**In-situ Water Management for the Optimization of Methanol Dehydration to Dimethyl Ether**

**Jillian Gannon ¹, JinYing Lin ¹, Danielle Wahl ¹**  
¹. Chemical and Molecular Engineering Program, Stony Brook University, Stony Brook NY 11794

**Abstract**  
The production of Dimethyl ether (DME) on a large scale is urgent as it is a promising clean fuel. This study focuses on DME production through methanol dehydration, which is catalyzed by a solid acid, typically γ-alumina ($\gamma$-$\text{Al}_2\text{O}_3$). Previous studies have found that the byproduct water inhibits methanol dehydration through competitive adsorption with methanol on the active sites of the catalyst. This poisons the catalyst and renders it inactive. In several published papers, simulations of in-situ water removal in methanol dehydration, which is designed to be accomplished by sweep-gas or membrane separation in fixed bed reactors, show that methanol conversion is improved with in-situ water removal. Sweep-gas and membrane separation methods cannot be performed in batch reactor so it was determined that using a water absorbent/adsorbent might be a solution for solving this issue. Molecular sieves have been found to be an excellent water adsorbent. This study aims to determine the ability of molecular sieves that have a 5Å pore size to adsorb the water as it is generated in the batch reactor experiment in order to improve the conversion of methanol to DME. In each of the nine experimental runs, the reactor pressure was found to increase isothermally at a stable set temperature of 280 °C and analyzing the product using gas chromatography (GC) gave results that proved that DME was produced. The GC results also helped to determine the methanol conversion baselines: the $\gamma$-$\text{Al}_2\text{O}_3$ baseline as 26.7% ± 8.8%, the molecular sieve baseline as 25.5% ± 6.2%, and the experiment, ran with both $\gamma$-$\text{Al}_2\text{O}_3$ and molecular sieves, as 47.5% ± 8.6%. The results proved that the molecular sieves improved methanol conversion. However, DME production data is needed for further evidence that the improvement in the conversion of methanol to DME was achieved by molecular sieves.

**Keywords**: Dimethyl ether, methanol dehydration, water removal, molecular sieves.

1. **Introduction**  
Due to an increasing energy demand and a reduction in the supply of fossil fuels, focus has shifted to the use of bioenergy to replace other energy sources. Due to its abundance and renewable properties, it has been shown that biomass could be a viable source for energy [1]. Dimethyl ether (DME) is a promising clean fuel alternative with similar thermal efficiencies to diesel fuel. At ambient conditions, DME is a colorless, non-toxic, highly flammable gas. It can be handled as a liquid when slightly pressurized [1][2]. Compared to traditional diesel fuel, DME has low NOx emissions, almost no smoke and less engine noise. In addition, DME is a useful chemical
intermediate for the preparation of many important chemicals including dimethyl sulfate and high value oxygenated compounds [1][2]. Moreover, DME has been used as an aerosol propellant to replace chlorofluorocarbons which can destroy the stratospheric ozone layer [3]. Consequently, the utilization of DME is environmentally favored.

DME can be produced through synthesis directly from CO, CO2, and H2, known as synthesis gas or syngas, or by methanol (MeOH) dehydration catalyzed by a solid acid, typically γ-alumina. For several decades, the production of DME has been focused on being synthesized directly from syngas. Because of this, the role of the active components and the reaction mechanism is well understood. However, the catalytic dehydration of methanol to DME has not been as well studied [1].

To address this issue, in-situ water removal is proposed to improve the yield of DME and avoid the poisoning of the catalyst. Due to the impact water has on the reaction, various methods have been analyzed to limit the amount of water present in the reaction. Many published papers have shown that limiting the amount of water present in the reactor can improve the conversion of methanol to DME when using methods such as the sweep-gas method in fixed bed reactors, membrane separation method in membrane reactors with hydrophilic membranes, or the combination of membrane and sweep gas [4][11]. In one simulation, methanol dehydration using a membrane reactor was modified with a high water perm-selective membrane and a conventional membrane reactor. The result showed methanol conversion in the conventional membrane reactor was 68%, while with the modified membrane reactor it was 82.5% [4]. The methods proposed in these previous papers are not applicable for a batch reactor, however these results suggest that inorganic water absorbents or adsorbents may be a suitable component useful for water removal in a batch reactor.

