



# Methanol to Olefins (MTO) & Dimethyl Ether to Olefins (DMTO) Processes

## Group 4

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## 1 Introduction

The extraction of unconventional gas has significantly increased the availability of natural gas over the past decade, driven by advancements in horizontal drilling and hydraulic fracturing. This innovation has unlocked vast quantities of shale gas, primarily composed of methane but often containing impurities like nitrogen, carbon dioxide, and light hydrocarbons, which require specialized treatment for effective processing. Traditional ethylene production typically involves the thermal cracking of naphtha or natural gas liquids (NGL). However, alternative methods using methane as a feedstock, such as Oxidative Coupling of Methane (OCM) and Methanol-to-Olefin (MTO), are gaining attention. The report consists of explanation of two methods of converting Methanol to Olefin which are :

- Traditional MTO Process
- DMTO Process

These process were simulated on DWSIM and analysed on yield of two olefins that are Ethene and Propene which are covered in following sections.

## 2 Objectives

- How to convert Methanol to Olefin effectively.
- Study how to make the process eco-friendly and sustainable.
- Comparing MTO and DMTO and finding which one is more efficient.

## 3 MTO : Methanol To Olefins

In the MTO process, natural gas is first reformed into synthesis gas, a mix of CO and H<sub>2</sub>, then converted into methanol. Finally, methanol undergoes a catalytic reaction to produce ethylene along with other low-weight olefins. This study focuses on assessing the profitability and environmental impact of using shale gas in the MTO processes for ethylene production.

### 3.1 Chemicals Required

- **Purified Shale Gas** – Primarily methane ( $\text{CH}_4$ ), which is reformed to produce synthesis gas (syngas).
- **Steam** ( $\text{H}_2\text{O}$ ) – Used in the steam methane reforming (SMR) process to convert methane into syngas.
- **Hydrogen** ( $\text{H}_2$ ) – Required to maintain the appropriate  $\text{H}_2/\text{CO}$  ratio during the syngas production stage.
- **Methanol** ( $\text{CH}_3\text{OH}$ ) – Produced from syngas, which is later converted into light olefins (ethylene and propylene) through the MTO reactor.
- **Catalysts** – Silicon aluminophosphates (SAPO-34) are used for high selectivity in converting methanol to light olefins. (Though not used in DWSIM simulation).

### 3.2 Chemical Equations

### 3.2.1 Methanol Dehydration to Ethylene



This reaction releases approximately  $-2.8$  kcal/mol at 700 K.

### 3.2.2 Methanol Dehydration to Propylene



This reaction releases approximately  $-7.4$  kcal/mol at 700 K.

### 3.2.3 Other Reactions

These reactions are catalyzed using SAPO-34 (silicon aluminophosphate) to produce ethylene and propylene selectively, along with water as a byproduct. and many side reactions of olefins converting into saturated hydrocarbons also takes place .

