Membrane Processes for Effective Methanol Synthesis in the Forest Based Biorefinery

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Abstract

A new promising way to produce synthesis gas from biomass is by black liquor gasification. In commencing forest based biorefineries, bio fuels such as methanol may be produced from the synthesis gas. However, biorefineries will produce relatively small quantities of bio fuels compared to traditional oil refineries producing fossil fuels. This calls for development of more efficient processes to reduce the production costs for production of bio fuels in small scale. Such processes could be membrane based. In the present work, ZSM-5 membrane reactors and ZSM-5 membrane modules, are explored and compared to traditional methanol synthesis processes. This is done through mathematical modelling. As basis for the calculations, a forest based biorefinery with a production of 70 000 tonne methanol per year was used. For a stoichiometric feed, the one-pass CO_x -conversion for a traditional methanol process is about 26 % per pass, which requires a recirculation loop with the associated disadvantages. The zeolite research group at Luleå University of Technology has prepared ZSM-5 membranes and evaluated their performance at atmospheric pressure and room temperature. By assuming that the same membrane performance could be obtained at industrial conditions for methanol synthesis, it was shown by mathematical modeling that a ZSM-5 membrane reactor with a membrane area of 400 m² could potentially reach 97% CO_x -conversion per pass, while a ZSM-5 membrane module process with the same membrane area could potentially reach 81% conversion per pass for a stoichiometric feed. As a result of the high conversion per pass for the membrane processes, one-pass design with the associated advantages is possible for these processes. A membrane module based system is preferable over a membrane reactor of practical reasons. However, similar performance to the membrane processes can of course be achieved with a one pass process comprised of a series of methanol reactors, reactor effluent heat exchangers, coolers and condensers.

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List of papers

1. **Membrane processes for effective methanol synthesis in the forest based biorefinery**, E. Sjöberg, L. Sandström & J. Hedlund, Keynote presentation at 9th International Conference on Catalysis in Membrane Reactors, Lyon, June 28th – July 2nd 2009. Abstract published in the conference proceedings
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1. Introduction

In recent years there has been much interest in bio-based transportation fuels. However, it is vital to find new and more effective ways of utilizing biomass for fuel production as efficient as possible. For example, effective production of fuels can be achieved in commencing forest based biorefineries, which is based on existing pulp mills by producing energy, fuels, chemicals, pulp and paper at the same site. In these commencing biorefineries, black liquor gasification might be a key technology. Black liquor is an internal biomass stream in pulp mills, which contains dissolved lignin and cooking chemicals. The only demonstration plant for pressurised black liquor gasification is operated at a large pulp mill in Piteå, Sweden. It is unlikely that the recovery boiler in existing plants can be replaced by gasification plants in the first step, since a recovery boiler represents a very large investment. However, the recovery boiler is often the bottleneck in a pulp plant and if as much as 25% of the black liquor produced in a large pulp mill is gasified in order to increase the pulp production capacity, about 70 000 ton of methanol can be produced per year. Due to the complexity of the processes and in order to arrive at favourable economy, the production capacity in new plants for production of methanol from fossil fuels exceeds 1 000 000 ton of methanol per year. The production capacity of bio-fuels in the example of a forest based biorefinery described above is thus less than 7% of the capacity of plants utilizing fossil fuels, which calls for development of more cost effective processes such as membrane processes. It has been shown earlier [1, 2] that the use of membrane reactors could increase the productivity of a conventional methanol synthesis process by increasing the one-pass conversion of a hydrogen rich synthesis gas.

1.1 The Forest Based Biorefinery

A biorefinery is an equivalent to a petroleum refinery. In a petroleum refinery crude oil is used as feedstock to produce a wide range of products such as fuels, fertilizers and synthetic materials. In a biorefinery, biomass would be used as feedstock to produce fuels, energy, pulp and paper, chemicals. The biomass can be either forest or agricultural based.

An advantage for the forest based biorefinery compared to an agricultural based is that it could be integrated with existing chemical pulp mills. The biorefinery could take use of already existing infrastructure, and also diversify the product mixture while utilizing more of the wood components, see Figure 1. The composition of wood is in general 42-45% cellulose, 27-30% hemicelluloses, 20-28% lignin and 3-5% extractives [3]. In

today's pulp mills basically only the cellulose, with a few exceptions, is sold as products while the residues are burned in the recovery boiler for energy. Thus, it makes sense converting the pulp mills to biorefineries that utilizes a larger fraction of the wood and produces more value from the wood.

Figure 1. A schematic overview of the forest based biorefinery.

The product streams in a forest based biorefinery can be divided into two main categories [4]: before and after digester. Before the digester, hemicelluloses can be leached from the wood. The extracted hemicelluloses can then be hydrolysed in order to produce mono-sugars, which can be used in fermentation to produce high value products such as succinic acid, that may be used to produce pharmaceuticals, solvents, biodegradable plastic and detergents. Hemicelluloses can also be used as fibre additives in the pulp mill, barriers in beverage packaging and hydrogels. The second product stream, after the digester, basically is the dissolved material (cooking chemicals and lignin) in the spent liquor (black liquor). The black liquor is normally burned in a recovery boiler to produce heat, electricity and recover the cooking chemicals. However, the black liquor could be gasified to produce synthesis gas instead of being burned in the recovery boiler. The synthesis gas could then be used to produce a large variety of products, such as methanol, dimethyl ether and mixed alcohols among others. However, instead of gasifying the black liquor, acid precipitation could be used to remove the lignin

from the liquor. This technique can be used to produce carbon fibres when mixed with polyester for example.

1.2 Methanol Synthesis

Methanol is one of many possible products that can be produced in commencing biorefineries. Methanol is an important feedstock for many chemicals. A great amount of the methanol produced in the world is converted to formaldehyde which is the base in for example explosives, paints and plastics. Methanol can also be used as fuel in Otto engines or converted to dimethyl ether, which can be used in Diesel engines.

1.2.1 Thermodynamics and reactions

When producing methanol from synthesis gas, usually a mixture of carbon monoxide, carbon dioxide and hydrogen is used. In such a mixture, methanol can form through two reactions (Equation 1-2).

It is also important to take the reverse water gas shift reaction (Equation 3) into account because it is catalyzed with the same catalyst at about the same temperature ranges [5].

Due to the exothermic nature of Equation 1-2 and that the reactions are accompanied by a decrease in volume, methanol formation is favoured by increasing pressure and decreasing temperature.

A generalization can be made that Equation 1 and 3 can be seen as independent reaction pathways while the conversion of carbon dioxide (Equation 2) is the overall reaction. The equilibrium constant $K_{x,2}$ can then be described as $K_{x,1}$ multiplied with $K_{x,3}$. If ideal gas behaviour is taken into account the equilibrium constant can then be expressed, for synthesis of methanol from carbon dioxide, as follows:

$$K_{x.2} = K_{x.1} K_{x.3} = \frac{P_{CH_3OH} P_{H_2O}}{P_{CO_2} P_{H_2}^3} \quad (4)$$

1.2.2 Kinetics and mechanism

The mechanism of methanol synthesis over Cu/ZnO/Al₂O₃, the catalysts used in the commercial low pressure process, has been under discussion for several years. Questions that have pervaded the literature are the reactive carbon containing component (CO or CO₂) and the overall mechanism.

