Glucose Hydrogenation in a Membrane Trickle-Bed Reactor

Victor Diakov and Arvind Varma
Dept. of Chemical and Biomolecular Engineering, and Center for Molecularly Engineered Materials, University of Notre Dame, Notre Dame, IN 46556

The concept of membrane distributed feed to a packed-bed reactor is applied to multiphase catalytic reaction systems. The expected benefits of this approach include enhanced reactant conversion. The concept may be applied to a wide variety of reactions conducted over trickle-beds and is supported experimentally for the reaction of glucose hydrogenation to sorbitol.

Introduction

Numerous advantages of membrane reactors over conventional reactor types have been discussed in the literature. These include enhancements of conversion, selectivity and/or yield in various reaction networks (cf. Dixon, 1999; Saracco et al., 1999), utilizing ceramic (Zhu et al., 1996), silica (Tsapatsis and Gavalas, 1994), palladium (Armor, 1998; Reich and Foley, 1998) and zeolite (Bernal et al., 2002) membranes. However, most prior work has been related to single-phase flows. In this work, the concept of a membrane reactor for multiphase systems is considered and supported experimentally.

An example that has received significant prior attention involves membrane distributed feed to catalytic packed-bed reactors, primarily for partial oxidation reactions (Reyes et al., 1993). Owing to continuous consumption of the distributed reactant, its concentration in a packed-bed membrane reactor (PBMR, Figure 1a) is usually smaller as compared with a conventional fixed-bed reactor (FBR, Figure 1b), where both reactants are co-fed at the reactor inlet. Further, the flow rate profile in the PBMR is also altered, resulting in higher residence time for the reactant fed directly to the catalyst bed (Tonkovich et al., 1996; Diakov et al., 2001). This effect enhances reactant conversion for oxidative dehydrogenation of methanol in a PBMR with oxygen distributed feed, as demonstrated recently both experimentally and by modeling (Diakov et al., 2002). The residence time increase due to membrane distributed gas feed can become more prominent in a packed-bed with multiphase flow.

The trickle-bed reactors (TBR, Figure 1d) are among the most industrially used multiphase reactor types, owing to their vast applications in petroleum processing (cf. Gianetto and Silveston, 1986) and more recently in the production of pharmaceuticals and fine chemicals (Mills and Chaudhari, 1997). For this reason, the reaction engineering aspects of TBR operation have been investigated extensively (cf. Dudukovic et al., 1999). In this article, we introduce the concept of a membrane trickle-bed reactor, which exploits the benefits of a PBMR for multiphase reaction systems.

The complexity of physical phenomena occurring in TBR results in a variety of correlations based on different models and approaches, providing useful relations between important characteristics of reactor operation, such as liquid holdup, mass-transfer rates, and catalyst wettability (Dudukovic and Mills, 1986; Al-Dahhan and Dudukovic, 1994; Iliuta et al., 1999). However, owing to a variety of significant factors, such as the modification of superficial velocities of the fluid phases involved, which may trigger changes in flow patterns, reaction rate, and fluid-phase compositions along the catalyst bed, it is not possible to predict the effect of membrane distributed gas feed in a multiphase reactor and the issue must be investigated experimentally.

Membrane Trickle-Bed Reactor Concept

The new membrane trickle-bed reactor (MTBR) is a packed-bed membrane reactor with multiphase cocurrent reactant flow (see Figure 1c), where a part of the gas feed is distributed along the reactor by the membrane, while the liquid reactant (along with remaining gas) is fed directly to the catalyst bed. A key concept for further development is conversion enhancement due to an increase in the residence time of one reactant, resulting from distributed addition of the other (that is, reactants B and A, respectively, in Figures 1a and 1c).

It is generally accepted that membrane distributed reactant feed lowers the conversion in a PBMR as compared with

---

Correspondence concerning this article should be addressed to A. Varma.

