# EXPERIMENTAL STUDY OF METHANOL SYNTHESIS IN A HIGH-PRESSURE MEMBRANE REACTOR

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*Abstract*

In this study a high-pressure membrane reactor (MR) was employed to carry-out the methanol synthesis (MeS) reaction. A commercial MeS catalyst was used in the MR shell-side, while the tube-side is swept with a high boiling point liquid with high solubility towards methanol. A mesoporous ceramic membrane was utilized, after its surface was modified to be rendered more hydrophobic. The efficiency of the MR was investigated under a variety of experimental conditions (different pressures, temperatures, and sweep liquid flow rates). The results revealed improved carbon conversion compared to the conventional packed-bed reactor.

*Keywords*

Membrane reactor, Methanol synthesis, Ionic liquid, [Emim][BF4], Sweep liquid, Conversion.

## Introduction

Methanol (MeOH) finds broad use as a transportation fuel and as an important raw material used in the production of other fuels and chemicals (Elvers, 2008). There are several commercial methanol synthesis (MeS) processes (e.g., Lurgi (Behr, 2014) and Haldor-Topsoe (Aasberg-Petersen et al., 2008)), but they are all challenged by low per-pass conversion that necessitates the recycling of the unreacted syngas. This challenge is especially problematic for MeOH production from renewable biomass, where the use of oxygen-blown gasifiers is not economic, and the available syngas has a large nitrogen content. One way to overcome the thermodynamic limitations of the MeS reaction, and thus increase the per-pass conversion is to utilize a membrane reactor (MR). In this study, a novel high-pressure MR is used, in which a membrane with the desired characteristics serves as an interface contactor between the MeS environment in the shell-side and a sweep liquid solvent flow in the membrane permeate-side. Two different sweep liquids have been employed in the study: A high boiling point (B.P.) petroleum-derived solvent (Li and Tsotsis, 2018) tetraethylene glycol dimethyl ether (TGDE) and an ionic liquid (IL) 1-Ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF4]). The choice of the TGDE and the IL as sweep liquids is because MeOH has high solubility in both of them, while the permanent gases like $H_2$ and CO have negligible solubility. Compared to TGDE, the IL has higher decomposition temperature (400 $^oC$), which implies less demanding downstream processing requirements for the separation of the MeOH from the solvent; its lower vapor pressure means lower solvent loss, and its higher thermal capacity affords a broader range of MeS operating conditions. The TGDE, on the other hand, is at present more readily available and less costly In this study, the conversion and yield of the MeS reaction in a MR using IL as the sweep liquid was measured at different conditions and the results were compared with the MR system employing TGDE as the sweep liquid.

## Experimental Procedure

The experimental set-up is described in detail elsewhere (Li and Tsotsis, 2018). It consists of the syngas

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delivery system, the MR, the liquid injection system employing a high-pressure HPLC pump, and the gas and liquid analysis sections utilizing GC/TCD and GC/FID instruments. A commercial mesoporous alumina membranes, whose surface is rendered hydrophobic via the application of an appropriate modifying agent, is installed in the reactor. During operation, the syngas mixture is fed into the membrane shell-side that operates under high pressure and temperature, where it contacts the MeS Cu-ZnO-$Al_2O_3$ catalyst to convert into MeOH. The sweep liquid is pumped through the membrane tube-side via a HPLC pump to continuously remove in situ the produced MeOH, and thus help increase the conversion and yield of the MeS reaction. Experiments were conducted in a broad range of pressures and temperatures, sweep liquid flow rates and for two different sweep liquids, TGDE and IL. The lab-scale system operates also as a conventional packed-bed reactor (PBR) when the inlet and outlet of the membrane tube-side are closed, so as to compare its behavior to that of the MR.

## Result and Discussion

The experiments in the project, which will be reported at a greater detail at the meeting, investigate the performance of the MR under different pressures, sweep liquid flow rates and syngas feed compositions (expressed in terms of the stoichiometric number SN = $(F_{H2}- F_{CO2})/(F_{CO} + F_{CO2})$ and the carbon factor CF = $F_{CO}/(F_{CO}+ F_{CO2})$ and compare the carbon conversion of the MeS reaction in the MR with that of the PBR under the same conditions.

Figure 1, for example, shows the effect of sweep liquid flow rate and reactor shell-side pressure on the carbon conversion of the MeS reaction at a temperature of 220 $^oC$, and at a fixed value of W/F (catalyst weight/total molar flow rate) = 170 kg*s/mol with a syngas with a SN=1.96 and CF=0.625. The effect of sweep liquid flow rate was investigated at a fixed pressure of 32 bar. As expected, the reactor conversion increases with increasing sweep liquid flow rate, with all MR conversions under these conditions exceeding the thermodynamic values. This is attributed to the fact that a higher sweep liquid flow rate helps to remove a larger amount of methanol from the reaction side. Moreover, the IL shows a higher conversion rate, which is likely related to the higher solubility of MeOH in IL compared to TGDE at high temperatures.

For the effect of pressure on conversion the sweep liquid flow rate in the lab-scale MR was kept equal to 1 cc/min and the MR shell-side pressure was varied in the range of 20-32 bar. As it can be seen in the figure, the MR exhibits conversions that are higher than that of the PBR. Also, measured conversions for both MR and PBR increase with increasing pressure because the MeS reaction results in an overall reduction in the number of moles that is thermodynamically favored at higher pressures. Another reason for the increase in the MR conversion with increasing pressure, in addition to more methanol being generated, is that the increase in pressure means that a higher amount of methanol transports through the membrane and is removed by the sweep liquid, thus further shifting the equilibrium towards the MeOH generation side. For the whole range of pressures studied, the IL attains higher conversions than the TGDE, which can be related to its higher methanol solubility.

Constrains with the size of the lab-scale system limit the gains in conversion afforded by the MR system. Modeling studies, however, indicate that conversions >90% are readily attainable. Economic evaluations indicate that such conversions would allow the proposed process to operate on biomass-derived syngas in an one-pass configuration without recycle of unreacted syngas needed.

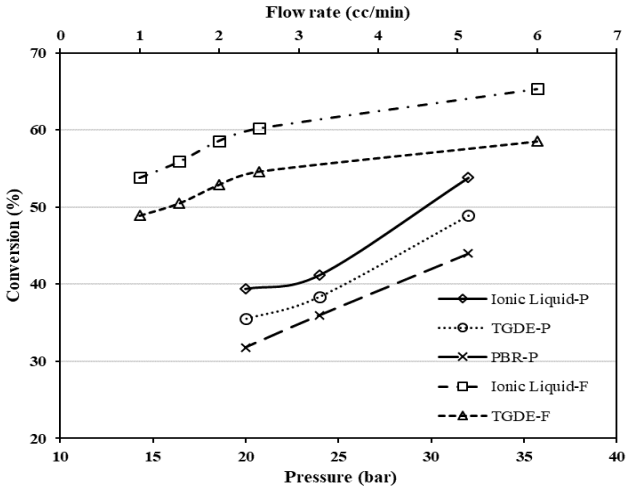


*Figure 1. Effect of liquid sweep flow rate ( F subscript) and effect of pressure (P subscript) on MR conversion*

## Conclusion

In this study a high-pressure MR was employed to carry-out the MeS reaction. The efficiency of the MR was investigated under a variety of experimental conditions with the results revealing improved carbon conversion compared to the conventional packed-bed reactor.

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