Mixtures of both H₂/CO and H₂/CO₂ will form methanol over a Cu/ZnO/Al₂O₃ catalyst and it was early believed that methanol synthesised from a mixture of H₂/CO/CO₂ was the product of CO hydrogenation [6]. However, it was discovered that the methanol synthesis was promoted by addition of small amounts of CO₂ to the H₂/CO mixture, while large CO₂/CO ratios inhibited the synthesis, thus providing a maximum in the reaction rate. This maximum was first concluded to exist due to an oxidized state and a reduced state of the catalyst, which could be controlled by the CO/CO₂ ratio in the feed (Equation 5) [7]. The intermediate reduced state is inactive and the oxidized state is active. The increase in reaction rate at high ratios of CO/CO₂ was explained by excessive reduction of the catalyst, inactivation of the sites, while at low ratios it were thought to be due to strong adsorption by CO₂. A mechanism was proposed building on an intuitive CO hydrogenation with a CO₂/CO redox-mechanism:

Based on these observations a rate expression was build up by two terms [7]; the first is the main term and relates the complete adsorption of CO₂ and CO or H₂ to the synthesis of methanol from CO under high pressures. The second term corresponds to the reaction directly from CO₂. This equation states that the reaction rate is zero for gases which contains no CO₂ (Equation 6).

$$r_{CH_3OH} = const \frac{K_{redox}^3 (p_{CO_2} / p_{CO})^3 (p_{CO} p_{H_2}^2 - p_{CH_3OH} / K_2^*)}{1 + K_{redox} (p_{CO_2} / p_{CO})^3 (F + K_{CO_2} p_{CO_2})^n} + k' (p_{CO_2} - (1/K_1^*) (p_{CH_3OH} p_{CO} / p_{H_2}^3)) \quad (6)$$

Through modelling of the methanol synthesis Villa et al. [8] found that the water-gas-shift reaction also should be accounted for in the modelling of the system, which was not accounted for in Equation 6. The set of equations (Equation 7-8) proposed assumes that

CO is the carbon containing source of methanol, and that the water gas shift reaction and hydrogenation of carbon monoxide occurs on different catalytic sites.

$$r_{CH_3OH} = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH} / K_2^*}{(A + Bf_{CO} + Cf_{H_2} + Gf_{CO_2})^3} \quad (7)$$

$$r_{WGS} = \frac{f_{CO_2}f_{H_2} - f_{CO}f_{H_2O}K_3^*}{M^2} \quad (8)$$

Evidence that the actual reactant in methanol synthesis is CO₂ was obtained using isotope labelled ¹⁴CO₂ in the feed [9]. At high space velocity the methanol product had similar ¹⁴C content as the ¹⁴CO₂ fed to the reactor. Due to interference from intermediate reactions in the water-gas-shift reaction, the results for low space velocity did not provide with any mechanistic information. It was also concluded that methanol synthesis and water-gas-shift does not have the same carbon containing intermediate on the catalyst surface.

Chinchen and Spencer [10] proposed a mechanism in which methanol and adsorbed oxygen was generated on the copper surface through hydrogenation of CO₂ and involving the formation of formats and their hydrogenolysis to methoxy groups (Equation 9-15). Since CO is a better reducing agent than H₂ it resulted in a linear relationship between CO₂/CO ratio and oxygen coverage and the adsorbed oxygen would promote chemisorption of CO₂. High CO₂/CO ratios would then cause excessive coverage of oxygen or chemisorbed species, which could explain the inhibition from large CO₂/CO ratios.

Despite the results of Chinchen and Spencer, Graaf et al. [11] derived kinetic expressions (Equation 16-18) based on the hydrogenation of CO and CO₂ together with the reverse water-gas-shift reaction. A dual-site Langmuir-Hinshelwood mechanism was proposed, which consisted of the adsorption of CO and CO₂ on one site while H₂ and H₂O adsorbs on another site.

$$r_{eq1} = \frac{k_1 K_{CO} (f_{CO_2} f_{H_2}^{3/2} - f_{CH_3OH} / (f_{H_2}^{1/2} K_{eq}^1))}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) (f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2} f_{H_2O}))} \quad (16)$$

$$r_{eq2} = \frac{k_2 K_{CO_2} (f_{CO_2} f_{H_2}^{3/2} - (f_{CH_3OH} f_{H_2O}) / (f_{H_2}^{1/2} K_{eq}^2))}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) (f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2} f_{H_2O}))} \quad (17)$$

$$r_{eq3} = \frac{k_3 K_{CO_2} (f_{CO_2} f_{H_2} - f_{CH_3OH} f_{CO} / K_{eq}^3)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) (f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2} f_{H_2O}))} \quad (18)$$

This model predicts that there are two different concentrations of one of the same species, like formyl and methoxy, since some intermediates occur in two different overall reactions.

Vanden Bussche and Froment [12] couples the rate of both overall reactions (Equation 19-21) through adsorbed oxygen intermediates, which also account for the water gas shift reaction, using a Langmuir-Hinselwood Hougen-Watson mechanism. The main source of carbon in methanol is assumed to be CO₂ and CO is the source of CO₂ through the water gas shift reaction.

$$r_{CH_3OH} = \frac{k'_{5a} K'_2 K_3 K_4 K_{H_2} p_{CO_2} p_{H_2} \left[1 - \frac{p_{H_2O} p_{CH_3OH}}{p_{H_2}^3 p_{CO_2} K_{eq}^1} \right]}{M^3} \quad (19)$$

$$r_{RWGS} = \frac{K'_1 p_{CO_2} \left[1 - \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2} K_{eq}^2} \right]}{M} \quad (20)$$

$$M = 1 + \left(\frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \right) \left(\frac{p_{H_2O}}{p_{H_2}} \right) + \sqrt{K_{H_2} p_{H_2}} + K_{H_2O} p_{H_2O} \quad (21)$$

1.2.3 Methanol production

The methanol synthesis process can be divided in four sections: feed purification, reforming, synthesis and distillation (Figure 2).

Figure 2. Schematic overview of methanol production

The feed purification step is important since the feedstock can contain sulphur and chloride which could poison the catalyst. For example, sulphur can be removed with a guard bed of zinc oxide or by using the Rectisol process.

Synthesis gas used for methanol synthesis is usually characterized by the stoichiometric number:

$$SN = ([H_2] - [CO_2]) / ([CO] + [CO_2]) \quad (22)$$

where the relevant components concentrations are expressed as volume percent. A stoichiometric number of 2.0 indicates that the gas mixture is stoichiometric in the aspect of methanol formation reaction. Should the stoichiometric number be above 2.0 it signals an excess of hydrogen. This stoichiometric number of the synthesis gas is regulated in the reforming process.