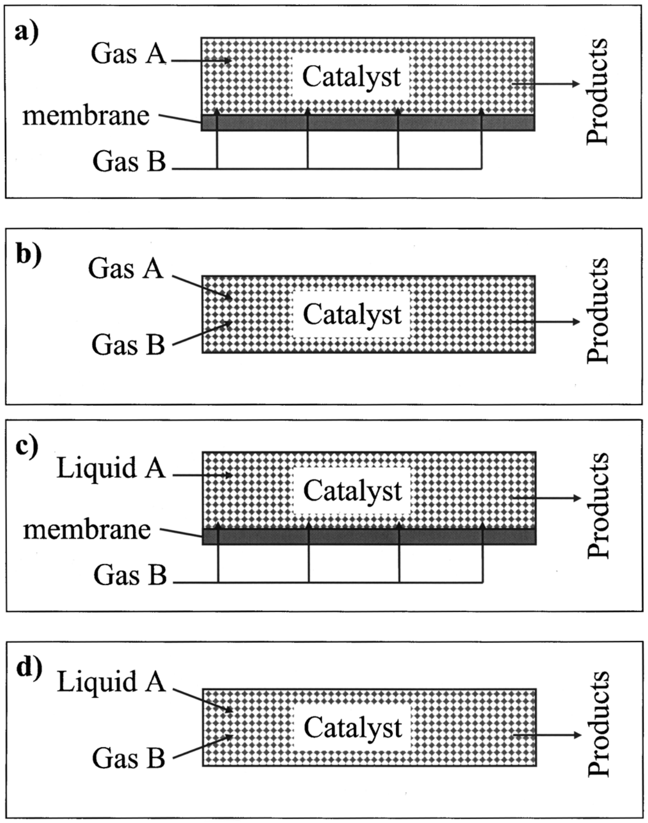


Figure 1. (a) Packed-bed membrane; (b) fixed-bed; (c) membrane trickle-bed; (d) trickle-bed reactors.

conventional FBR at overall equal feed conditions (cf. Reyes et al., 1993; Dixon, 1999). However, in the particular case of methanol partial oxidation over Fe/Mo oxide catalyst, the PBMR with oxygen feed distributed via membrane (PBMR-O) exhibits higher methanol conversion than the FBR (Diakov et al., 2002). There are two reasons for this behavior. The first is related to the fact that the reaction is zero-order with respect to oxygen, so that its decreased concentration over the catalyst bed owing to its distributed addition does not incur a penalty in the reaction rate. Secondly, conversion is enhanced by methanol residence time, a concept used by Tonkovich et al. (1996) and further developed in our work (Diakov et al., 2001). It is clear that for the same overall feed conditions in PBMR and FBR (Figure 1a and 1b, respectively), the local volumetric flow rate in the former is lower owing to the distributed feed of reactant B, leading to higher residence time for reactant A over the catalyst bed and higher conversion.

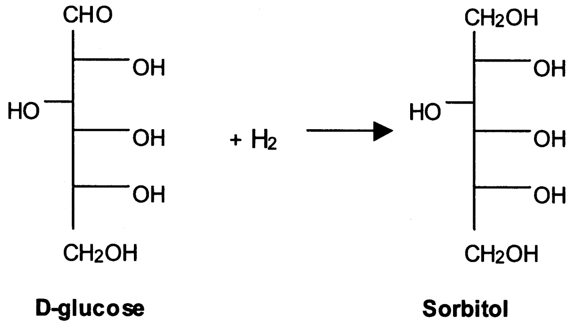
A qualitatively similar conversion enhancement is expected for the MTBR with gas distributed feed (Figure 1c), as compared with the conventional TBR (Figure 1d). Membrane distributed gas feed lowers gas volume over the catalyst bed, allowing the liquid to occupy a larger volume. Therefore, increased liquid reactant residence time and enhanced conversion are expected. In the absence of transport limitations, the concentration of gaseous reactant in the liquid phase depends only on its partial pressure, so that the decrease in gas volume in the MTBR should not reduce the reaction rate, similarly to the zero-order kinetics for the PBMR discussed above. Thus, our recent findings for gas-solid catalytic reactions in a PBMR lead to the concept of membrane distributed feed for multiphase catalytic reaction systems.