### 3.3 Flowsheet

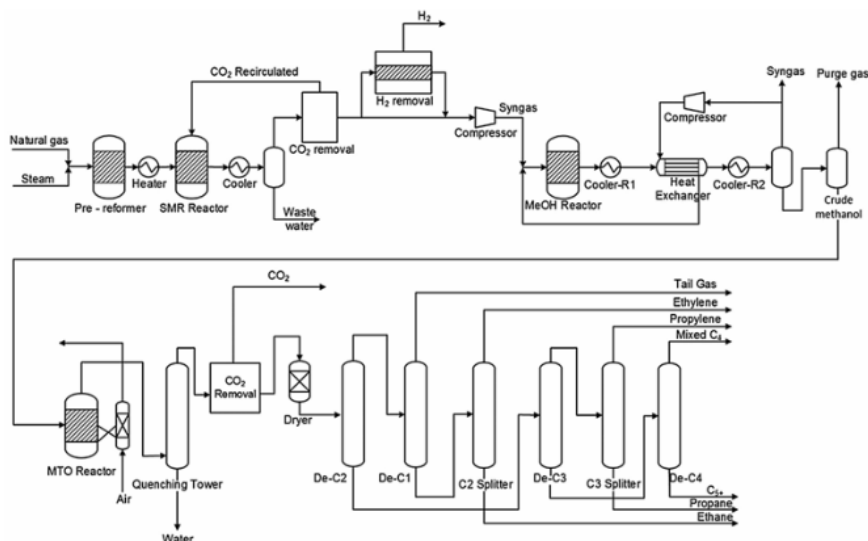


Figure 1: MTO FLOWSHEET

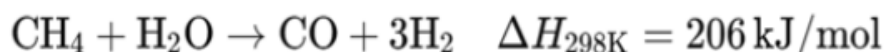
### 3.4 Methodology

The Methanol-to-Olefins (MTO) process transforms shale gas into valuable olefins, mainly ethylene and propylene, through three key stages: reforming, methanol synthesis, and methanol-to-olefins conversion. This process features specific catalytic reactions, separations, and recycling methods.

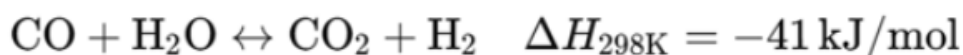
#### 3.4.1 Reforming Stage

In the first stage, purified shale gas, primarily composed of methane, is converted into synthesis gas (syngas), which is a blend of hydrogen (H<sub>2</sub>) and carbon monoxide (CO). Steam Methane Reforming (SMR) is chosen as the reforming technique due to its proven commercial viability. Key Reactions are:

- Methanol reforming:



- Water-Gas shift reaction:

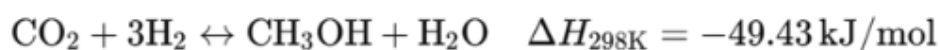


During this phase, CO<sub>2</sub> is extracted from the outlet of the SMR reactor and recycled. A hydrogen removal unit is utilized to achieve the necessary H<sub>2</sub> ratio for methanol synthesis.

#### 3.4.2 Methanol Synthesis

After compression, the syngas is sent to a catalytic reactor for methanol production. The operating conditions are set at 260°C and 83 bar to optimize efficiency, leading to the following reactions:

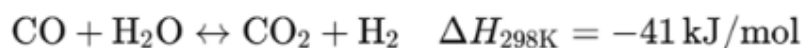
- Methanol Formation from CO<sub>2</sub>:



- Methanol Formation from CO:



- Water-Gas Shift Reaction (repeated for balancing syngas):



The methanol reactor is modelled with an conversion reactor model in DWSIM. Following cooling, any unreacted syngas is separated in a flash unit and recycled back to the reactor, maintaining a 0.5 recycle ratio.

#### 3.4.3 Methanol-to-Olefins (MTO) Conversion

In the final stage, crude methanol is converted into light olefins (primarily ethylene and propylene) using a silicon aluminophosphate (SAPO-34) catalyst, which ensures high selectivity for smaller olefins. Key Reactions :

- **Ethylene Formation:**



- **Propylene Formation:**



The MTO reactor operates at 450°C and 1.5 bar, modeled as an RYield reactor in DWSIM. The output is rapidly cooled in a quenching tower, followed by a purification process where CO<sub>2</sub> and water are removed in an absorber and dryer, respectively. Distillation columns (demethanizer, de-ethanizer, depropanizer, debutanizer, and C<sub>2</sub>/C<sub>3</sub> splitters) are used to separate and purify the final ethylene and propylene product streams.

### 3.5 Advantages

- **Economic Viability:** The MTO process showcases a strong Return on Investment (ROI), especially when shale gas prices are low, positioning it as a competitive choice for olefin production. Compared to alternatives like the Oxidative Coupling of Methane (OCM) process, the MTO process offers a more appealing ROI due to its effective conversion stages.
- **Energy Integration Potential:** The MTO process also has significant potential for energy integration, which can lead to lower operating costs. It enables the reuse of heat at various stages, reducing the reliance on external energy sources. This capability for energy optimization facilitates cogeneration, which decreases cooling utility needs and allows for electricity generation from surplus process heat.
- **Selective Catalysis:** Utilizing a silicon aluminophosphate (SAPO-34) catalyst, the MTO process achieves high selectivity for small olefins, particularly ethylene and propylene. This selectivity is beneficial for maximizing the yield of desired products, further enhancing the economic efficiency of the process.
- **Environmental Adjustments:** While the MTO process may initially present a higher carbon footprint due to CO<sub>2</sub> emissions from purge streams, modifications—such as increasing the recycling ratio of syngas after methanol synthesis—can help reduce its environmental impact. These adjustments enable the MTO process to reach environmental performance levels similar to those of alternative methods.
- **Flexibility in Byproducts Management:** The design of the MTO process incorporates effective separation units for managing various byproducts (e.g., de-methanizers, de-ethanizers, and C<sub>2</sub>/C<sub>3</sub> splitters). This flexibility allows for the efficient handling and purification of byproducts, improving overall process efficiency and product quality.