Since methanol synthesis is equilibrium limited, only about 50% of the synthesis gas is converted per-pass in modern processes. A simplified flow-sheet is shown in Figure 3. The recycled gas is first mixed with fresh synthesis gas, the mixture is then compressed to operating conditions, i.e. about 50-100 bar. A heat exchanger is then used to transfer heat from the gas in the product stream of the reactor to the gas entering the reactor. The reaction inside the reactor is exothermic and the temperature inside the reactor is about 200- 300°C. After passing through the heat-exchanger, crude methanol (methanol and water) in the product stream is separated from the unreacted synthesis gas in a separator and flashed before the distillation step.

Figure 3. A schematic overview of the methanol synthesis loop A) Compressor, B) Separator, C) Reactor, D) Heat Exchanger.

In commercial processes it is mainly the reactor design that differs. The most common reactor types are adiabatic or quasi-isothermal. The adiabatic reactor consists of a single catalyst bed. By adding cold synthesis gas at several points over the reactor the reaction is quenched, giving the temperature profile over the reactor a sig-sag shape. The quasi-isothermal reactors consists mainly of tubes filled with catalyst (packed bed reactor), which is cooled by boiling water. The cooling water flows over the catalyst filled tubes and the temperature of the cooling water is adjusted by the pressure.

The crude methanol that is separated from the unreacted synthesis gas is generally separated from impurities in two stages. In the first stage all components that boil at a lower temperature than methanol (light ends) are removed. The light ends normally consist of acetone, methyl formate, dimethyl ether and dissolved gases. After the removal of the light ends, pure methanol is distilled out in distillation columns.

1.3 Zeolite Membranes

Zeolites are crystalline aluminosilicates with a three-dimensional structure and open channels within the network [13]. The three-dimensional structure of zeolites consists of SiO_4^{4-} and AlO_4^{5-} tetrahedra, where the centres consist of either a silicon atom or an aluminum atom. The structural formula that represents zeolites can be written as:

$$\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O} \quad (23)$$

where the M is a metal cation with valence n. The purpose of the metal cation is to balance the negative charge introduced by the aluminum tetrahedra. The ratio of y and x, y/x , is the $\text{SiO}_2/\text{AlO}_2$, and w is the number of water molecules. The porous framework of the zeolites is determined by oxygen rings, which consists of 4, 5, 6, 8, 10 or 12 oxygen atoms. However, the pore size is also determined by the volume of the charge balancing cation. The channel diameters in known zeolites range from 0.3 to 1.3 nm [14].

Zeolites have four major areas of application. These are catalysis, ion exchange, gas separation and adsorption. The zeolites most important properties as catalysts are the high activity and selectivity. The selectivity is a result of the microporous framework, which either prevents larger reactants to enter the porous structure or prevents larger products to either form or the leave the pores [14].

A promising zeolite for membrane reactors and membrane modules is ZSM-5, a synthetic zeolite with high silicon to aluminium ratio. High ratios give the structure high thermal stability and make the zeolite hydrophilic. Thus it will adsorb water molecules from organic solutions containing water, while a more hydrophobic zeolite will adsorb the organic molecules in a water solution. The channel structure of ZSM-5 is two-dimensional, with rings consisting of 10 oxygen atoms, and straight channels (0.51x0.55 nm) and intersecting zig-zags channels (0.54x0.56 nm) [14].

A membrane process is characterised by the use of a membrane to achieve a specific separation. A membrane is a permeable material that acts as a selective barrier between two phases. The separation over a zeolite membrane can occur in different ways, see Figure 4. Molecular sieving is when larger molecules are inhibited to permeate over the zeolite membrane due to their size, while smaller can diffuse through the zeolite pores. Adsorption is when high concentration of strongly adsorbing molecules inhibiting other molecules from permeating, while the adsorbed molecules diffuse through. The third way is when molecules with high diffusivity are separated from molecules with lower diffusivity.

Figure 4. Three different types of separation in a zeolite membrane.

1.3.1 Membrane reactors

In general the separation unit in chemical processes follows the reactor in a separate unit. However, membranes offer the possibility to integrate the reactor and separation into one unit, a membrane reactor. A membrane reactor could be a packed bed reactor with the bed surrounded of a membrane. The advantage of such a design is that it would be favourable for equilibrium limited reactions since the membrane can selectively remove one or more products from the reactor and a higher conversion per-pass can be reached. It also offers the possibility to increase the selectivity of the reaction in the reactor, by either removing an intermediate product or dosing a reactant through the membrane.

1.3.2 Membrane modules

Membranes can also be used as replacements for traditional separation units such as condensers. A way to do this is by using a membrane module. The benefit of a membrane module compared to a membrane reactor is that it offers more degrees of freedom, since it is possible use different operation condition in the reactor and separation. A membrane module may also perform separations to a lower energy cost then, for example, a condenser.

1.4 Objectives of this work

In the present work, hypothetical processes utilizing ZSM-5 zeolite membrane reactors and membrane modules are compared to a traditional methanol synthesis processes at the basis of a forest based biorefinery. Also a high temperature and high pressure test-facility for zeolite membranes was to be build.

2. High pressure Membrane test facility

A schematic overview of the high pressure test facility that was constructed at Energy Technology Centre (ETC) in Piteå is shown in Figure 5. Most of the test facility was built during the course of the work, but some work is necessary before the test facility is complete and ready for use. The purpose of the facility is to allow evaluation of zeolite membranes at high temperature and high pressures, i.e. up to 300 °C and 100 bar. The current test facility at LTU is restricted to tests up to 400 °C and 5 bar. To drive the research further and evaluate the membranes under realistic conditions, tests at higher pressure are necessary.

In the centre of the rig a membrane cell is installed, see Figure 5. The cell is sealed with copper washers so that leakages of gas cannot occur. Mass flow controllers are used to dose gas in different ratios to the membrane cell. A syringe pump is installed between the membrane cell and the mass flow controllers to allow for addition of methanol or other alcohols, which are subjects of evaluation. Finally the whole system is connected to a gas chromatograph. Pictures from the laboratory at ETC are shown in Figure 6.

Figure 5. Schematic overview of the membrane test-setup at ETC

Figure 6. Pictures from the laboratory at ETC

3. Mathematical modelling

The mathematical model for simulating the processes considered in the present work was developed using the following assumptions: one dimensional plug flow in the reactors and membrane modules, ideal gas, no radial diffusion in the catalyst pellets, no axial dispersion of heat along the reactors. In the overall systems, the energy balances were neglected. In all reactors, the catalyst was diluted (35 %) compared to a conventional reactor due to the large heat development associated with a stoichiometric feed. Also, the activity of the catalyst was assumed to be 70% of that of a fresh catalyst. The tube diameter is 38 mm in the Lurgi process [15]. A smaller diameter was used here for all three processes for better temperature control. As basis of the calculations a forest based biorefinery with a production of 70 000 tonne methanol was used.