Molecular sieves have shown to perform well in the adsorption of water.

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**Figure 1:** Production of DME from syngas [10]
Molecular sieves are a type of desiccant primarily composed of alumina, silica, and other metal oxides, with uniform pore-size distributions. They are widely used in heterogeneous catalysis [9]. It has been shown that using molecular sieves alongside a catalyst in the production of DME from methanol can not only improve diffusion in the pores, but also improve activity, selectivity, and stability [6]. Additionally, molecular sieves have been used to separate water-based azeotropic mixtures such as ethanol in water and isopropanol in water [7]. Molecular sieves of 5Å diameter are often used in the petroleum industry specifically for separating compounds in chemistry laboratories and drying starting materials in a reaction. Due to the precise and uniform sized pores, these molecular sieves are commonly used as adsorbents for both gases and liquids [9].

Our study focuses on the in-situ water management for the optimization of methanol dehydration to DME using \( \gamma \)-\( \text{Al}_2\text{O}_3 \). We hypothesize that in situ water removal can be assisted by using a molecular sieve 5Å desiccant which can improve the conversion of methanol to DME when using a batch reactor. To accomplish in-situ water removal in a batch reactor, molecular sieves with a 5 Å pore size were used as a water adsorbent. Such molecular sieves have been found to be particularly suitable to absorb water [8]. In this study, molecular sieves of a 5 Å diameter were placed in a batch reactor in order to limit the amount of water present to prevent the poisoning of the catalyst. Methanol dehydration reactions were run both with and without the water adsorbent. The methanol conversions of these products were compared in order to confirm that molecular sieve use improves the conversion of methanol to DME.

2. Materials and Methods

2.1 Chemicals

Methanol (99.8%, anhydrous, 322415) and polyethylene glycol (PEG-400, 81172), were purchased from Sigma-Aldrich and were used as the reactant and solvent, respectively, for the synthesis of DME in a standard batch reactor. Commercial gamma-alumina, purchased from Acros Chemicals, was used as a catalyst. Molecular sieves (5 Å, 8 to 12 mesh, 197295000), purchased from Acros Chemicals, were used as water adsorbents. Nitrogen gas, purchased from Airgas, was used for purging and pressurizing the system. DME (≥99%, anhydrous, 295299), purchased from Sigma Aldrich, was used as a reference sample for GC-TCD analysis.

For GC-TCD analysis, Helium gas, purchased from Airgas, was used as the carrier. The molecular sieves 5A and \( \gamma \)-\( \text{Al}_2\text{O}_3 \) were dried in a Thermo Scientific HeraTherm oven at 120 °C before being used for moisture removal.

2.2 Batch Reactor Setup

The batch reactor used to run all experiments was a Parr model 4547 batch unit fitted with a 300 mL pressure vessel. This batch unit was connected to a model 4848 process controller and a Parr model 4831 temperature controller. The batch reactor setup is shown in Figure 2 below. In each run, the reaction took place in the reactor vessel (A) that connected to the
reactor head (B) and placed on the reactor stand (C). The reactor controller (D) controlled the stirring speed and monitored the reactor conditions. The heating mantle (E) was connected to the temperature controller (F) to control the temperature of the system due to heating mantle incompatibility with the reactor controller. As shown in Figure 3, the reactor head had a pressure transducer (1) and an automatic stirrer (2), which was connected to the reactor controller, a secondary pressure gauge (3), and two thermocouples (4). One of the thermocouples was connected to the reactor controller for reporting the system temperature and the other was connected to the temperature controller for controlling the temperature of the system. The reactor head also included a gas inlet (5), gas outlet (6), and dip tube (7).

