diagram**

  The plant can be divided into three main sections: reaction, quench and compression, and product fractionation\(^{(16)(17)}\).

  ![Proposed Process Flow Diagram](image)

  **Figure 6: Reaction Section of the Plant\(^{(16)(17)}\)**

  In the first section, reaction, the feed, which is pure methanol, is first vaporized then combined with recycled methanol and dimethyl ether (DME) then superheated before entering the DME reactor. In the DME reactor, methanol is dehydrated, the product is a mixture of DME, water, and unreacted methanol. The product, with some recycled hydrocarbons, is then fed into the MTP reactors on several stages to increase the conversion and maintain isothermal conditions in the reactors. There are two reactors to conduct the reaction, and one reactor for regeneration.
The product mixture from the reactors is then cooled and sent to the quench and compression section.

Figure 7: Quench and Compression Section of the Plant$^{(16)(17)}$

In the quench unit, water is separated from the hydrocarbon mixture. The water-methanol mixture is then sent to the methanol recovery column, while the hydrocarbon mixture is compressed, partially condensed and sent to a flash separator to separate the light hydrocarbons from the heavier hydrocarbons.
The light hydrocarbons are compressed and condensed before entering the DME recovery column [1]. In the DME recovery column, the three carbon and less molecules are distilled at the top, while the four carbon molecules are extracted in the bottom as liquid petroleum gas, LPG. The distillate is then sent to another flash separator to remove any remaining water and methanol from the stream and recycle it back to the methanol recovery column. The vapor from the flash separator is then compressed and condensed before entering the Deethanizer column [4]; in the Deethanizer column the two carbon molecules are distilled out as fuel gas while the three carbon molecules are sent to the carbon three splitter [5]. In the carbon three splitter, polymer grade
propylene is distilled out at the top of the column while propane is extracted in the bottom as LPG.

Figure 9: Product Fractionation for the Heavy Hydrocarbons\(^{(16)}(17)\)

The heavy hydrocarbons, is sent to a Debutanizer column [2]; trace amounts of the light hydrocarbons are distilled at the top of the column and are to be mixed with the vaper stream coming out of the second flash separator. The bottom product, mainly the heavy hydrocarbons, are sent to a Dehexanizer column [3] where the bottoms product is gasoline, and the top product is some trace amounts of lighter hydrocarbons that are recycled to the MTP reactors.
The bottoms product from the quench unit, water methanol, is mixed with the recycle stream from the second flash separator and sent to a methanol recovery column [6]. Methanol, with trace amounts of DME, is distilled in the top of the column and is sent to be mixed with the feed before entering the DME reactor, while the bottoms water stream is to be reused in the plant to utility purposes.

- **Process Design Simulation:**

  The plant will be designed through Aspen plus V8.8. The units needed, reactants and products are all defined in Aspen database. Propylene that is the main product of the design will be send to Sadara for downstream products. In addition to that, all the bi-products will be transported and sold.
• References


10) http://www.sadara.com/