3.1 Process description

The traditional reactor process (TRP), represented here by the Lurgi low-pressure process [15], see Figure 7a, consists of a water-cooled tubular reactor in which the feed-effluent heat exchanger preheats the recycled synthesis gas to the reactor inlet. Crude methanol is condensed from the reactor effluent while unreacted synthesis gas is recycled using a compressor. A recycle ratio of 3.7 is used here (for a stoichiometric feed). A fraction (2 %) of the recycled gas is purged.

Figure 7. Methanol synthesis using a traditional reactor process (a), a membrane reactor process (b) and a membrane module process (c).

In the membrane reactor process (MRP) considered here, see Figure 7b, the synthesis gas is not recycled as in the TRP. The synthesis gas is fed to the reactor and permeate from the membrane is sent to the condenser and the synthesis gas from the condenser is used as sweep gas. The retentate from the reactor is purged. The membrane module process (MMP) evaluated in the present work, see Figure 1c, consists of four 4 meter long water-cooled tubular reactors placed in series with membrane modules after each reactor. In each reactor the cooling water temperature is set independently. The

membrane modules consist of several membrane tubes that separate methanol and water from the synthesis gas at reaction temperature. Methanol is condensed from the membrane permeate streams and the retentate from the last membrane module is purged. Synthesis gas from the condenser is used as sweep gas in the membrane modules.

3.2 Water-cooled tubular reactor

The traditional reactor (in the TRP) consists of steel tubes, which are filled with catalyst pellets. The tubes are cooled with boiling water generating medium pressure steam. The dimensions and properties of the reactor and catalyst are listed in Table 1. The mass and energy balance and the Ergun equation for the water cooled tubular reactor are:

$$\frac{dF_i}{dz} = r_i \rho_b \quad (24)$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + \sum_{i=1}^{n_r} r_i (-\Delta H_i^{rx}) \rho_b \right) \quad (25)$$

$$\frac{dP}{dz} = \frac{G_0^2}{\rho_G D_p} \frac{(1-\phi)}{\phi^3} \left(\frac{150}{Re} + 1.75 \right) \cdot 10^{-5} \quad (26)$$

The boundary conditions for the water cooled tubular reactor are:

$$P|_{z=0} = P_0, F_i|_{z=0} = F_{i0}, T|_{z=0} = T_0 \quad (27)$$

The overall heat transfer coefficient, U, between the circulating boiling water on the shell side and the gas flow on the reaction side was estimated from:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{(D_o - D_i)}{(D_o + D_i)} \frac{D_i}{k_s} + \frac{D_i}{D_o} \frac{1}{h_o} \quad (28)$$

where h_i is the heat transfer coefficient between the packed bed and the tubular wall of the reactor and h_o is the heat transfer coefficient between the tubular wall on the outer side and the cooling water, which is obtained by the correlations [16, 17]:

$$h_i = \frac{2.06 \rho_G V_0}{\phi C_{pG}} \left(\frac{V_0 D_P \rho_G}{\mu_G} \right)^{-0.575} \left(\frac{C_{pG} \mu_G}{k_G} \right)^{-2/3} \quad (29)$$

$$h_o = \frac{0.020 k_w}{D_o} \left(\frac{V_T D_H}{\mu_w} \right)^{0.8} \left(\frac{C_{pw} \mu_G}{k_w} \right)^{1/3} \left(\frac{D_T}{D_o} \right)^{0.53} \quad (30)$$

Table 1. Catalyst, feed, reactor and membrane specifications.

Parameter	Value	Parameter	Value
Catalyst		Reactor	
Catalyst density	1775 kg/m ³	Tot. reactor length	16 m
Catalyst pellet diameter	0.0042 m	Reactor tube I.D.	0.0254 m
Void fraction of bed	0.4	Membrane	
Feed		Tot. memb. area	450 m ²
Stoichiometric number of feed	2	Memb. tube O.D.	0.01 m
CO/CO ₂ ratio in feed	2.75	Membrane module length	4 m
Concentration of inert in feed	2 %	Sweep & Cooling	
Inlet temperature of feed	513 K	Sweep gas per MRP tube	1.200 mol/s
Inlet pressure of feed	80 bar	Sweep gas per MMP tube	0.450 mol/s
Fresh feed to each TRP tube	0.170 mol/s	Sweep gas pressure	70 bar
Feed to each MRP tube	0.270 mol/s	C.W. temp. TRP	533 K
Feed to each MMP tube	0.390 mol/s	C.W. temp. MRP	513 K
		C.W. temp. MMP	513, 523, 533K

3.2 Membrane reactor

The membrane reactor consists of steel tubes, which are filled with catalyst. A zeolite membrane supported on the outer side of an alumina tube is placed in the centre of each steel tube [18]. The reactor is cooled with boiling water on the outer side of the steel tubes generating medium pressure steam. The dimensions and properties of the membrane reactor are listed in Table 1. The mass and energy balance for the membrane reactor are:

$$\frac{dF_i}{dz} = r_i \rho_B - f_i \Delta P_i a_m \rho_B \quad (31)$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_B \quad (32)$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + a_m U_s (T_s - T) + \sum_{i=1}^{n_r} r_i (-\Delta H_i^{rx}) \rho_b \right) \quad (33)$$

$$\frac{dT_s}{dz} = \frac{a_m U_s (T_s - T)}{\sum_{i=1}^{n_c} F_{si} C_{pi}} \quad (34)$$

The boundary conditions for the membrane reactor are:

$$P|_{z=0} = P_0, F_i|_{z=0} = F_{i0}, T|_{z=0} = T_0, F_{si}|_{z=0} = F_{si0}, T_s|_{z=0} = T_{s0} \quad (35)$$

The overall heat transfer coefficient, U_s , between the gas flow on the reaction side and the sweep gas flow on the inside of the membrane tube was estimated in the same way as in Equation 28, where the heat transfer coefficient between the sweep gas and the membrane with support was obtained by the correlation [17]:

$$h_m = 3.66 \frac{k_G}{D_m} \quad (36)$$

3.2 Membrane module

The membrane module consists of a steel housing that contains zeolite membrane tubes. The sweep gas is fed co-currently in the module while the synthesis gas from the reactor is fed to the centre of each membrane tube. The module consists of 6 equally large sections in which the sweep gas is fresh for each section, while the retentate from each section is sent to the next section. The dimensions and properties of the membrane module are listed in Table 1. The mass balance with boundary conditions for the membrane modules are:

$$\frac{dF_i}{dz} = -f_i \Delta P_i a_m \rho_B \quad (37)$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_B \quad (38)$$

$$F_i|_{z=0} = F_{i0}, F_{si}|_{z=0} = F_{si0} \quad (39)$$

3.3 Membrane properties

The ZSM-5 membranes prepared by the zeolite group at LTU are shown in Figure 8. These membranes have the observed permeances at room temperature of 0.3, 1, 12 and $18 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for H_2 , CO_2 , CH_3OH and H_2O , respectively[18]. The separation

factor α methanol/ H_2 is about 30, and α methanol/ CO_2 about 9. In the present work, it was assumed that the same membrane performance would be obtained at reaction conditions as that experimentally observed at room temperature and atmospheric pressure. It was also assumed that the CO and N_2 permeances were identical to the H_2 permeance. These permeances were used in the mathematical model.