**Figure 2.** Parr batch reactor setup

**Figure 3.** Reactor head setup

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>1 (Control Group 1)</th>
<th>2 (Control Group 2)</th>
<th>3 (Experimental Group)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>γ-Al₂O₃ Baseline</td>
<td>Molecular Sieves Baseline</td>
<td>Experiment</td>
</tr>
<tr>
<td>Methanol (mL)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>PEG-400 (mL)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>γ-Al₂O₃ (g)</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>Molecular Sieve 5A (g)</td>
<td>0</td>
<td>11.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>
2.3 **Synthesis of Dimethyl Ether**

Using the batch reactor, three experiments were run using the same quantities of methanol and PEG-400, but with differing amounts of γ-Al₂O₃ and molecular sieves. Specific amounts are listed in Table 1. Each experiment was run three times. In the experimental run, 60 mL of PEG, 10 mL of methanol, 1.0 g of γ-Al₂O₃ and/or 11.0 g of molecular sieves were placed into the 300 mL vessel. The reactor was sealed and purged with N₂. During purging, the stirrer was turned on to ensure that the dissolved air leaves the system. After purging, the reactor was pressurized to 64 psig using N₂ gas. The mixture was stirred for fifteen minutes and an initial liquid sample was obtained from the vessel through the dip tube valve. Each reaction started with initial conditions of 25 °C, 60 psig, and 300 rpm. Temperature and pressure were monitored using the reactor controller and were recorded every fifteen minutes throughout each experiment. All experiments were run isothermally at 280 °C for three hours. After three hours, the batch reactor was cooled to room temperature and a final liquid sample was obtained. A gas sample was obtained from the gas outlet valve.

2.4 **Methanol Adsorption Test**

In order to determine the amount of methanol that would be adsorbed by the molecular sieves, 6 mL PEG-400, 1 mL methanol, and 1.1 g molecular sieve were added to a small glass vial. In another glass vial, 6 mL PEG-400 and 1 mL methanol were added. These two vials were stirred and placed in the sonicator bath until the mixture became uniform. Methanol concentration in the vials was measured by GC after a three-day period.

2.5 **Calibration for Methanol concentration and peak area**

In order to calibrate the methanol peak area from the GC results and the methanol concentration in the sample, five methanol/PEG-400 samples containing different methanol concentrations were prepared by mixing different volumes of methanol with 6 mL PEG-400 in small vials. The samples were placed in the sonicator bath until the mixture became uniform.

2.6 **Gas Chromatography (GC)**

A Gow Mac series 580 Gas Chromatograph with Thermal Conductivity Detector (TCD) (column 8’, packing OV101) was used to measure the methanol and DME concentrations in the samples. Helium gas was used as the carrier gas with flow rate measured by the ProFLOW 6000 from Restek and was adjusted to 20-30 mL/hr. The GC injector temperature, detector temperature, and column temperature were set to 150 °C, 190 °C, and 150 °C, respectively. The detector current was set to 200 mA. For data acquisition and analysis, the Clarify PC chromatography software was set to collect the voltage output data for 10 minutes. For liquid samples, a 5 μL sample was measured using a 10 μL Hamilton model gas tight 1801 glass syringe and was used to inject the sample into the injector port. In the analysis of gas samples, the sample size was 5 μL initially, but was later increased to a sample size of 0.5 mL. After a sample was injected into the GC, the
Software was started for data acquisition. Samples of pure methanol and pure DME were used for calibration because GC is based on comparative analysis. For each sample, three measurements were made.

3. **Results and Discussion**

3.1 **Batch Reactor Run Data**

For the purpose of this study, the $\gamma$-Al$_2$O$_3$ (catalyst) baseline is defined as Experiment 1 and the molecular sieve baseline is defined as Experiment 2. Three runs were performed for each of the three experiments, totaling nine experimental runs. In each experimental run, reactor temperature and pressure were recorded every 15 minutes, as shown in Figure 4.