These characteristics position the MTO process as a strong candidate for large-scale, efficient production of light olefins from shale gas, particularly in contexts where economic and energy efficiency are crucial.

### 3.6 Challenges faced During Simulation

There were many challenges made during the simulation process

- No catalyst can be used so adjusted the reaction accordingly .
- There were no Packed Bed Reactor so we used a conversion reactor and calculated the conversion rate .

- De ethanizer and separator were interchanged by gas liquid separator .

These problems were tackled by trial and TA's help making the below flowsheet work .

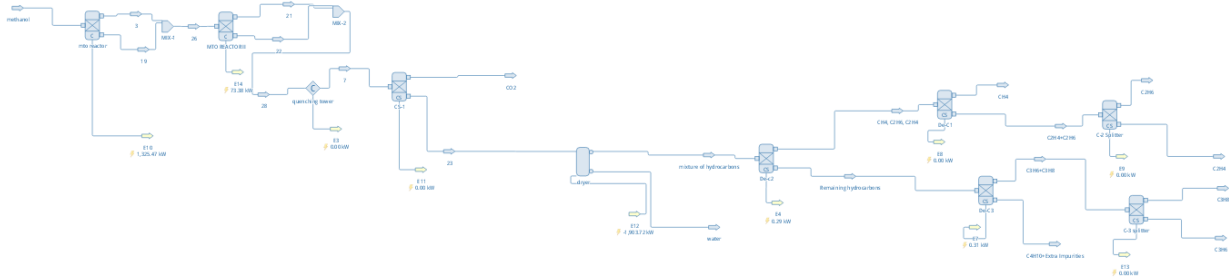


Figure 2: MTO SIMULATION

### 3.7 Results Of MTO

Input/Output material balance for a MTO process			
	Input	Output	
	Flow Rate (kg/s)	Yield (%w)	Flow Rate (kg/s)
C2H4		55.7	0.142
C3H6		39.3	0.179
<b>Total Olefins</b>			<b>0.241</b>
MeOH	1		0
CH4		0	0
C2H6		3	0.007609
C3H8		2	0.00505
<b>Total hydrocarbon</b>	<b>1</b>	<b>100</b>	<b>0.012659</b>
Water			0.7001
Impurities			0.028
<b>Total (kg/h)</b>	<b>1</b>		<b>1</b>

## 4 DMTO :DiMethyl-Ether to Olefins Process

The DMTO (Dimethyl Ether to Olefins) process is an innovative petrochemical method used to convert dimethyl ether (DME) into light olefins like ethylene and propylene, which are essential building blocks for the plastics and synthetic materials industries. This technology emerged as an alternative route for olefin production, especially valuable in regions with limited petroleum resources but abundant coal or natural gas. The DMTO (Dimethyl Ether to Olefins) process originated as an extension of methanol-to-olefins (MTO) technology, developed initially by Mobil in the 1970s to reduce dependency on oil. In the early 2000s, China's Dalian Institute of Chemical Physics (DICP) and Sinopec advanced this technology, optimising it for regions rich in coal and natural gas. The first commercial DMTO plant was established in China in 2010, providing an alternative pathway to produce essential olefins like ethylene and propylene.

### 4.1 Chemical Required

The main chemicals used in the DMTO (Dimethyl Ether to Olefins) process include:

- **Dimethyl Ether (DME):** The primary feedstock, derived from methanol. DME is converted into light olefins in the process.
- **Methanol:** Initially used to produce DME via dehydration. Methanol is often sourced from coal, natural gas, or biomass.
- **Zeolite Catalyst:** A specialized catalyst, typically based on SAPO-34 (Silicoaluminophosphate), which facilitates the conversion of DME to olefins like ethylene and propylene.
- **Olefins (Ethylene and Propylene):** The primary products of the process, separated and purified after the catalytic reaction.

