EXPERIMENTAL INVESTIGATION OF THE APPLICATION OF IONIC LIQUIDS TO METHANOL SYNTHESIS IN MEMBRANE REACTORS

Fatemeh Sadat Zebarjad, Sheng Hu, Zhongtang Li, and Theodore T. Tsotsis*

Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, University Park, Los Angeles, CA 90089-1211, United States

KEYWORDS

Methanol synthesis, membrane reactor, ionic liquid, [EMIM][BF4], sweep liquid, catalyst, membrane surface modification

ABSTRACT

In this study a high-pressure membrane reactor (MR) was employed to carry-out the methanol synthesis (MeS) reaction. Syngas was fed into the MR shell-side where a commercial MeS catalyst

^{*}Corresponding Author. E-mail: tsotsis@usc.edu

was used, while the tube-side is swept with a high boiling point liquid with good solubility towards methanol. A mesoporous alumina ceramic membrane was utilized, after its surface had been modified to be rendered more hydrophobic. The efficiency of the MR was investigated under a variety of experimental conditions (different pressures, temperatures, sweep liquid flow rates, and types of sweep liquids). The results reveal improved per single-pass carbon conversions when compared to the conventional packed-bed reactor. An ionic liquid (IL), 1-ethyl-3methylimidazolium tetrafluoroborate ([EMIM][BF4]) was utilized in the MR as the sweep liquid. The experimental results are compared to those previously reported by our Group (Li and Tsotsis, J. Membrane Sci., 2019) while using a conventional petroleum-derived solvent as sweep liquid, tetraethylene glycol dimethyl ether (TGDE). Enhanced carbon conversion (over the petroleumderived solvent) was obtained using the IL.

1. INTRODUCTION

Since the industrial revolution human activities like fossil-fuel combustion have produced CO_2 , thought to contribute to global warming, thus leading to an increase in its atmospheric concentration of ~40% ¹. During the same period, the world's rising demand for energy increased the use of fossil fuels, such as oil, gas, and coal; combined with the limited availability of these resources, this has intensified the need for finding new technologies to meet the world's energy needs. CO_2 capture and utilization (CCU) to produce fuels and chemicals, and the use of renewable energy resources (e.g., biomass) in the place of fossil fuels are two approaches intensively studied today for reducing the CO_2 environmental impact and for diminishing the world's reliance on fossil fuels.

Recently, CO₂ conversion into methanol (MeOH), as a CCU process, and MeOH production from biomass have attracted increased attention. MeOH is one of the most commonly used industrial chemicals; its widespread applications includes utilizing it as a feedstock for producing chemicals (e.g., C₂-C₄ olefins and aromatics ^{2.4}), fuels and fuel additives (e.g., DME, MTBE and DMC ⁵⁻⁷), and as a H₂ carrier in energy storage. The most common method to produce MeOH is from a mixture of CO, CO₂ and H₂ known as syngas; it is generated from the catalytic reforming of natural gas or the gasification of coal and biomass. The following three global reactions are thought to take place during MeOH synthesis (MeS) (though there are differing opinions among researchers on the carbon source for MeOH during MeS, and all three reactions are noted in the literature, only two out of three are linearly independent. It is noted that only the first and third reactions are considered in the kinetics part of this study, to be discussed later).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
 $\Delta H^o = -49.5 \text{ (kJ/mol)}$ (R1)

$$CO + 2H_2 \rightarrow CH_3OH$$
 $\Delta H^\circ = -90.6 \text{ (kJ/mol)}$ (R2)

$$CO + H_2O \rightarrow CO_2 + H_2$$
 $\Delta H^o = -41.2 \text{ (kJ/mol)}$ (R3)

Today's commercial MeS processes ⁸⁻⁹ utilize the so-called low-pressure (pressures range from 50-80 bar) Cu-ZnO-Al₂O₃ MeS catalyst (also employed in this study) which is highly selective (selectivity, typically, >99 %), with DME being the main by-product ¹⁰. They have different technical features, but are all designed to overcome two key challenges: first, low per-pass conversions dictating recycle of unreacted syngas ⁸, and second, the need to remove the reaction heat efficiently. Newer MeS processes have also been developed ¹¹⁻¹⁵, but none has, as yet, to reach commercial maturity. The first, and foremost, challenge (low per-pass conversion) is particularly problematic for MeOH production from small-scale, distributed-type renewable biomass sources, for which the use of oxygen-blown gasifiers is not economically justified, with the resulting syngas thus containing large concentration of N₂. For such applications, increasing the per-pass conversion (to ~85%) is essential for commercial adaptation. Such requirement motivates the consideration of reactive separations for such an application, including membrane reactors (MR), since they are capable to overcome the aforementioned thermodynamic limitations of MeS.

Several prior studies report the use of MR for MeS to increase the conversion rate and thermal efficiency ¹⁶⁻²³. Galucci et al. ¹⁸, for example, investigated a packed-bed membrane reactor (PBMR) for MeS using a commercial Cu-Zn catalyst and a zeolite-A membrane. For similar reactor conversions, the PBMR showed higher selectivity than the conventional PBR, which was attributed to the selective removal of H₂O and CH₃OH by the membrane. Earlier, Barbieri et al. ¹⁹ had predicted such behavior via simulation. Struis et al. ²⁴ used a Nafion® membrane for selective separation of MeOH in a MR; syngas was fed in the membrane tube-side, while sweep gas was directed to the shell-side in a counter-current direction of flow. Their experiments were performed using membranes with different counter-ions for temperatures up to 200 °C. Their studies showed that the higher the pressure is, the better is the reactor performance; it was also found that

optimizing the membrane structure and the module configuration can lead to a significant improvement in reactor performance. The experimental results were also validated in a modeling study ²¹. In another study that was conducted employing a silicone rubber composite membrane, a higher conversion rate was reported for thr PBMR compared to the conventional reactors ²³. The experiments showed conversions of less than 10%, and the stability of these membranes is doubtful long-term under the high pressure/high temperature MeS conditions. A modeling study of the use of a MR for MeS employing a water-permselective silica membrane ²⁵ revealed a slight improvement (~4 %) in conversion over equilibrium; removing the water was reported, however, as a key factor to improve catalyst lifetime, since its presence was claimed to intensify catalyst deactivation via sintering.