While the complexity of hydrodynamics in multiphase reactors is challenging (cf. Sundaresan, 2000), it is possible to assess the upper limit for conversion enhancement in a MTBR based on literature data (Dudukovic and Mills, 1986; Al-Dahhan and Dudukovic, 1994), which suggest that the liquid holdup (that is, fraction of reactor volume occupied by liquid) is inversely proportional to 0.2–0.8 power of gas-flow rate. When comparing TBR (Figure 1d) and MTBR (Figure 1c) fed with a 2 mol/L solution of liquid reactant (stoichiometrically equivalent to approximately 40 times larger volume of gaseous reactant at normal conditions), with the consumption of gaseous reactant compensated by its distributed addition along the reactor, the MTBR requires a minimal reactor volume occupied by gas. Thus, a theoretical 40-fold reduction in local gas-flow rate within the reactor, achieved by complete gaseous reactant consumption, would result in a significant two- to ten-fold increase in liquid holdup and residence time, and, consequently, reactant conversion. Note, this effect is expected to be less pronounced at elevated pressures.

Unlike liquid reactant residence time, the effect of membrane on transport limitations in a TBR is more difficult to assess. It may be expected that increased liquid holdup will affect catalyst contacting efficiency and gas transfer through the liquid film. Specifically, the liquid-phase Sherwood number exhibits little or no correlation with gas-flow rate related dimensionless groups (see Table 2 of Iliuta et al. (1999)); thus, the beneficial effect of liquid holdup increase caused by reduced gas-flow rate is unlikely to be offset by transport limitations through the liquid film. Another important factor for TBR performance is the catalyst wettability (Mazzarino et al., 1987; Burghart et al., 1990; Horowitz et al., 1999), which is likely to be influenced by decreased gas-flow rate. Depending on whether liquid or gas is the limiting reactant, increased wettability may be either beneficial or detrimental (Dudukovic, 1999).

We may conclude by noting that, despite the abundance of literature data on the subject, the influence of the above factors on the reaction rate in a trickle bed for a specific catalytic reaction may only be determined experimentally. This is particularly true for a new configuration, such as membrane distributed gas feed.

To demonstrate the MTBR concept experimentally, glucose to sorbitol hydrogenation reaction



was selected for the following reasons. It is an industrially important reaction, where sorbitol is used as an artificial sweetener and conservant in foods, for Vitamin C production in pharmaceuticals, and also in cosmetics, textiles, and polymers (Lawson, 1991). The reactant (glucose), the product (sorbitol), and the solvent (water) are all environmentally benign chemicals. Finally, the reaction has been studied previously in a TBR (Dechamp et al., 1995), where no internal diffusion limitations were detected for small catalyst particles (approximately 0.5 mm in diameter).

Experimental

To obtain preliminary experimental data to support the concept, a membrane reactor for glucose hydrogenation was designed and constructed. The catalyst used was supported Ni extrudates, approximately 0.5 mm in diameter and 7–10 mm in length, supplied by Engelhard Corp (Ni-3288E). The gaseous feed (H_2) was distributed to the catalyst bed by a cylindrical porous stainless steel membrane (Mott Metallurgical Corp.), 14 cm long, outer diameter 12.5 mm, and 2 mm thick with 0.2 μm pores. The membrane ended with an impermeable cap, which ensured that all gas fed to the membrane permeated the pores. The reactor was made entirely from stainless steel (Figure 2), with all parts assembled by thread connections rather than by welding, to enhance reactor ruggedness and facilitate catalyst loading, as well as parts replacement. The catalyst bed, with 34 g of extrudates packed in 60 mL volume, filled the annulus between the membrane and the reactor wall.

The MTBR was incorporated in the experimental setup (Figure 3), which allowed one to control operating temperature and pressure, gas and liquid feed flow rates, and to distribute the gas feed between the membrane and direct catalyst bed flows. When there was no gaseous feed via membrane, the capillary forces effectively plugged membrane pores (approximately 12 psi differential pressure was needed to unplug them), transforming the MTBR into a conventional TBR.

D-glucose monohydrate and D-sorbitol from Aldrich Chemicals and de-inonized distilled water were used to form solutions of reactant (40 wt. % glucose) and product (40 wt. % sorbitol, for FTIR calibration measurements). Zero grade hydrogen (Matheson Gas Products) was used as gaseous feed and to barbotate the liquid feed prior to experiments. The catalyst bed was pre-wetted (cf. Jiang et al., 1999) with liquid before feeding both gas and liquid to the reactor.