In Figure 4a, the reactor temperature reached the desired set point of 280 °C in roughly 30 minutes and generally maintained that temperature for the remainder of the reaction. In Figure 4b, the reactor pressure increased sharply in the first half hour due to the quick increase in temperature. After $t = 30$ minutes, pressure continued to increase gradually and then leveled off at $t = 90$ minutes.

The increase in reactor pressure after the temperature stabilized at the set point indicated that methanol was converted to DME. This is due to the fact that the vapor pressure of DME is much higher than that of methanol. When the pressure leveled off and even slightly dropped, it indicated that the equilibrium was reached and the reverse reaction took place. Additionally, the results show that the experiment time could be shorten to 2 hours due to the leveling off of the pressure.

![Reactor Temperature Vs. Experiment Time](image)

- Cat. Bas. Run 1
- Cat. Bas. Run 2
- Cat. Bas. Run 3
- MS Bas. Run 1
- MS Base Run 2
- MS. Base. Run 3
- Experi. Run 1
- Experi. Run 2
- Experil. Run 3
Figure 4. Reactor Temperature (a) and Pressure (b) as a function of time for nine runs. Dotted lines with square markers represent runs for Experiment #1 Catalysis Baseline, Dashed lines with diamond markers represent runs for Experiment #2 Molecular Sieve Baseline, Solid lines with circular dot markers represent runs for Experiment #3.

3.2 GC Results

GC-TCD was used to determine the methanol concentration in the liquid samples and the DME concentration in the gas samples. Pure methanol and DME samples were used as references. Figure 5 shows the voltage output was collected during GC data acquisition. The software recorded the peaks and reported the retention time, peak intensity, and peak area. The recorded peaks for different molecules have different retention times which are listed in Table 2.

Table 2. Retention times of different molecules

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Water</th>
<th>MeOH</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention time (min)</td>
<td>~2</td>
<td>6-8</td>
<td>5-6</td>
</tr>
</tbody>
</table>
The GC results for the gas sample (5 μL) of Experiment #1 and #2 only have a water peak present. After the gas sample size was changed to 0.5 mL, the GC result of the gas sample (0.5 mL) showed peaks for water, DME, and a very small amount of methanol. The GC results for the gas samples (0.5 mL) of Experiment #1 and #2 also showed a huge water peak and a small DME peak.

The DME peak in gas samples also helped to confirm that DME was produced in all three experiments. The water peak is higher than the DME peak in the 0.5mL GC results and only a water peak was present in the GC result of a 5 μL gas sample. This is because water has a higher thermal conductivity than DME. The gas samples were collected using a syringe at different pressures and flow rates because the flow rate could not be controlled using the gas outlet valve present in Figure 3. This means that the gas samples were collected at different conditions. Consequently, the DME peaks in the GC results for gas samples could not be compared to each other, nor to pure DME. DME and water concentrations and yields in the gas sample could not be determined.

Experiment #2, involving only molecular sieves, was not expected to have any methanol conversion to DME, due to a lack of a catalyst. However, the GC results suggested that DME was produced. Molecular sieves are primarily composed of alumina and silica [9]. Methanol dehydration to DME generally is catalyzed by a solid acid catalyst. The catalyst activity of a silica-alumina catalyst in DME production was studied in previous work [1]. Therefore, DME production in Experiment #2 should be a result of the methanol conversion catalyzed by alumina and silica molecular sieves.
The reported areas under the methanol peak in the GC data of liquid samples were used in the calculation of the methanol conversion for the experiments. By measuring the methanol peak areas for five methanol/PEG-400 solution samples containing different methanol concentrations, a calibration of methanol peak area and methanol concentration (wt%) was performed (Figure 6). A fitting curve was generated to determine the linear trend line. The slope was 220.8 ± 2.3 and y-intercept was -4.4 ± 18.2.

Table 3 shows the average methanol peak areas of the initial and final liquid samples for the three experiments and the methanol concentration, which was converted using the calibration above. The percent methanol conversion was determined by comparing the concentration difference between the initial and final liquid samples to the initial concentration.