Studies also exist on the use of distributor-type MR's (in these reactors, reactants flow on either side of the membrane, that provides a means through which one reactant is dosed into another) for the Fischer-Tropsch (FT) process and for alcohol synthesis ^{20, 22, 26-31}, including MeS. A Pd-membrane based distributor-type MR for MeS was simulated by Rahimpour and coworkers ²⁰; they also modeled dual-reactor systems ³²⁻³⁶ including a distributor-type MR ³⁷⁻³⁹ that coupled MeS with cyclohexane dehydrogenation via a Pd/Ag membrane, but to date none of these systems have been validated experimentally. Bradford et al. ⁴⁰ studied the FT reaction in a contactor-type MR using a catalytic porous alumina membrane running in a "flow-through" mode (FTCMR). The results showed a higher C2+ hydrocarbon yield and a lower olefin/paraffin ratio attained in the MR than in the conventional reactor, which they explained to be due to a higher H₂/CO-ratio prevailing within the catalytic membrane. Khassin et al. ⁴¹ also investigated the FT reaction in a similar MR and obtained high selectivity toward C5+ hydrocarbons, a higher space-time yield of

liquid hydrocarbons, and up to three times higher catalyst activity with the FTCMR when compared with a slurry reactor.

Our Group previously investigated ⁴² a different MR methanol synthesis process; a hightemperature inorganic membrane was utilized in MeS as a porous selective barrier in between the reaction side and a liquid solvent flowing in its tube-side (permeate-side). Tetraethylene glycol dimethyl ether (TGDE) was used as the sweep liquid, in which MeOH has good solubility, while other components of syngas (like H₂ and CO) do not. Removing the MeOH in situ from the reaction side, allows achieving conversion for MeOH beyond its equilibrium value. An advantage of this over other MR processes for alcohol synthesis, is that the selective separation is done by the sweep liquid; thus commercial, off-the-self inorganic membranes can be used (as in this study), which require no further development effort beyond needing to modify the hydrophobicity of their surface. Thus, one is no longer constrained by the limited commercial availability (or lack of robustness) of appropriate membranes, and can, instead, rely on the greater range of available solvents to attain desired selective properties.

Though employing a petroleum-derived solvent like TGDE in a MR system (but even in a conventional trickle-bed reactor) shows good benefit, there are still disadvantages relating to its application to the MeS reaction. Its relatively low boiling point (275 °C) dictates that the reaction temperature is kept rather low. In addition, though its vapor pressure is quite low (<0.001kPa at 20 °C) it is still finite. For these reasons, here we investigate, instead, a different sweep liquid, specifically an ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]). It has been demonstrated to date that certain ILs are highly polar compounds; as a result, MeOH has considerably higher solubility than CO and H₂ in them ⁴³. Dissolution of the MeOH produced during MeS into the ILs enables its in situ removal from the reactor, and this (similarly to using

the TGDE) enhances the conversion. The IL solvent's advantages over the competing organic solvents (e.g., TGDE) for the specific MeS reactive separation process under study are: (1) their extremely low vapor pressures ($<10^{-9}$ bar), which prevents significant loss of the sweep solvent into the gas phase, and simplifies downstream separations of the MeOH in the IL sweep stream; (2) the thermal properties of the IL solvents, including their broad operating range, and their high decomposition temperatures, which permit their use for a broader region of conditions in MeS that, typically, takes place commercially in the temperature range of (220~300 °C). Specifically, the high MeOH solubility ⁴³ and decomposition temperature (447 °C) ⁴⁴ of the [EMIM][BF4] compared to other ILs have made it a good choice of sweep liquid for our MR design.

In summary, in this study the conversion 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. In what follows, we first describe the experimental system utilized, and the method to modify the commercial inorganic membrane used to make it more appropriate for the proposed application. Experimental results are then presented and discussed.

2. EXPERIMENTAL SECTION

2.1. MATERIALS

Gases. Ultra high purity (UHP) Nitrogen (N₂, 99.999% pure), and UHP Hydrogen (H₂, 99.999% pure) were purchased from Praxair. The CO/CO₂ (37.5% CO₂) mixture was purchased pre-mixed from Praxair with the purity of 99.999%.

Ionic Liquid. 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) with a reported purity of ≥98% was purchased from Zhejiang Arts & Crafts Imp. & Exp. Company, China. Upon

being received at USC, the purity of the IL was confirmed via 400 MHz ¹H and the 375 ¹⁹F NMR analysis (the analysis results can be found in the Supplementary materials section).

Membrane. A multilayer ceramic membrane from Media and Process Technology, Inc. (M&PT) of Pittsburgh, PA, whose properties, as reported by the manufacturer, are shown in Table 1 has been utilized. The porosity of the membrane was measured to be 22.8% with the helium expansion method, employing a helium porosimeter apparatus and measurement procedures which are described elsewhere ⁴⁵.

Layer	Material	Thickness (µm)	Average pore size (Å)			
Support	α- Alumina	1100	2000-4000			
First layer	α- Alumina	10-20	500			
Second layer	γ- Alumina	2-3	100			
Outer diameter: 5.7 mm, Inner diameter: 4.7 mm						

Table 1. Properties of the ceramic membrane

Catalyst. A commercial Cu-based MeS catalyst (MK-121, purchased from Haldor-Topsoe) was utilized (properties, as provided by the manufacturer, are presented in Table 2). The as received catalyst was in a pellet form. Prior to being loaded into the reactor, 30 g of the catalyst were ground into powder with particle sizes in the range from 650 μ m to 850 μ m, which were then diluted with quartz particles of the same size. Further details about how the catalyst is loaded into the reactor are provided below.