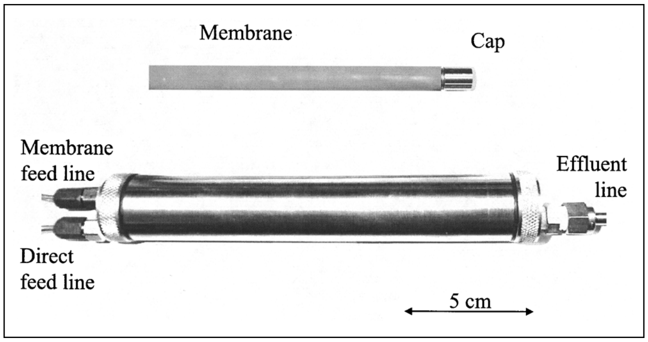


Figure 2. Membrane trickle-bed reactor.

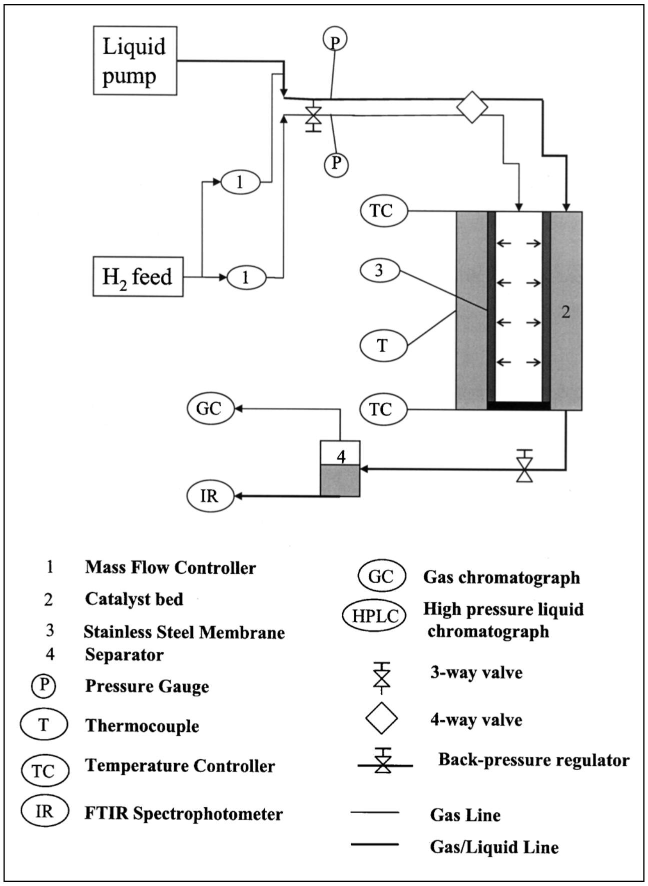


Figure 3. Experimental setup incorporating the membrane trickle-bed reactor.

A syringe pump (KdScientific) provided liquid feed at pressure up to 2 bar. The liquid effluent from the reactor was analyzed using FTIR Satellite 5000 spectrophotometer (MattsonIR) within the wave length range 2,500–2,800 cm^{-1} in a ZnSe optical cell. The effluent mixture absorbance spectra were linearly deconvoluted into the spectra of individual components. The experimental error for glucose and sorbitol concentration measurements was within ± 0.5 wt. %.

Conversion Enhancement in the MTBR

Glucose hydrogenation to sorbitol in a TBR over a supported Ni catalyst was studied by Dechamp et al. (1995) at pressures of 40–120 bar and temperatures of 70–130°C. In the present case, the higher catalyst activity allows one to obtain significant glucose conversion at ambient pressure and temperature of 90°C. The experimental results for several values of hydrogen feed flow rate (Figure 4) show reactor performance enhancement by distribution of gaseous feed via a membrane. As expected, increased gas-flow rate decreases glucose conversion, since it reduces glucose residence time. It may be seen that, for the same overall feed conditions and gas-flow rate, the MTBR provides higher glucose conversion to sorbitol than the TBR. For example, at 40 sccm H_2 flow, the MTBR increases glucose conversion by a substantial factor of 1.5, demonstrating the potential usefulness of membrane distributed gas feed in multiphase catalytic reactors.