Figure 8. SEM images of (a) the surface and (b) the cross section of a ZSM-5 membrane.

3.4 Kinetic expression

Methanol formation occurs through two independent reactions, i.e. hydrogenation of carbon dioxide and the reverse water-gas shift reaction. Here, the kinetics for these reactions are described by a Langmuir-Hinselwood Hougen-Watson model [20] by the following equations with constants in Table 2:

$$r_{CH_3OH} = \frac{k_D p_{CO_2} p_{H_2} \left[1 - \frac{p_{H_2O} p_{CH_3OH}}{p_{H_2}^3 p_{CO_2} K_{eq}^1} \right]}{M^3} \quad (40)$$

$$r_{RWGS} = \frac{k_E p_{CO_2} \left[1 - \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2} K_{eq}^2} \right]}{M} \quad (41)$$

$$M = 1 + k_C \left(\frac{p_{H_2O}}{p_{H_2}} \right) + k_A \sqrt{p_{H_2}} + k_B p_{H_2O} \quad (42)$$

Table 2. Kinetic and equilibrium constants [20].

$k=A\exp(B/RT)$	A	B
$k_A [\text{bar}^{-1/2}]$	0.499	17 197
$k_B [\text{bar}^{-1}]$	6.62e-11	124 199
$k_C [-]$	3 453.38	-
$k_D [\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-2}]^*$	1.07	36 696
$k_E [\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-1}]^*$	1.22e10	-94 765
$K_{eq}=10^{(A/T-B)}$	A	B
$K_{eq}^1 [\text{bar}^{-2}]$	3066	10.592
$K_{eq}^2 [-]$	2073	2.029

*The rate constants k_D and k_E are multiplied with 0.7 in the model to reflect the activity of a used catalyst.

3.5 Numerical evaluation

To solve the ordinary differential equations above an implicit Runge-Kutta method was used. Permeation rates depend on the partial pressures, and the composition of the feed to reactor depends on the recycled flow. An iterative method was thus used to determine these variables and MATLAB R2008b (MathWorks, Inc.) was used for numerical solution.

4. Results and discussion

Based on the experimental data for membrane performance and literature data for catalyst performance, the processes described in Figure 7 were evaluated, for a production of 70 000 ton methanol per year using a stoichiometric feed with 2% inert (N₂) and a feed pressure of 80 bar. A steady-state model validation against published data on a traditional reactor process (Lurgi low-pressure process) showed that the model prediction was satisfactory [15].

Table 3 shows results from simulations of the modeled processes. The total flow to the condensers is about 1.4 and 1.1 times higher for the MMP and MRP compared to the TRP. A lower total flow to the condensers is an advantage for the TRP due to the lower cost in cooling water. In principle, the sweep gas flow rate can be reduced further to minimize the flow to the condensers. However, for an effective membrane process, the sweep gas flowrate must be sufficiently high, to maintain sufficient driving force for transport through the membrane. For more selective membranes, the flow to the condensers would be reduced further.

Table 3. Comparative data for the different processes.

Specification	TRP	MRP	MMP
Flow to condenser [kmol/h]	3810	4200	5230
Catalyst mass [ton]	11.3	5.9	5.9
Hydrogen loss [kmol/h]	38.0	21.5	178.4
Pressure drop [%]	17.3	1.3	1.0
Recycle ratio [-]	3.8	0	0
Inert concentration [%]	21-23	2-17	2-8
Reactor tubes	1460	810	3020
Membrane tubes	0	810	3180
Length of membrane tubes [m]	0	16	4
CO _x -conversion per pass [%]	26	97	81
CO _x -conversion overall [%]	98	97	81

The membrane processes require 1.9 times less catalyst mass than the TRP due to the selective removal of products, which increases the reaction rate, and due to that no recirculation, which would lead to accumulation of inert, is applied. The hydrogen loss is highest in the MMP due to that some reactants leave through the membrane, which also impede the membrane processes to reach 100% CO_x-conversion, and the lower CO_x-conversion. However, the reactants will leave with the purge and energy could be

recovered in a boiler. Obviously, with a more selective ZSM-5 membrane, the hydrogen loss would be reduced and the maximum CO_x -conversion would increase for the MMP.

The pressure drop is quite high in the TRP due to the high flow rate in this reactor, which is caused by the recirculation of synthesis gas, while the pressure drop is almost insignificant in the membrane processes. In addition, a compressor is needed in the TRP to recompress the recycled gas, which is not needed in the membrane processes (MMP and MRP) due to the one pass design.

Figure 3a shows the temperature along the reactor length for the three processes. The temperature reaches the catalyst sintering temperature after about one meter in the TRP and levels out at the cooling water temperature (533 K) in the last part of this reactor. In the MRP and the MMP, the reaction rate is higher due to a more concentrated feed, the different cooling water temperatures and the removal of products, which results in more uneven temperature profiles. Due to the high reaction rate in the membrane processes, it was necessary to reduce the tube diameter from 38 (as in the Lurgi process) to 25 mm and to dilute the catalyst 35 % in the first 4 meters of the reactors to limit the maximum catalyst temperature below the sintering temperature. For the sake of simplicity, this reactor tube diameter and catalyst dilution were used in all cases. It was necessary to reduce the cooling water temperature 20 K to 513 K in the MRP to reduce the maximum catalyst temperature below the sintering temperature. In the MMP the cooling water temperature was reduced with 20K to 513K in the first two reactors (to reduce the maximum catalyst temperature and keep it below the sintering temperature), and then increased with 10K and 20K for the two remaining reactors in order to compensate for the decrease in the reaction rate. The temperature in the MRP reaches its maximum after about one meter and is then quickly approaching the cooling water temperature, while in the MMP the the maximum temeratures varies more due to the different conditions in each reactor.

Fig 3. Temperature profiles (a) and methanol concentration profiles (b) for the three processes

Figure 3b shows the methanol concentration along the reactor length of the three processes. The highest methanol concentration is observed for the MMP, which is explained by the more concentrated feed with less inert compared to the TRP and that methanol is not continuously removed as for the MRP. The MMP could be optimized by a more suitable distribution of membrane area in the four membrane modules (larger area in the first module), which may allow complete removal of methanol between each reactor in the MMP. The MMP could also be optimized with respect to the reactor length and since a large part of the catalyst mass operates close to equilibrium in the last two reactors. However, for the sake of simplicity, the feed temperature was set to 513 K for all reactors and the membrane area in each module was set to 1/4 of the total membrane area, which is not optimal for the MMP.