The process also involves some auxiliary chemicals, like nitrogen or steam, for purging and controlling the reactor environment, but these are not reactants.

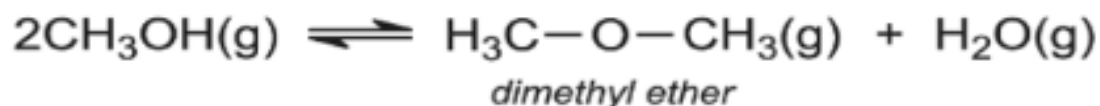
### 4.2 Flowsheet

### 4.3 Methodology

#### 4.3.1 Methanol to Dimethyl Ether (DME) Conversion

First, methanol is converted into dimethyl ether (DME) through a dehydration reaction using a catalyst, typically alumina.

**Reaction:**



This is an equilibrium reaction, where two molecules of methanol combine to form one molecule of DME and one molecule of water.

#### 4.3.2 DME to Olefins Conversion

Dimethyl Ether (DME) is fed into a reactor containing a SAPO-34 zeolite catalyst (Silicoaluminophosphate-34), which is highly selective for producing light olefins. In the presence of heat (400-500°C) and the catalyst, DME undergoes several complex reactions to produce a mixture of ethylene (C<sub>2</sub>H<sub>4</sub>), propylene (C<sub>3</sub>H<sub>6</sub>), and other hydrocarbons.