A methanol adsorption test was conducted by comparing the methanol concentration of the sample with molecular sieves to the one without molecular sieves. The relative difference is 9.4 % ± 1.1 %. This result showed that 9.4% of the methanol in the sample was adsorbed by molecular sieves. Methanol conversions of Experiment #2 and #3 were adjusted based on the adsorption test result. This adjustment can be seen in Table 3.

Figure 7 shows that methanol conversion in Experiment #3 is about twice that of each of the baselines. The results indicate that methanol conversion is improved by the addition of molecular sieves. However, in order to confirm that methanol was only consumed in its conversion to DME, additional DME
Table 3. Determination of methanol conversion

<table>
<thead>
<tr>
<th>Sample</th>
<th>MeOH Peak Area Avg. (mV*s)</th>
<th>Area meas. error (mV*s)</th>
<th>MeOH wt%</th>
<th>MeOH wt% error</th>
<th>MeOH Conversion %</th>
<th>MeOH Conversion % error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial liquid</td>
<td>2484.0</td>
<td>±130.9</td>
<td>11.3</td>
<td>± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Exp. #1 Final liquid</td>
<td>1820.4</td>
<td>±122.3</td>
<td>8.3</td>
<td>± 0.7</td>
<td>26.7</td>
<td>± 8.8</td>
</tr>
<tr>
<td>Exp. #2 Final liquid</td>
<td>1618.1</td>
<td>±40.0</td>
<td>7.3</td>
<td>± 0.3</td>
<td>25.5</td>
<td>± 6.2</td>
</tr>
<tr>
<td>Exp. #3 Final liquid</td>
<td>1071.8</td>
<td>±128.2</td>
<td>4.9</td>
<td>± 0.7</td>
<td>47.5</td>
<td>± 8.6</td>
</tr>
</tbody>
</table>

production data is needed. It in unconfirmed whether the amount of DME produced is equivalent to amount of methanol consumed in each experiment. It is also necessary to characterize the fresh and used molecular sieve samples in order to determine its function in water removal and methanol conversion.

Figure 7. Methanol conversion % for Experiment #1 (with γ-Al2O3 only), Experiment #2 (with molecular sieves only) and Experiment #3 (with both γ-Al2O3 and molecular sieves).

4. Conclusions

In this study, three experiments were run with the same amount of methanol and PEG-400. Experiment #1 was run with γ-Al2O3 only, Experiment #2 with molecular sieves only, and Experiment #3 with both γ-γ-Al2O3 and molecular sieves. From the experiment data, the increase in pressure at an isothermal temperature of 280 °C indicated the conversion of methanol to DME. The stabilization and then decrease in pressure after 2 hours shows that the experiment time could be reduced to 2 hours. This will reduce energy input.

The GC results indicated that DME was produced in all three experiments. The production of DME in Experiment #2 was the result of methanol conversion catalyzed by the alumina and silica components in the molecular sieves. The methanol conversion of three experiments was also determined from the GC results: Experiment #1, 26.7 % ± 8.8%; Experiment #2, 25.5% ± 6.2%; Experiment #3, 47.5% ± 8.6%.

The high methanol conversion in Experiment #3 indicated that methanol conversion is improved by the addition of molecular sieves. However, additional DME production data is needed in order to
confirm whether the amount of DME produced is equivalent to amount of methanol consumed in each experiment. This information is needed to confirm that methanol is only consumed in the conversion to DME.

Future work would include additional runs for each of the three experiments to obtain sufficient DME production data and the characterization of fresh and used molecular sieves to establish its role as an in-situ water removal material during conversion of methanol to DME. The particle diameter of the molecular sieves in relation to the particle size of methanol should also be considered. The molecular sieve used was 5 Å and the diameter of water is only 3 Å. It could potentially be beneficial to use a molecular sieve with a smaller pore size (3 Å or 4 Å) in order to reduce the amount of methanol absorbed by the molecular sieves while still being able to absorb water.

5. Acknowledgements

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6. References