Table 2. MK-121 catalyst properties (catalyst cylinders with domed ends, 6*4 mm)

Property	Value
Chemical composition	

Cu	>43	%
Zn	20±3	%
Al	5±1	%
Axial crush strength	>220	kg/cm ²
Expected filling density	1	kg/l

2.2. EXPERIMENTAL SET-UP

Figure 1 shows the schematic of experimental set-up. The gas delivery system, the reactor module, and the gas analysis section are the three main components of the set-up. The inlet syngas feed-stream is prepared by mixing pre-determined flows of H₂ and the aforementioned CO/CO₂ gas mixture, with their flow rates being controlled by individual Mass Flow Controllers (MFC, Brooks 5400). After pre-heating, the resulting syngas mixture is fed into the high-pressure/high-temperature lab-scale MeS reactor. The MeS experiments were carried-out over a pressure range of 20-30 bar and a temperature range of 200-240 °C. The reactor's temperature was controlled by temperature controllers and monitored by a three-point thermocouple (from OMEGA). Further details about the experimental apparatus can be found elsewhere ⁴².



Figure 1. Schematic of the experimental set-up

Figure 2 shows a schematic of the MR itself, showing that the reactor is divided into two zones by a tubular ceramic membrane: the shell-side (reject-side) and the tube-side (permeate-side). The shell-side contains a packed-bed of catalysts and the MeS reaction occurs in this zone. The methanol produced is then transported through the membrane and is dissolved into a sweep liquid that flows in the tube-side. A back-pressure regulator (BPR) is used to control the pressure of the MR shell-side. A condenser is installed at the outlet of the shell-side to ensure that complete condensation takes place of the methanol, H₂O, and other potential by-products in the gas phase exiting the reactor. Glass beads are used in the condenser for improving cooling of the gas stream; a cooling bath containing dry-ice and acetone with the fixed temperature of -78 °C is also used in which the condenser is immersed. No methanol and other organic compounds were detected (using a Gas Chromatograph equipped with a Thermal Conductivity Detector (GC-TCD)) in the gas stream exiting the condenser, which verifies that complete condensation of such compounds takes place in the condenser. CO, CO₂ and H₂ were the only compounds detected in the gas stream by GC-TCD. A Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID) was used to analyze the composition of the liquid phase collected in the condenser.



Figure 2. Schematic of the membrane reactor

The sweep liquid is injected into the membrane permeate-side using a HPLC pump, with a BPR (installed in the exit line) being employed for controlling the pressure. Due to the potential of gases being dissolved in the sweep liquid, it is directed after the BPR into a condenser/separator operating at atmospheric pressure and room temperature, to separate any such gas components from the sweep liquid. For the purpose of properly closing mass balances, the gas stream from the liquid condenser is recombined with the gas stream exiting the BPR in the MR shell-side, the resulting total gas stream then being fed into the shell-side condenser. The same experimental set-up, as described above (and also described in greater detail elsewhere ⁴²), is used for performing

the packed-bed reactor (PBR) experiments; this is accomplished by closing both the inlet and outlet lines in the tube-side of the membrane.

2.3. EXPERIMENTAL PROCEDURE

As shown in Figure 2, the ceramic membrane is installed in the center of the reactor, which is an autoclave made of stainless steel. It is attached to the top of the autoclave with flexible stainless steel tubing that accommodates potential thermal expansion; it is connected to that tubing via Swagelok fittings and Teflon O-rings. The bottom of the reactor is first loaded with quartz particles (150 µm to 650 µm in diameter, see Figure 2) up to a level reaching the bottom of the membrane. The reactor is then packed along the length of the membrane with a mixture of catalyst and quartz (650 µm to 850 µm in diameter, as described above). A bed of quartz particles (850 µm to 1000 µm in diameter, see Figure 2) is then packed from the top of the membrane all the way to the top of the autoclave The syngas is fed into the reactor by means of a tube that traverses the length of the reactor from the top of the autoclave into the middle of the fine quartz particle bed at the bottom of the reactor. The liquid sweep flows through the flexible tubing connected, on either side to the membrane (in the PBR mode of operation, the inlet and outlet of the membrane tube-side are closed). The reactor (in both the PBR and the MR experiments) operates isothermally (temperature difference across the reactor length: less than 2 °C), and isobarically (pressure drop: less than 0.1 bar).

After calibration of the MFC's and GC's, the set-up is tested to ensure that it is leak-free (for that, the system is pressurized at 30 bar with N_2 , and the target for leak-free operation is a pressure drop of <0.2 bar over a 24 h period). Then, the catalyst is activated in situ, following a hydrogenation treatment protocol recommended by its manufacturer (for further details, see Li

and Tsotsis ⁴²). After the catalyst activation step and before starting the experiments, the reactor is purged with N_2 at a flow rate of 600 cc/min for about 1 h; after that, the operating conditions are adjusted according to the design of experiments. The IL chosen ([EMIM][BF4]) has a relatively high viscosity at room temperature (~45 cP), therefore, to reduce its viscosity to facilitate pumping, it is preheated to 50 °C (via a water bath) prior to pumping via the HPLC pump. In order to achieve a steady-state condition, the outlet composition and flow rate should have negligible variations (the acceptable range: less than 5% for the concentration and less than 2% for the outlet flow rate); therefore, beside the pressure and temperature of the reactor, the composition and flow rate of the outlet gas are monitored accurately via GC-TCD and bubble-flow meters, respectively.