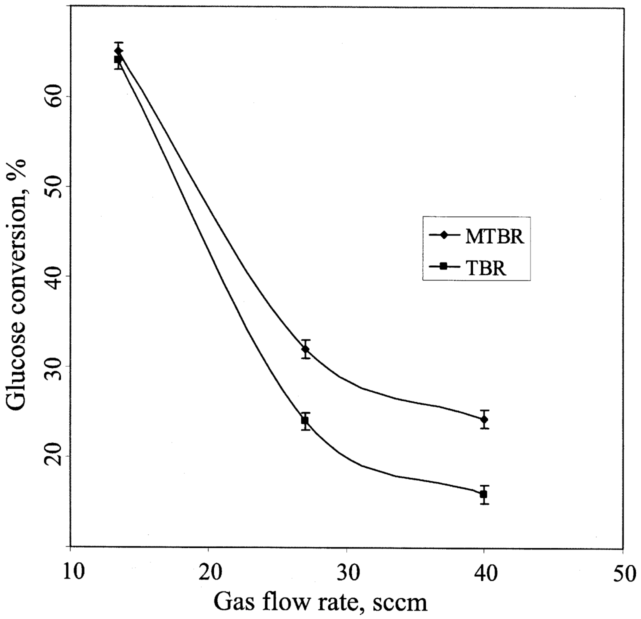


Figure 4. Conversion enhancement in the membrane trickle-bed reactor: gas feed flow rate dependence.

Ambient pressure, temperature 90°C; liquid feed: 5 mL/h of 40 wt.% D-glucose in water.

Concluding Remarks

The concept of membrane distributed gas feed to trickle-bed reactors is presented. The use of a membrane alters liquid residence time within the reactor. While the factors contributing to reactor performance are not fully understood, when compared with conventional trickle-bed reactors, the novel membrane reactor provides higher overall reaction rate. This conclusion is supported experimentally in the case of glucose hydrogenation over Ni catalyst.

Acknowledgments

We gratefully acknowledge financial support from the National Science Foundation (grant CTS-9907321). We also thank Engelhard Corporation for supplying the catalyst free of charge.

Literature Cited

Al-Dahhan, M. H., and M. P. Dudukovic, "Pressure Drop and Liquid Holdup in High Pressure Trickle-Bed Reactors," *Chem. Eng. Sci.*, **49**, 5681 (1994).

Armor, J. N., "Applications of Catalytic Inorganic Membrane Reactors to Refinery Products," *J. Membr. Sci.*, **147**, 217 (1998).

Bernal, M. P., J. Coronas, M. Menendez, and J. Santamaria, "Coupling of Reaction and Separation at the Microscopic Level: Esterification Processes in a H-ZSM-5 Membrane Reactor," *Chem. Eng. Sci.*, **57**, 1557 (2002).

Burghart, A., A. S. Koldziej, and M. Jaroszinsky, "Experimental Studies of Liquid-Solid Wetting Efficiency in Trickle-Bed Cocurrent Reactors," *Chem. Eng. Prog.*, **28**, 35 (1990).

Dechamp, N., A. Gamez, A. Perrerd, and P. Gallezot, "Kinetics of Glucose Hydrogenation in a Trickle-Bed Reactor," *Catalysis Today*, **34**, 29 (1995).

Diakov, V. E., D. Lafarga, and A. Varma, "Methanol Oxidative Dehydrogenation in a Catalytic Packed-Bed Membrane Reactor," *Catalysis Today*, **67**, 159 (2001).

Diakov, V. E., B. Blackwell, and A. Varma, "Methanol Oxidative Dehydrogenation in a Catalytic Packed-Bed Membrane Reactor: Reaction Kinetics and Reactor Model," *Chem. Eng. Sci.*, **57**, 1563 (2002).