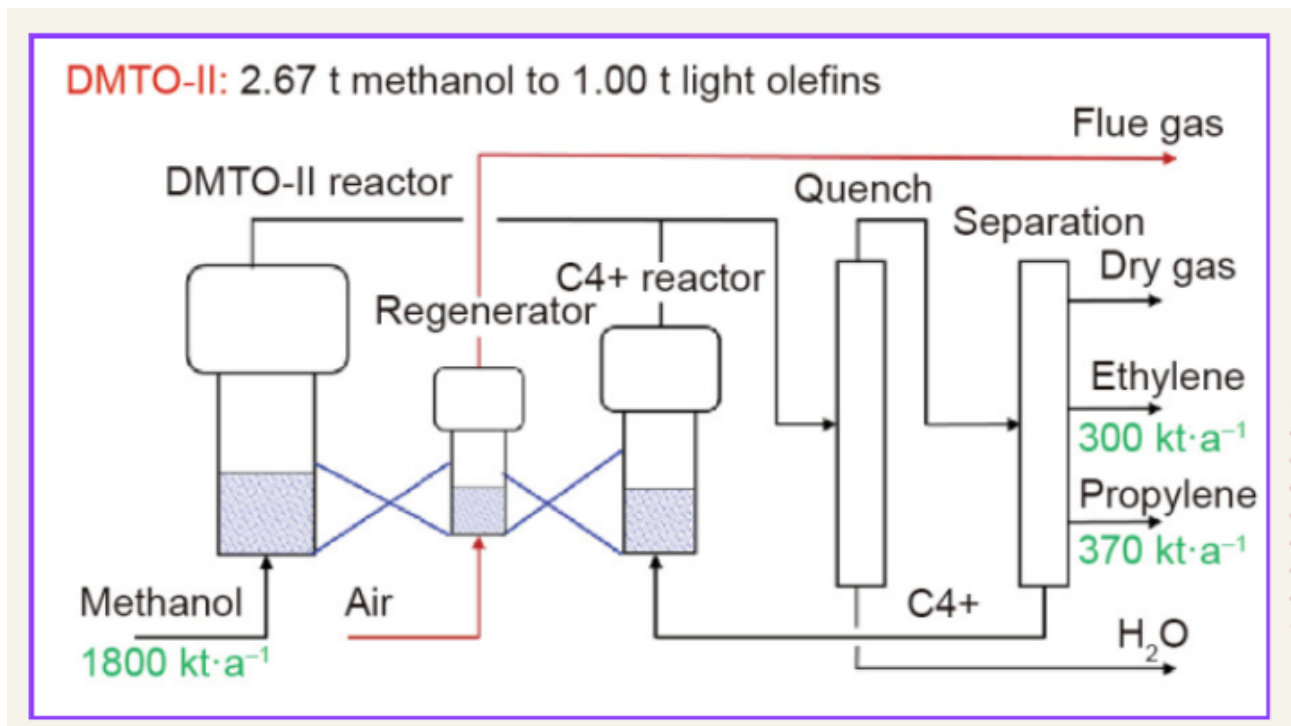


Figure 3: DMTO FLOWSHEET

- **Initial Cracking and Methylation:** DME can break down into methane and other intermediates.  
Reaction:



- **Methylation Reactions:** DME and other intermediates add methyl (CH<sub>3</sub>) groups to form larger hydrocarbons that contribute to the formation of olefins.
- **Hydrocarbon Pool Mechanism:** The zeolite catalyst facilitates a hydrocarbon pool mechanism, in which cyclic and aromatic hydrocarbons act as intermediates for producing olefins. These intermediates break down in the catalyst, releasing ethylene and propylene.
- **Paraffin and Olefin Formation:** Larger hydrocarbons formed in the hydrocarbon pool break down into paraffin (alkanes) and olefins (alkenes).

**Overall major reactions:**



## 4.4 Product Separation and Purification

The reactor's output contains a mix of ethylene, propylene, butenes, methane, carbon monoxide, water, and minor byproducts. This mixture is then cooled and condensed to separate the olefins (ethylene and propylene) from other hydrocarbons and byproducts. Further distillation and purification steps are employed to meet the commercial standards of olefins.

## 4.5 Advantages of DMTO Process

The DMTO (Dimethyl Ether to Olefins) process offers several advantages, especially for regions with abundant coal or natural gas resources but limited access to oil. Here are the key benefits:

- **Feedstock Flexibility:** The DMTO process can utilize methanol derived from coal, natural gas, or biomass, making it a versatile option for producing olefins in areas with abundant non-oil resources. This flexibility reduces dependence on crude oil and aligns with the energy availability of specific regions, particularly coal-rich countries like China.
- **High Selectivity and Efficiency:** The process is highly selective for producing ethylene and propylene, which are essential feedstocks for plastics and other chemical products. The use of SAPO-34 zeolite catalysts ensures an efficient conversion of DME to olefins, maximizing yields while minimizing byproducts.
- **Lower Carbon Footprint with Cleaner Feedstocks:** While the process generates CO<sub>2</sub> emissions if coal is used to produce methanol, it has a lower carbon footprint when using natural gas or biomass. Furthermore, technological advancements are making the process more environmentally friendly by reducing waste and emissions.
- **Reduced Dependency on Steam Cracking:** Traditional steam cracking of naphtha to produce olefins requires a large amount of energy and is dependent on oil-derived feedstocks. The DMTO process, on the other hand, reduces reliance on this energy-intensive method, providing a viable alternative with relatively lower energy consumption.

## 4.6 Challenges faced during Simulation

The challenges faced in this simulation were almost same as stated in MTO .