2.4. MEMBRANE MODIFICATION

The membrane's key role during the reaction is to provide a well-defined interface between the sweep liquid (permeate-side) and the gas phase in the reactor side (shell-side) for the reaction products to dissolve into and be carried away by the sweep liquid. Complete wetting of the membrane by the liquid is not desirable, however, since that creates a large transport resistance. The ideal configuration, instead, is shown schematically in Figure 3 whereby the liquid is confined only in the top membrane layer creating an impermeable layer preventing the gas from simply bubbling through.



Figure 3. Gas-liquid interface in a hydrophobic membrane

The M&PT mesoporous ceramic membrane is intrinsically relatively hydrophilic and the sweep liquids are polar compounds capable to remove the MeOH from the reaction zone; they, thus, have affinity towards hydrophilic surfaces and are non-wetting toward hydrophobic ones. In order to prevent the solvent from completely penetrating through, prior to its use in the MR experiments the membrane surface must be modified to become more hydrophobic. For that, a surface modification method ⁴⁶ has been developed, which uses a fluoroalkylsilane (FAS) compound as a surface modifier that has both hydrolysable groups and hydrophobic ends ⁴⁷ (the structure of the FAS compound employed in this study is shown in Figure 4). The mechanism for the surface through a reaction between its hydrolysable groups with the surface hydroxyl groups, as shown in Figure 4.



Figure 4. FAS attachment mechanism during membrane modification ⁴⁷

Prior to the modification of its surface, the membrane tube is cleaned by ultra-sonification with ethanol for 30 min and then with de-ionized (DI) water for an additional 30 min (the membrane is glazed on both ends, ~1 cm, before any modification takes place, to ensure complete sealing when installed inside the reactor, with the glazing procedure being explained in greater detail in ⁴⁸). Then, the membrane is soaked in an ethanol/DI water solution (2:1 volume ratio) for 24 h, and is then dried in air at 60 °C for 24 h. The dry membrane is then immersed into a FAS/hexane (0.1 mol/l) solution, which is prepared by dissolving FAS into hexane at room temperature under vigorous stirring for 12 h, ultra-sonicated for 30 min and then left in the FAS solution for an additional 24 h to allow the surface coupling reaction to complete. The unreacted FAS on the surface of the membrane is removed by rinsing with hexane solution for several times and then placed in an oven for 12 h at 100 °C to dry. The aforementioned steps (soaking the membrane in the FAS/hexane solution, washing and drying) are then repeated four times. As the final step, the modified membrane gets heated at 200 °C in a furnace for 6 h in flowing Argon.

As it can be seen in Figure 5, which shows DI water droplets on the membrane, the surface becomes hydrophobic after the modification procedure. In order to quantify the ability of the FAS modification method to alter the wettability of the membrane surface toward a more hydrophobic

one, a number of characterization tests were performed during the initial development of method. They included break-through pressure tests, contact angle tests, membrane morphology testing via electron microscopy (SEM), FTIR-DRIFTS characterization, and thermogravimetric analysis (TGA), the latter to assess whether the surface modification is robust at the temperatures employed in MeS. Further details regarding the results of the studies can be found elsewhere ⁴⁹.

We report here contact angle tests with both the modified and unmodified membranes with DI water, TGDE and IL at room temperature and pressure using a Rame-Hart (Model #290) automated goniometer, to validate the ability of the method to modify the hydrophilicity characteristics of the membrane surface. For such testing, the membrane to be studied was cut into numerous small pieces, each used in a single contact angle measurement. For the unmodified membranes, liquid droplets placed on their surface (due to the relatively low hydrophobicity of the surface) vanish quickly, typically after 10 min. Therefore, the contact angle measurements reported here are taken within the first few seconds after the droplet's placement on the surface. On the other hand, the droplets placed on the modified membranes' surface remain stable for over an hour. For each droplet, an average of 6 contact angle measurements on different membrane pieces is reported in the following section.



Figure 5. DI water droplets on the surface of the modified membrane

During the MR experiments, the pressure in the tube-side is kept a bit higher (typically, 0.5-1 bar) than that of the shell-side, to assure that the liquid will penetrate into the membrane to block gas transport. Complete infiltration of the membrane by the solvent is not desirable, however, because it creates a large resistance for the MeOH molecules to permeate through. To assure than no solvent penetration and leak-through occurs during the MR experiments, after the membrane is installed in the reactor and prior to loading the catalyst, the reactor shell-side is pressurized with N₂ at a temperature of 210 °C and a pressure 25 and 7 bar, while the sweep liquid is flowing through the tube-side (at a flow rate of 0.5 ml/min) at a sufficiently high overpressure to prevent the gas from bubbling through, but not exceedingly high so that the liquid itself breaks through (typically <1 bar). After passing through the membrane, the solvent is redirected into a reservoir, and it is then recycled to the membrane tube-side. The recycling of the sovent enables us to estimate its loss (leak-through) rate by monitoring the change in the solvent mass in the reservoir. If less than 1 ml of the IL liquid is lost over a-12 hour period, it is considered that the membrane surface modification and the membrane sealing are satisfactory, and the membrane overpressure is sufficiently high.

3. RESULTS AND DISCUSSION

3.1. PBR EXPERIMENTAL RESULTS

In addition to the MR experiments reported here, we have also carried-out PBR experiments to provide a basis for comparison for the MR experiments, i.e., whether the MR is less or more efficient than the PBR under the same experimental conditions. These experiments were performed in the same lab-scale reactor (Figure 2) with the membrane in place but with the permeate-side inlet and outlet being closed. In the PBR experiments, the effect of five parameters on the performance of the reactor were investigated, including the temperature (T), pressure (P), catalyst weight to inlet molar flow-rate ratio (W/F), the carbon factor in the feed (CF = mol CO/(mol CO + mol CO₂)), and the feed stoichiometric number (SN = (mol H₂- mol CO₂)/(mol CO + mol CO₂)). The exact experimental conditions investigated and the obtained carbon conversions (defined by Eq. 1 below) are shown in Table S1 in the Supplementary Materials section.

$$X_{carbon} = \frac{(F_{inlet\ CO}+F_{inlet\ CO_2}) - (F_{outlet\ CO}+F_{outlet\ CO_2})}{(F_{inlet\ CO}+F_{inlet\ CO_2})} * 100$$
(1)

where F_i is the molar flow rate (mol/s) of species i at the designated location.