As illustrated by Figure 4, it is possible to reach about 97%, 81% and 26% CO_x -conversion per pass, for a MRP, MMP and TRP, respectively. However, the overall CO_x -conversion is equal to the one pass conversion for the membrane processes but for the TRP it is as high as 98%. The high overall CO_x -conversion is due to the recycle of the synthesis gas. Consequently, one pass operation is possible for the membrane processes if the CO_x -conversion for the membrane processes could be as high as for the TRP. Due to CO_x and H_2 loss through the membranes, it is not possible to reach 100% CO_x -conversion using the membrane processes. However, with a more selective ZSM-5 membrane, higher conversion could be achieved using the membrane processes.

Fig 4. CO_x-conversion for the three processes.

5. Conclusions

Provided that the same performance as observed at room temperature and atmospheric pressure is obtained at reaction conditions, the performance of our current ZSM-5 membranes seems sufficient in order to improve the methanol synthesis process. This work shows that the MRP is the best alternative with the highest conversion per pass enabling one pass operation for a stoichiometric feed in commencing biorefineries, and even more selective membranes would of course improve the membrane processes (MRP and MMP) even further. A membrane module configuration (MMP) is better from a practical point of view since catalyst and membrane is separated and by adding more membrane units, the performance of the MMP will approach the MRP. Also, a MRP would have less degrees of freedoms compared to a MMP. However, a similar system to the MMP could be designed by replacing each membrane module by a reactor effluent heat exchanger, a cooler and a condenser. A disadvantage with the latter process would be a higher complexity of the processes and higher flows through the heat exchangers, coolers and condensers. Membrane processes would be more preferable in systems that not only are limited by thermodynamic equilibrium, but also have selectivity issues, such as in the synthesis of higher alcohols from synthesis gas.

6. References

- [1] G. Barbieri, G. Marigliano, G. Golemme, E. Drioli, *Simulation of CO₂ hydrogenation with CH₃OH removal in a zeolite membrane reactor*, Chem. Eng. J., 85 (2002) 53-59.
- [2] F. Gallucci, L. Paturzo, A. Basile, *An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor*, Chem. Eng. Proc., 43 (2004) 1029-1036.
- [3] H. Karlsson, *Fibre Guide*, AB Lorentzen & Wettre, Kista (2006) p. 22
- [4] P. Söderholm, R. Lundmark, *The development of forest-based biorefineries: implications for market behavior and policy*, Forest Products Journal, 52 (2009) 6-16
- [5] M. V. Twigg, *Catalyst handbook*, 2nd edition, London (1996)
- [6] I. Wender, *Reactions of synthesis gas*, Fuel Processing Technology, vol. 48, pp. 189-297, 1996.
- [7] K. Klier and H. P. a. P. B. W. D.D. Eley, *Methanol Synthesis*, Advances in Catalysis, vol. Volume 31: Academic Press, 1982, pp. 243-313.
- [8] P. Villa, *Synthesis of alcohols from carbon oxides and hydrogen. 1. Kinetics of the low-pressure methanol synthesis*, Industrial & engineering chemistry process design and development, vol. 24, pp. 12, 1985.
- [9] G. C. Chinchin, P. J. Denny, D. G. Parker, M. S. Spencer, and D. A. Whan, *Mechanism of methanol synthesis from CO₂/CO/H₂ mixtures over copper/zinc oxide/alumina catalysts: use of ¹⁴C-labelled reactants*, Applied Catalysis, vol. 30, pp. 333-338, 1987.
- [10] G. C. Chinchin and M. S. Spencer, *Sensitive and insensitive reactions on copper catalysts: the water-gas shift reaction and methanol synthesis from carbon dioxide*, Catalysis Today, vol. 10, pp. 293-301, 1991.
- [11] G. H. Graaf, E. J. Stamhuis, and A. A. C. M. Beenackers, *Kinetics of low-pressure methanol synthesis*, Chemical Engineering Science, vol. 43, pp. 3185-3195, 1988.
- [12] K. M. V. Bussche and G. F. Froment, *A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al₂O₃ Catalyst*, Journal of Catalysis, vol. 161, pp. 1-10, 1996.
- [13] G. Rayner-Canham, T. Overton, *Descriptive Inorganic Chemistry*, W. H. Freeman & co, New York, 3rd edition, (2002) 251, 306-308
- [14] C. N. Satterfield, *Heterogeneous catalysis in industrial practice*, McGraw- Hill Inc., New York, 2nd edition, (1996) 226-252
- [15] F. Harting, F.J. Keil, *Large-scale spherical fixed bed reactors: modeling and optimization*, J. Ind. Eng. Chem. Res., 32 (1993) 424-437.

- [16] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, 1997.
- [17] F. P. Incropera, D. P. DeWitt, *Fundamentals of heat and mass transfer*, Wiley, New York, 2007.
- [18] Linda Sandström, Jonas Lindmark, Jonas Hedlund, *Separation of Methanol and Ethanol from Synthesis gas using MFI Membranes*, Manuscript to be submitted to Journal of Membrane Science
- [19] M.R. Rahimpour, A. Khosravanipour Mostafazadeh, M.M. Barmaki, *Application of hydrogen-permselective Pd-based membrane in an industrial single-type methanol reactor in the presence of catalyst deactivation*, Fuel Proc. Technol.. 89 (2008) 1396-1408.
- [20] K.M. Vanden Bussche, G. F. Froment, *A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst*, J. Catal.. 161 (2006) 1-10.

PAPER 1

Membrane processes for effective methanol synthesis in the forest based biorefinery

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Keywords: methanol synthesis, membrane reactor, membrane module, biorefinery, ZSM-5

Introduction

Black liquor is an internal biomass stream in pulp mills, which contains dissolved lignin and cooking chemicals. The only demonstration plant for pressurised black liquor gasification is operated at a large mill in Piteå, Sweden. If as much as 25% of the black liquor produced in a large pulp mill is gasified, about 70 000 ton of methanol can be produced per year. However, due to the complexity of the processes and in order to arrive at favourable economy, the production capacity in new plants for production of methanol from fossil fuels exceeds 1 000 000 ton of methanol per year. The production capacity of bio-fuels in a forest based biorefinery is thus less than 7% of the capacity of plants utilizing fossil fuels, which calls for development of more cost effective processes such as membrane processes.

It has been shown earlier [1, 2] that the use of membrane reactors could increase the productivity of a conventional methanol synthesis process by increasing the one-pass conversion of a hydrogen rich synthesis gas. However, there are a number of possible designs and feed gas compositions for this process and these have not been evaluated and compared as will be done in the present work. Furthermore, previous works mostly consider hypothetical membranes, while the present work is based on permeation data for a real ZSM-5 membrane.

Fig 1. (a) Methanol synthesis process with a traditional reactor (b) Membrane module process for methanol synthesis (c) Membrane reactor process for methanol synthesis.