Dixon, A. G., "Innovations in Catalytic Inorganic Membrane Reactors," *Catalysis*, **14**, 40, Royal Society of Chemistry, Cambridge, U.K. (1999).

Dudukovic, M. P., "Trends in Catalytic Reaction Engineering," *Catal. Today*, **48**, 5 (1999).

Dudukovic, M. P., F. Larachi, and P. L. Mills, "Multiphase Reactors—Revisited," *Chem. Eng. Sci.*, **54**, 1975 (1999).

Dudukovic, M. P., and P. L. Mills, "Contacting and Hydrodynamics in Trickle-Bed Reactors," *Encyclopedia of Fluid Mechanics, Vol. 3: Gas-Liquid Flows*, N. P. Cheremisinov, ed., Gulf Publishing Corp., Houston, pp. 969–1017 (1986).

Gianetto, A., and P. L. Silveston, *Multiphase Chemical Reactors: Theory, Design, Scale-up*, Springer-Verlag, New York (1986).

Horowitz, G. I., O. Martinez, A. L. Cukierman, and M. C. Cassanello, "Effect of the Catalyst Wettability on the Performance of a Trickle-Bed Reactor for Ethanol Oxidation as a Case Study," *Chem. Eng. Sci.*, **54**, 4811 (1999).

Iliuta, I., F. Larachi, B. P. A. Grandjean, and G. Wild, "Gas-Liquid Interfacial Mass-Transfer in Trickle-Bed Reactors: State-of-the-Art Correlations," *Chem. Eng. Sci.*, **54**, 5633 (1999).

Jiang, Y., M. N. Khadilkar, M. H. Al-Dahhan, and M. P. Dudukovic, "Two-Phase Flow Distribution in 2D Trickle-Bed Reactors," *Chem. Eng. Sci.*, **54**, 2409 (1999).

Lawson, M. E., "Sugar Alcohols," *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 23, Mary Howe-Grant, ed., Wiley, New York, pp. 93-119 (1991).

Mazzarino, I., S. Sicardi, and G. Baldi, "Hydrodynamics and Solid–Liquid Contacting Effectiveness in an Upflow Multiphase Reactor," *Chem. Eng. J.*, **36**, 151 (1987).

Mills, P. L., and R. V. Chaudhari, "Multiphase Catalytic Reactor Engineering and Design for Pharmaceuticals and Fine Chemicals," *Catal. Today*, **37**, 367 (1997).

Reich, B. A., and H. C. Foley, "Ethanol Dehydrogenation with a Palladium Membrane Reactor: an Alternative to Wacker Chemistry," *Ind. Eng. Chem. Res.*, **37**, 3888 (1998).

Reyes, S. C., E. Iglesia, and C. P. Kelkar, "Kinetic-Transport Models of Bimodal Reaction Sequences—I. Homogeneous and Heterogeneous Pathways in Oxidative Coupling of Methane," *Chem. Eng. Sci.*, **48**, 2643 (1993).

Saracco, G., H. W. J. P. Neomagus, G. F. Versteeg, and W. P. M. van Swaaij, "High-Temperature Membrane Reactors: Potential and Problems," *Chem. Eng. Sci.*, **54**, 1997 (1999).

Sundaresan, S., "Modeling the Hydrodynamics of Multiphase Flow Reactors: Current Status and Challenges," *AIChE J.*, **46**, 1102 (2000).

Tonkovich, A. L. Y., D. M. Jiménez, J. L. Zilka, and G. L. Roberts, "Inorganic Membrane Reactors for the Oxidative Coupling of Methane," *Chem. Eng. Sci.*, **51**, 3051 (1996).

Tsapatsis, M., and G. Gavalas, "Structure and Aging Characteristics of H_2-Permselective SiO_2-Vycor Membranes," *J. Membr. Sci.*, **87**, 281 (1994).

Zhu, Y., R. G. Minet, and T. T. Tsotsis, "A Continuous Pervaporation Membrane Reactor for the Study of Esterification Reactions Using a Composite Polymeric/Ceramic Membrane," *Chem. Eng. Sci.*, **51**, 4103 (1996).

Manuscript received Oct. 5, 2002, and revision received Apr. 1, 2003.