In these studies, after the reactor reaches steady-state (based on the gas phase measurements), the experiment was run for an additional time period during which time a liquid sample was collected in the condenser (its volume measured and its composition determined via GC-FID analysis). This is done in order to close mass balances (by determining the quantity of liquid products and comparing with the carbon reacted determined via the gas-phase measurements), and to measure reactor selectivity toward MeOH. For the experiments reported here, both the selectivity and carbon balance are always higher than 98 %.

The experimental results were also fitted to global rate expressions for reactions R1 and R3 from the technical literature ⁵⁰⁻⁵², and to available data for the thermodynamic parameters ⁵³. Figure 6 shows comparison of experimental and calculated carbon conversions (Eq. 1), indicating a reasonable agreement between the experimental and modeling data.



Figure 6. Comparison of experimental vs. calculated carbon conversions

3.2. MEMBRANE REACTOR EXPERIMENTS

Prior to being installed in the reactor for the MR experiments, the surface of the membrane must be rendered sufficiently hydrophobic to prevent complete wetting of the membrane structure by the solvent and break-through into the shell-side. A routine means to assess the hydrophobicity of the surface is via contact-angle measurements. Such data with one of the membranes for TGDE, the IL, and DI water are shown in Figure 7. It is clear from Figure 7, that the wettability of the surface has been altered towards being more hydrophobic, since the contact angles measured for all three liquids have increased after the modification. For instance, for the IL the contact angle has changed from 78 degrees (relatively hydrophilic) to 122 degrees (strongly hydrophobic). The lowest values of contact angle among the three fluids were obtained with the TGDE (TGDE also has the lowest viscosity and density at room temperature and pressure). IL has the highest contact angle among the three liquids, but also the highest viscosity, which further diminishes the chance of breaking through the membrane and leaking into the shell-side.



Figure 7. Comparison of measured contact angles on modified and unmodified membranes

During the MR experiments, the liquid sweep flowing in the tube-side removes in situ the methanol generated in the reactor (shell-side), leading to equilibrium shift and enhanced methanol production. Another important role of the sweep liquid is carrying away the exothermic heat of reaction. The membrane acts as an interphase contactor in between the reactor side and the product-removing solvent, without requiring the solvent to come directly in contact with the catalyst, as in the case of employing a trickle-bed reactor for the same purpose. This, then, helps to reduce the potential impact of the catalyst on solvent stability, or of the solvent on catalyst activity, thus extending both their life-times.

In this part of the study, the performance of the membrane reactor was investigated at different experimental conditions (variables: T, P, sweep liquid flow rates, and W/F) and the results were

compared with the PBR under the same conditions (for all such experiments, we kept the stoichiometric number and the carbon factor constant, i.e., SN = 1.96 and CF=0.625). We have previously reported [41] experiments with the same catalyst bed and membrane employing TGDE as the sweep solvent. For this study, prior to carrying-out the experiments with the IL we repeated several of these experiments with the TGDE as the solvent to verify the state of the membrane and catalyst. Excellent repeatability in carbon conversion with the previous tests [41] was observed (error $\leq 2\%$).



Figure 8. Effect of W/F on MR and PBR conversion. P = 32 bar, T = 220 °C

Figure 8 shows the carbon conversion for both the MR and PBR as a function of W/F under a pressure of 32 bar, a temperature of 220 °C, and for two different sweep liquid flow rates (LF), namely 1 cc/min and 6 cc/min. In this study, the catalyst weight and syngas composition are both constant, therefore, increasing the W/F means reducing the syngas flow rate. Predictably, the increase of W/F leads to enhancement in conversions for both the MR and PBR . As it can be seen

from the figure, for larger W/F the PBR conversion approaches the equilibrium value. The membrane reactor conversions, on the other hand, with both sweep liquids manage to exceed the equilibrium values. When the IL is used as the sweep liquid, the observed conversions consistently exceed those measured with the TGDE being employed as the solvent, and are on a relative basis 22.2 - 51.3% higher than the PBR conversions. In addition, the IL offers the advantage of a significantly lower vapor pressure, which simplifies downstream separation requirements when compared to TGDE, and also means diminished solvent losses due to vaporization.



Figure 9. Effect of flow rate (liquid sweep) on MR conversion. P = 32 bar, T = 220 °C, W/F = 47.2 g*h/mol

To further investigate the effect of varying the sweep liquid flow rate, a series of experiments were performed at different sweep liquid flow rates and constant pressure (32 bar), temperature (220 °C), and W/F (47.2 g*h/mol). The results are presented in Figure 9. For both sweep liquids, the MR conversion increases with increasing sweep liquid flow rates, attributed to the fact that a greater amount of methanol is extracted from the shell-side as a result of increasing liquid sweep

flow rate, thereby, pushing further the equilibrium conversion to the right toward methanol generation. The sweep liquid flow rate plays a crucial role in process design optimization: a higher flow rate results in higher conversions, as Figure 9 amply manifests but, on the other hand, the resulting solutions have a lower MeOH concentration, and thus are more challenging to separate the alcohol from.



Figure 10. Effect of temperature on PBR, MR and equilibrium conversion. P = 32 bar, liquid sweep rate = 1 cc/min, W/F =47.2 g*h/mol.