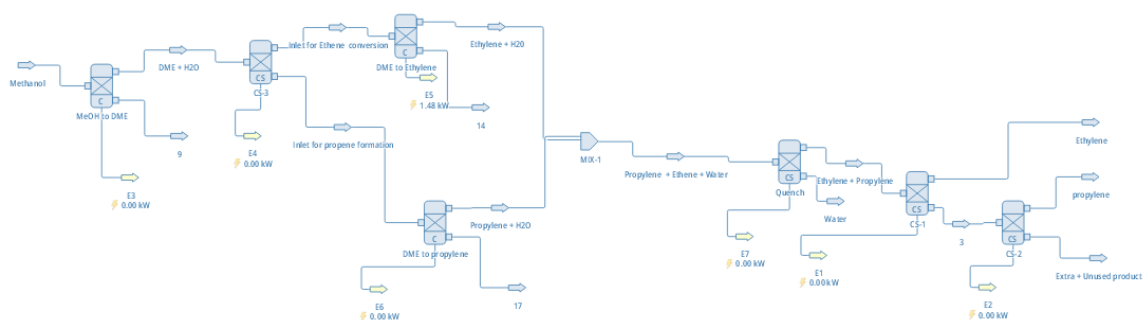


Figure 4: DMTO SIMULATION



#### 4.7 Results of DMTO Simulaton :

Input/Output material balance for a DMTO process			
	Input	Output	
	Flow Rate (kg/s)	Yield (%w)	Flow Rate (kg/s)
C <sub>2</sub> H <sub>4</sub>		29.7	0.15831
C <sub>3</sub> H <sub>6</sub>		36.6	0.19492
<b>Total Olefins</b>			<b>0.35323</b>
MeOH	1.0		
C <sub>2</sub> H <sub>6</sub> O		5.7	0.03055
<b>Total hydrocarbon</b>	<b>1.0</b>	<b>100</b>	<b>0.53378</b>
Water			0.46622
<b>Total (kg/h)</b>	<b>1.0</b>		<b>1.0</b>

## 5 Eco-Friendly Approach for MTO and DMTO Processes

Both the MTO and DMTO processes can be made more eco-friendly by focusing on several key strategies:

- **Renewable Feedstocks:** Using biomass-derived methanol or CO<sub>2</sub>-captured methanol instead of fossil-based methanol reduces carbon emissions.
- **Energy Efficiency:** Optimizing the process with advanced reactors, heat integration, and renewable energy sources (e.g., solar, wind) reduces overall energy consumption and emissions.
- **Carbon Capture:** Implementing carbon capture and storage (CCS) technologies to trap CO<sub>2</sub> emissions makes the processes more sustainable.
- **Green Catalysts:** Developing non-toxic, recyclable catalysts helps minimize waste and reduce environmental impact.
- **Waste Minimization:** Recycling by-products, improving catalyst life, and optimizing product recovery reduce waste and resource consumption.
- **Advanced Process Control:** Using real-time monitoring and AI-based optimization improves efficiency, minimizes waste, and reduces resource usage.

In essence, both MTO and DMTO can be made eco-friendly by reducing reliance on fossil fuels, improving energy efficiency, and minimizing waste through sustainable practices.

## 6 Conclusion

The Methanol-to-Olefins (MTO) and Direct Methanol-to-Olefins (DMTO) processes are both effective routes for the production of light olefins such as ethylene and propylene. The conclusion we came out stated below :

- **MTO (Methanol-to-Olefins) Process:** The MTO process converts methanol into light olefins, primarily ethylene and propylene. Methanol can be derived from various feedstocks, such as natural gas, coal, or biomass, making this process widely used across the globe.

- **DMTO (Direct Methanol-to-Olefins) Process:** The DMTO process is an advanced version of the MTO process that uses dimethyl ether (DME) as a feedstock. DME can be more easily produced from methanol and serves as a more efficient precursor for olefins production than methanol itself. This results in higher olefin yields compared to MTO.
- **Higher Yield Efficiency:** The DMTO process generally exhibits better yield efficiency due to the selective and efficient conversion of DME into light olefins. The use of DME as feedstock minimizes side reactions and enhances olefin yields compared to the MTO process though the yield percent of reactor is more in MTO results but the mass yield is more in DMTO and we get more in DMTO process.
- **Feedstock Flexibility:** Both processes offer significant feedstock flexibility, particularly in coal and gas-rich regions. These regions benefit from the ability to produce methanol from local resources, such as coal or natural gas, providing an alternative to petroleum-based feedstocks.
- **Lower Dependency on Oil-Based Resources:** Both the MTO and DMTO processes reduce reliance on crude oil for olefin production. This makes them attractive in regions aiming to decrease dependence on oil while utilizing abundant local coal or natural gas resources.

## Citation

- **Energy-efficient methanol-to-olefins process** by Alexandre C. Dimian. Available at: <https://www.sciencedirect.com/science/article/abs/pii/S0263876217306123>
- **Methanol to Olefins (MTO): From Fundamentals to Commercialisation** by the American Chemical Society. Available at: [https://pubs.acs.org/doi/epdf/10.1021/acscatal.5b00007?ref=article\\_openPDF](https://pubs.acs.org/doi/epdf/10.1021/acscatal.5b00007?ref=article_openPDF)