Experimental

ZSM-5 membranes were prepared as described earlier [3]. The permeation performance of the membranes was evaluated for a feed of 40 kPa H_2 , 5.8 kPa CH_3OH , 10 kPa CO_2 , 0.6 kPa H_2O and 45 kPa He. Except for the helium balance and the absence of CO, the composition of this feed mimics the composition of a methanol reactor effluent. High pressure and high temperature tests of the membranes are commencing.

Mathematical modelling

Flowsheets of the evaluated systems are presented in Figure 1. The traditional reactor process (TRP), Figure 1(a), consists of a water-cooled tubular reactor in which the feed-effluent heat exchanger preheats the recycled synthesis gas to the reactor inlet. Crude methanol is condensed from the reactor effluent while unreacted synthesis gas is recycled and reheated and a fraction of the gas is purged. The membrane module process (MMP) evaluated in the present work, Figure 1(b), consists of four water-cooled tubular reactors placed in series with membrane modules after each reactor. The membrane modules consist of several membrane tubes that separate methanol and water from the synthesis gas at reaction temperature. Methanol is condensed from the membrane permeate streams and the retentate from the last membrane module is purged. Synthesis gas from the condenser is used as sweep gas in the membrane modules. In the membrane reactor process (MRP), Figure 1(c), a tubular membrane is surrounded with catalyst, which is in turn surrounded by cooling water [4]. In this configuration, permeate from the membrane is sent to the condenser and the synthesis gas from the condenser is again used as sweep gas. Unlike the traditional process (TRP), the membrane processes (MMP and MRP) are thus one pass designs without recirculation of synthesis gas.

The tubular reactors were modelled using a one-dimensional pseudo-homogeneous model based on a Langmuir-Hinshelwood mechanism [5]. Steady state conditions, ideal gas and plug flow were assumed. All processes were designed for a production of 70 000 ton methanol/year. The results discussed in this abstract are for a stoichiometric feed with 2% inert and a hydrogen rich feed will be considered as well in the full manuscript. The feed pressure was 80 bar in both cases. The inner diameter of the catalyst tubes were 25 mm and the inner diameter of the membrane tubes were 10 mm. A total membrane area of 400 m² was applied in the membrane processes and the pressure on the permeate side was set to 70 bar.

Results and discussion

The permeances at room temperature for the ZSM-5 membranes were 0.3, 1, 12 and 18·10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ for H₂, CO₂, CH₃OH and H₂O, respectively, which resulted in a separation factor α methanol/H₂ of about 30. The methanol permeance is five times higher than for previously reported membranes [6, 7]. Based on the experimental data for membrane performance and literature data for catalyst performance, the processes described in Figure 1 were evaluated using mathematical modelling and the results are illustrated in Figure 2. This Figure illustrates that it is possible to reach more than 96%, 89% and 30% CO_x conversion per pass for a MRP, MMP and TRP, respectively. Consequently, one pass operation is possible for the membrane processes.

Table 1 shows data from the modelled processes. The total flow to the condensers are about 1.6 times larger for the membrane processes (MMP and MRP) compared to the TRP, which is due to the sweep gas used in the membrane processes. In principle, the sweep gas flowrate can be set to any value. However, for an effective membrane process, the sweep gas flowrate must be sufficiently high.

Table 1. Comparative data for the different processes

Specification	TRP	MMP	MRP
Flow to condensor	3300	5200	5200
Catalyst mass	23.8	4.9	4.9
Hydrogen loss	32	93	28
Pressure drop	6.6	0.4	0.1
Recycle ratio	3.4	0	0

The membrane processes (MMP and MRP) require less catalyst mass than the TRP due to the selective removal of products, that increase reaction rate, and due to that no re-circulation that would lead to accumulation of inert, is applied in the former processes.

The hydrogen loss is lowest in the MRP due to its higher conversion compared to the MMP and lack of purge of the recycle gas with respect to the TRP.

Fig 2. CO_x-conversion profiles for the different processes

The pressure drop is quite high in the TRP due to the high flowrate in this reactor, which is caused by the recirculation of synthesis gas, while the pressure drop is insignificant in the membrane processes. In addition, a compressor is needed in the TRP to recompress the recycled gas, a unit operation that is not needed in the membrane processes (MMP and MRP) due to the one pass design.

This work shows that the MRP is the best alternative with the highest conversion per pass enabling one pass operation for a stoichiometric feed. However, from a practical point of view, a MMP is preferable, since the membrane and the reactor are not integrated and membrane and catalyst can be replaced separately, which is an advantage. By adding more membrane units, the performance of the MMP will approach the MRP.

Conclusions

Provided that the same performance as observed at room temperature and atmospheric pressure is obtained at reaction conditions, the performance of our current ZSM-5 membranes seems sufficient in order to improve the methanol synthesis process significantly. A ZSM-5

membrane reactor configuration (MMP or MRP) can enable one pass operation in methanol synthesis in commencing biorefineries. A membrane module configuration (MMP) is better from a practical point of view since catalyst and membrane is separated.

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References

- [1] G. Barbieri, G. Marigliano, G. Golemme, E. Drioli, *Simulation of CO₂ hydrogenation with CH₃OH removal in a zeolite membrane reactor*, Chem. Eng. J.. 85 (2002) 53-59.
- [2] F. Gallucci, L. Paturzo, A. Basile, *An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor*, Chem. Eng. Proc.. 43 (2004) 1029-1036.
- [3] S.A.S. Rezai, Lindmark J, Andersson C, et al., *Water/hydrogen/hexane multicomponent selectivity of thin MFI membranes with different Si/Al ratios*, Microporous Mesoporous Mater. 108 (2008) 136-142.
- [4] M.R. Rahimpour, A. Khosravanipour Mostafazadeh, M.M. Barmaki, *Application of hydrogen-permselective Pd-based membrane in an industrial single-type methanol reactor in the presence of catalyst deactivation*, Fuel Proc. Technol.. 89 (2008) 1396-1408.
- [5] K. M. Vanden Bussche, G. F. Froment, *A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst*, J. Catal.. 161 (2006) 1-10.
- [6] M.D. Jia, B. Chen, R. D. Noble, and J. L. Falconer, *Ceramic-zeolite composite membranes and their application for separation of vapor/gas mixtures*, J. Memb. Sci. 90 (1994) 1-10.
- [7] K. Sato, K. Sugimoto, Y. Sekine, M. Takada, M. Matsukata, and T. Nakane, *Application of FAU-type zeolite membranes to vapor/gas separation under high pressure and high temperature up to 5 MPa and 180°C*, Micro. Meso. Mat.. 101 (2007) 312-318.