Figure 10 shows the carbon conversion for the MR and PBR as a function of temperature for a constant pressure (32 bar), W/F (47.2 g*h/mol), and sweep liquid flow rate (1 cc/min). The rather narrow range of temperatures studied was due to the fact that the FAS coating gets damaged at higher temperatures; and because temperatures lower than 200 °C may lead to catalyst deactivation. In Figure 10, the PBR conversion first increases, passes through a maximum at a

certain temperature, and then decreases at the higher temperatures (e.g., reaching a lower conversion at T=220 °C compared to that of T=214 °C). This can be explained by the fact that at the higher temperatures the reactor conversion starts "tracking" the thermodynamic equilibrium conversion (shown also on the Figure) of this exothermic reaction.



Figure 11. Effect of pressure on PBR, MR and equilibrium conversion. T = 220 °C, liquid sweep rate = 1 cc/min, W/F = 42.7 g*h/mol

The conversion of MR, on the other hand, increases steadily with increasing temperature for either sweep solvent employed, which can be attributed to the increased reaction rate as well as enhanced methanol transport across the membrane, as the temperature rises. For all temperatures studied in Figure 10, the MR conversions (for both the TGDE and IL) are higher than the corresponding PBR values. From a certain temperature and beyond, in fact, the MR conversion exceeds the thermodynamic equilibrium conversion value as well. Moreover, the IL results in higher

conversion due to its higher solubility towards methanol at the reaction conditions, likely, due to its more polar nature.

Figure 11 shows the effect of changing the reactor pressure on the MR (for both types of sweep solvent, IL and TGDE) and PBR conversion as well as the thermodynamic equilibrium conversion while keeping constant the reactor temperature (220 °C), the sweep liquid flow rate (1 cc/min), and W/F (47.2 g*h/mol). Predictably, both the thermodynamic equilibrium and PBR conversions (which at this relatively high temperature closely track the equilibrium values) increase with increasing pressure, due to the fact that the total number of moles reduces as a result of MeS reaction which is thermodynamically favored at higher pressures. The MR conversion also increases with increasing pressure, the added reason for that being that a greater pressure means that a higher amount of methanol will also transport through the membrane to be removed by the sweep liquid, thereby the equilibrium condition is further shifted towards the methanol generation. Comparing the MR performance when employing the two different sweep liquids, higher conversions are obtained for the IL over the whole range of pressures studied, thus manifesting the advantage in terms of MeS reactor efficiency of using the IL when compared to TGDE. As noted previously, using the IL portends additional advantages related to diminished solvent loss, lower potential for damage to the catalyst, and simplified downstream separation requirements.

4. CONCLUSIONS

This paper presents experimental data in support of a novel concept of carrying-out MeS in a MR. In this reactor, the membrane divides its volume into two sections, the membrane shell-side and tube-side. A Cu-based commercial MeS catalyst is packed in the shell-side where the reaction takes place, while a sweep liquid flows in the membrane tube-side; its role is to remove the produced MeOH from the reaction zone in-situ, thus allowing the reactants to produce more MeOH

("breaking the equilibrium"). A commercial alumina membrane is employed, whose surface is rendered hydrophobic via modification with a FAS agent, in order to prevent any liquid leakage, thus avoiding solvent loss and potential catalyst deactivation. In our previous work [41], we used a petroleum-derived solvent (TGDE) as the sweep liquid to conduct the MR experiments. Though employing the TGDE allowed the MR to attain higher conversion and yield compared to the PBR, there are disadvantages relating to its use. They include its relatively low boiling point (275 °C) that dictates the reaction temperature to be kept rather low. Moreover, though its vapor pressure is quite low it is still finite, and this creates a concern for potential solvent loss due to vaporization. Therefore, in this paper we have investigated, instead, a new sweep liquid, specifically the ionic liquid [EMIM][BF4], that demonstrated during MeS in the MR high solubility towards MeOH, whose in situ removal from the reactor, similarly to when using the TGDE, resulted in enhanced MR conversion. The IL solvent's advantages over TGDE for our MR design include: (1) its extremely low vapor pressures, which eliminates potential loss of solvent and substantially simplifies downstream separations; (2) its broad operating temperature range, and high decomposition temperature, which permit the operation of the MR for a broader region of MeS conditions. In addition, when using the IL, the observed conversions consistently exceeded those measured with the TGDE.

One of the key goals of the proposed MeS-MR technology is to attain a sufficiently high perpass syngas conversion and yield into MeOH (>85%) to avoid the need for syngas recycle. This is particularly important, when the aim is to produce alcohols from renewable biomass. Though limitations with the lab-scale system did not allow in this study to meet the target per-pass yield (>85%), preliminary process scale-up simulations employing a data-validated model indicate the potential of the proposed concept to meet such a target. We presently continue to investigate the MeS-MR technology by focusing on optimization and on technical and economic analysis (TEA) for process scale-up. There are several important optimization conditions one must consider, such as syngas composition, gas and liquid flow rates, temperature, pressure, catalyst weight and activity, membrane area, the concentration of MeOH in the solvent, and the fraction of the MeOH product recovered in the product stream. In our studies, we employ a MR model validated by our MR experimental data that allows us to investigate process performance under operating conditions that are not readily accessible by the lab-scale experimental system. Results of these studies will be presented in an upcoming publication.

ACKNOWLEDGEMENT

The support of the National Science Foundation (Award# CBET-1705180) is gratefully acknowledged.

AUTHOR INFORMATION

Corresponding Author

* Email address: tsotsis@usc.edu

ABBREVIATIONS

1; MR, membrane reactor 2; MeS, methanol synthesis 3; IL, ionic liquid 4; PBR, packed-bed reactor 5; FAS, fluoroalkylsilane 6; DI, deionized 7; W/F, catalyst weight/total molar flow rate 8; TEA, technical and economic analysis.

5. REFERENCES

1. Stocker, T., Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change. Cambridge University Press: 2014.

2. Unneberg, E.; Kolboe, S., Formation of p-Xylene from Methanol over H-ZSM-5. In *Studies in Surface Science and Catalysis*, Elsevier: 1988; Vol. 36, pp 195-199.

3. Conte, M.; Lopez-Sanchez, J. A.; He, Q.; Morgan, D. J.; Ryabenkova, Y.; Bartley, J. K.; Carley, A. F.; Taylor, S. H.; Kiely, C. J.; Khalid, K., Modified zeolite ZSM-5 for the methanol to aromatics reaction. *Catalysis Science & Technology* **2012**, *2* (1), 105-112.

4. Zeng, D.; Yang, J.; Wang, J.; Xu, J.; Yang, Y.; Ye, C.; Deng, F., Solid-state NMR studies of methanol-to-aromatics reaction over silver exchanged HZSM-5 zeolite. *Microporous and mesoporous materials* **2007**, *98* (1-3), 214-219.

5. Elvers, B., Handbook of fuels. *Viley-VCH, Wienhaim* **2008**.

6. CMAI. World Methanol Analysis. <u>https://www.chemicalonline.com/doc/cmai-completes-</u> 2010-world-methanol-analysis-0001, accessed 2010.

7. CMAI. World Butylenes Analysis. <u>https://ihsmarkit.com/industry/chemical.html</u>, accessed 2010.

8. Behr, A., Methanol: The Basic Chemical and Energy Feedstock of the Future. Asinger's Vision Today. Edited by Martin Bertau, Heribert Offermanns, Ludolf Plass, Friedrich Schmidt and Hans-Jürgen Wernicke. *Angewandte Chemie International Edition* **2014**, *53* (47), 12674-12674.

9. Aasberg-Petersen, K.; Nielsen, C. S.; Dybkjær, I.; Perregaard, J., Large scale methanol production from natural gas. *Haldor Topsoe* **2008**, *22*.

10. Kirk, R. E.; Othmer, D. F., *Encyclopedia of Chemical Technology. Vol. 2*. The Interscience Encyclopedia, Inc; New York: 1953.

11. Zhang, Q.; He, D.; Zhu, Q., Recent progress in direct partial oxidation of methane to methanol. *Journal of Natural Gas Chemistry* **2003**, *12* (2), 81-89.

12. Choudhary, T.; Goodman, D., Methane decomposition: production of hydrogen and carbon filaments. *Catalysis* **2006**, *19*, 164-183.

13. Abbas, H. F.; Daud, W. W., Hydrogen production by methane decomposition: a review. *International journal of hydrogen energy* **2010**, *35* (3), 1160-1190.

14. Muradov, N.; Veziroğlu, T., From hydrocarbon to hydrogen–carbon to hydrogen economy. *International Journal of Hydrogen Energy* **2005**, *30* (3), 225-237.

15. Merkx, M.; Kopp, D. A.; Sazinsky, M. H.; Blazyk, J. L.; Müller, J.; Lippard, S. J., Aktivierung von Disauerstoff und Hydroxylierung von Methan durch lösliche Methan-Monooxygenase: eine Geschichte von zwei Eisenatomen und drei Proteinen. *Angewandte Chemie* **2001**, *113* (15), 2860-2888.

16. Espinoza, R.; Du Toit, E.; Santamaria, J.; Menendez, M.; Coronas, J.; Irusta, S., Use of membranes in Fischer-Tropsch reactors. In *Studies in Surface Science and Catalysis*, Elsevier: 2000; Vol. 130, pp 389-394.

17. Soltani, M. S., ; Tsotsis, T., Catalytic membrane reactors. . *Encyclopedia of Membrane Science and Technology* **2013**.

18. Gallucci, F.; Paturzo, L.; Basile, A., An experimental study of CO2 hydrogenation into methanol involving a zeolite membrane reactor. *Chemical Engineering and Processing: Process Intensification* **2004**, *43* (8), 1029-1036.

19. Barbieri, G.; Marigliano, G.; Golemme, G.; Drioli, E., Simulation of CO2 hydrogenation with CH3OH removal in a zeolite membrane reactor. *Chemical Engineering Journal* **2002**, *85* (1), 53-59.

20. Rahimpour, M.; Ghader, S., Theoretical investigation of a Pd-membrane reactor for methanol synthesis. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology* **2003**, *26* (8), 902-907.

21. Struis, R.; Stucki, S., Verification of the membrane reactor concept for the methanol synthesis. *Applied Catalysis A: General* **2001**, *216* (1-2), 117-129.

22. Rohde, M. P.; Unruh, D.; Schaub, G., Membrane application in Fischer–Tropsch synthesis reactors–Overview of concepts. *Catalysis today* **2005**, *106* (1-4), 143-148.

23. Chen, G.; Yuan, Q., Methanol synthesis from CO2 using a silicone rubber/ceramic composite membrane reactor. *Separation and purification technology* **2004**, *34* (1-3), 227-237.

24. Struis, R. P. W. J.; Stucki, S.; Wiedorn, M., A membrane reactor for methanol synthesis. *Journal of membrane science* **1996**, *113* (1), 93-100.

25. Farsi, M.; Jahanmiri, A., Dynamic modeling of a H2O-permselective membrane reactor to enhance methanol synthesis from syngas considering catalyst deactivation. *Journal of Natural Gas Chemistry* **2012**, *21* (4), 407-414.

26. Rohde, M. P.; Unruh, D.; Schaub, G., Membrane application in Fischer– Tropsch synthesis to enhance CO2 hydrogenation. *Industrial & engineering chemistry research* **2005**, *44* (25), 9653-9658.

27. Leonard, S.; Miachon, S.; Vanhove, D., In *Effet de la nature de la membrane sur la synthèse de Fischer-Tropsch en réacteur membranaire à lit fixe*, MemPro2, 14/05/03-16/05/03, 2003.

28. Vanhove, S., Synthese de Fischer-Tropsch en alimentations separees (IMPBR). *Recents Progres en Genie des Procedes*. **2003**, *89*, 194-198.

29. Rahimpour, M.; Mirvakili, A.; Paymooni, K., A novel water perm-selective membrane dual-type reactor concept for Fischer–Tropsch synthesis of GTL (gas to liquid) technology. *Energy* **2011**, *36* (2), 1223-1235.

30. Marvast, M. A.; Sohrabi, M.; Zarrinpashne, S.; Baghmisheh, G., Fischer-Tropsch Synthesis: Modeling and performance study for Fe-HZSM5 bifunctional catalyst. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology* **2005**, *28* (1), 78-86.

31. Vakili, R.; Rahimpour, M.; Eslamloueyan, R., Incorporating differential evolution (DE) optimization strategy to boost hydrogen and DME production rate through a membrane assisted single-step DME heat exchanger reactor. *Journal of Natural Gas Science and Engineering* **2012**, *9*, 28-38.

32. Bayat, M.; Rahimpour, M., Simultaneous hydrogen injection and in-situ H2O removal in a novel thermally coupled two-membrane reactor concept for Fischer–Tropsch synthesis in GTL technology. *Journal of Natural Gas Science and Engineering* **2012**, *9*, 73-85.

33. Bayat, M.; Rahimpour, M., Simultaneous hydrogen and methanol enhancement through a recuperative two-zone thermally coupled membrane reactor. *Energy Systems* **2012**, *3* (4), 401-420.

34. Bayat, M.; Rahimpour, M.; Taheri, M.; Pashaei, M.; Sharifzadeh, S., A comparative study of two different configurations for exothermic–endothermic heat exchanger reactor. *Chemical Engineering and Processing: Process Intensification* **2012**, *52*, 63-73.

35. Bayat, M.; Rahimpour, M., Simultaneous utilization of two different membranes for intensification of ultrapure hydrogen production from recuperative coupling autothermal multitubular reactor. *international journal of hydrogen energy* **2011**, *36* (12), 7310-7325.

36. Rahimpour, M.; Bayat, M., Production of ultrapure hydrogen via utilizing fluidization concept from coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor. *international journal of hydrogen energy* **2011**, *36* (11), 6616-6627.

37. Khademi, M.; Rahimpour, M.; Jahanmiri, A., Differential evolution (DE) strategy for optimization of hydrogen production, cyclohexane dehydrogenation and methanol synthesis in a hydrogen-permselective membrane thermally coupled reactor. *international journal of hydrogen energy* **2010**, *35* (5), 1936-1950.

38. Khademi, M.; Setoodeh, P.; Rahimpour, M.; Jahanmiri, A., Optimization of methanol synthesis and cyclohexane dehydrogenation in a thermally coupled reactor using differential evolution (DE) method. *international journal of hydrogen energy* **2009**, *34* (16), 6930-6944.

39. Khademi, M.; Rahimpour, M.; Jahanmiri, A., A comparison of a novel recuperative configuration and conventional methanol synthesis reactor. *Chemical Engineering Communications* **2012**, *199* (7), 889-911.

40. Bradford, M. C.; Te, M.; Pollack, A., Monolith loop catalytic membrane reactor for Fischer–Tropsch synthesis. *Applied Catalysis A: General* **2005**, *283* (1-2), 39-46.

41. Khassin, A.; Sipatrov, A.; Yurieva, T.; Chermashentseva, G.; Rudina, N.; Parmon, V., Performance of a catalytic membrane reactor for the Fischer–Tropsch synthesis. *Catalysis today* **2005**, *105* (3-4), 362-366.

42. Li, Z.; Tsotsis, T. T., Methanol synthesis in a high-pressure membrane reactor with liquid sweep. *Journal of Membrane Science* **2019**, *570*, 103-111.

43. Domańska, U.; Marciniak, A., Solubility of ionic liquid [emim][PF6] in alcohols. *The Journal of Physical Chemistry B* **2004**, *108* (7), 2376-2382.

44. Nishida, T.; Tashiro, Y.; Yamamoto, M., Physical and electrochemical properties of 1alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *Journal of Fluorine Chemistry* **2003**, *120* (2), 135-141.

45. Yu, Y. An experimental method to measure the porosity from cuttings: Evaluation and error analysis. 2013.

46. Lu, J.; Yu, Y.; Zhou, J.; Song, L.; Hu, X.; Larbot, A., FAS grafted superhydrophobic ceramic membrane. *Applied surface science* **2009**, *255* (22), 9092-9099.

47. Wei, C. C.; Li, K., Preparation and characterization of a robust and hydrophobic ceramic membrane via an improved surface grafting technique. *Industrial & Engineering Chemistry Research* **2009**, *48* (7), 3446-3452.

48. Li, Z., Methanol Synthesis in a Contactor-Type Membrane Reactor. *PhD Thesis USC*. 2017.

49. Soltani, S., Methanol Synthesis in a Membrane Reactor. University of Southern California, 2014.

50. Rozovskii, A. Y.; Lin, G. I., Fundamentals of methanol synthesis and decomposition. *Topics in Catalysis* **2003**, *22* (3-4), 137-150.

51. Bussche, K. V.; Froment, G., A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3Catalyst. *Journal of Catalysis* **1996**, *161* (1), 1-10.

52. Chinchen, G.; Denny, P.; Parker, D.; Spencer, M.; Whan, D., Mechanism of methanol synthesis from CO2/CO/H2 mixtures over copper/zinc oxide/alumina catalysts: use of14C-labelled reactants. *Applied Catalysis* **1987**, *30* (2), 333-338.

53. Graaf, G.; Stamhuis, E.; Beenackers, A., Kinetics of low-pressure methanol synthesis. *Chemical Engineering Science* **1988**, *43* (12), 3185-3195.

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