PAPER 2

Membrane Processes for Effective Methanol Synthesis in the Forest Based Biorefinery

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Abstract

ZSM-5 membranes were prepared and their performance for methanol separations from synthesis gas were evaluated. The experimentally observed permeances at room temperature for the ZSM-5 membranes were 0.3, 1, 12 and $18 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for H_2 , CO_2 , CH_3OH and H_2O , respectively, which resulted in a separation factor α methanol/ H_2 of about 30. For a stoichiometric feed, the one-pass CO_x -conversion for a traditional methanol process is about 26 % per pass, which requires a recirculation loop with the associated disadvantages. By assuming that the same membrane performance could be obtained at industrial conditions, it was shown by mathematical modeling that a ZSM-5 membrane reactor could potentially reach 97% CO_x -conversion per pass, while a ZSM-5 membrane module process could potentially reach 81% conversion per pass for a stoichiometric feed. As a result of the high conversion per pass for the membrane processes, one-pass design with the associated advantages is possible for these processes. A membrane module based system is preferable over a membrane reactor of practical reasons. However, similar performance to the membrane processes can of course be achieved with a one pass process comprised of a series of methanol reactors, reactor effluent heat exchangers, coolers and condensers.

Keywords: methanol synthesis, membrane reactor, membrane module, biorefinery, ZSM-5

1. Introduction

Black liquor is an internal biomass stream in pulp mills, which contains dissolved lignin and cooking chemicals. The only demonstration plant for pressurised black liquor gasification is operated at a large mill in Piteå, Sweden. It is unlikely that the recovery boiler in existing plants can be replaced by gasification plants in the first step, since a recovery boiler represents a very large investment. However, the recovery boiler is often the bottleneck in a pulp plant and if as much as 25% of the black liquor produced in a large pulp mill is gasified in order to increase the pulp production capacity, about 70 000 ton of methanol can be produced per year. Due to the complexity of the processes and in order to arrive at favourable economy, the production capacity in new plants for production of methanol from fossil fuels exceeds 1 000 000 ton of methanol per year. The production capacity of bio-fuels in the example of a forest based biorefinery described above is thus less than 7% of the capacity of plants utilizing fossil fuels, which calls for development of more cost effective processes such as membrane processes.

It has been shown earlier [1, 2] that the use of membrane reactors could increase the productivity of a conventional methanol synthesis process by increasing the one-pass conversion of a hydrogen rich synthesis gas. However, there are a number of possible designs for this process and these have not been evaluated and compared as will be done in the present work. Also, the advantages of membrane processes are greatest for stoichiometric feeds rather than for hydrogen rich synthesis gas. Furthermore, previous works mostly consider hypothetical membranes, while the present work is based on permeation data for a real ZSM-5 membrane.

2. Experimental

Porous graded α -alumina discs (Inocermic GmbH, Germany) were used as membrane supports. The supports were masked and seeded as described previously [3] and were subsequently hydrothermally treated in a hydrolyzed synthesis solution at 100°C for 27 hours, under atmospheric pressure and reflux. The molar composition of the synthesis mixture was 3 TPAOH: 0.25 Al_2O_3 : Na_2O : 25 SiO_2 : 1600 H_2O : 100 EtOH. After synthesis, the membranes were rinsed in a 0.1 M NH_3 solution for 24 hours, and calcined at 500°C for 6 hours. The heating and cooling rates for calcination were 0.2°C/min and 0.3°C/min, respectively.

A Wicke-Kallenbach setup was used for the separation experiments. The membranes were mounted in a stainless steel cell with graphite gaskets. In order to remove adsorbed species, the membranes were heated overnight at 300°C in a flow of pure helium. The separation experiments were performed at 25°C. Three mass flow controllers and two saturators in thermostat baths were used to achieve a feed gas composition of 5.8 kPa methanol, 40 kPa H_2 , 10 kPa CO_2 and 0.6 kPa H_2O , with helium balance to atmospheric pressure. Except for the absence of CO and the helium balance, this feed mixture is similar in composition to a methanol reactor effluent. The feed flow rate was 1000 ml/min and the sweep gas (helium) flow rate was 150 ml/min. Quantitative analysis of the gas compositions was performed online using a Varian 3800 GC equipped with a thermal conductivity detector.

3. Process and model description

The mathematical model for simulating the processes considered in the present work was developed using the following assumptions: one dimensional plug flow in the reactors and membrane modules, ideal gas, no radial diffusion in the catalyst pellets, no axial dispersion of heat along the reactors. In the overall systems, the energy balances were neglected. In all reactors, the catalyst was diluted (35 %) in the first four meters of the reactors compared to a conventional reactor due to the large heat development associated with a stoichiometric feed. Also, the activity of the catalyst was assumed to be 70% of that of a fresh catalyst. The tube diameter is 38 mm in the Lurgi process [4]. A smaller diameter was used here for all three processes for better temperature control.

The traditional reactor process (TRP), represented here by the Lurgi low-pressure process [4], see Figure 1a, consists of a water-cooled tubular reactor in which the feed-effluent heat exchanger preheats the recycled synthesis gas to the reactor inlet. Crude methanol is condensed from the reactor effluent while unreacted synthesis gas is recycled using a compressor. A recycle ratio of 3.8 is used here (for a stoichiometric feed). A fraction (2 %) of the recycled gas is purged.

Fig 1. Methanol synthesis using a traditional reactor process (a), a membrane reactor process (b) and a membrane module process (c).

The traditional reactor consists of steel tubes, which are filled with catalyst pellets. The tubes are cooled with boiling water generating medium pressure steam. The dimensions and properties of the reactor and catalyst are listed in Table 1.

The mass and energy balance and the Ergun equation for the water cooled tubular reactor are:

$$\frac{dF_i}{dz} = r_i \rho_b \quad (1)$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + \sum_{i=1}^{n_r} r_i (-\Delta H_i^{rx}) \rho_b \right) \quad (2)$$

$$\frac{dP}{dz} = \frac{G_0^2}{\rho_G D_p} \frac{(1-\phi)}{\phi^3} \left(\frac{150}{Re} + 1.75 \right) \cdot 10^{-5} \quad (3)$$

The boundary conditions for the water cooled tubular reactor are:

$$P|_{z=0} = P_0, F_i|_{z=0} = F_{i0}, T|_{z=0} = T_0 \quad (4)$$

The overall heat transfer coefficient, U , between the circulating boiling water on the shell side and the gas flow on the reaction side was estimated from:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{(D_o - D_i)}{(D_o + D_i)} \frac{D_i}{k_s} + \frac{D_i}{D_o} \frac{1}{h_o} \quad (5)$$

where h_i is the heat transfer coefficient between the packed bed and the tubular wall of the reactor and h_o is the heat transfer coefficient between the tubular wall on the outer side and the cooling water, which is obtained by the correlations [5, 6]:

$$h_i = \frac{2.06 \rho_G V_0}{\phi C_{pG}} \left(\frac{V_0 D_P \rho_G}{\mu_G} \right)^{-0.575} \left(\frac{C_{pG} \mu_G}{k_G} \right)^{-2/3} \quad (6)$$

$$h_o = \frac{0.020 k_w}{D_o} \left(\frac{V_T D_H}{\mu_w} \right)^{0.8} \left(\frac{C_{pw} \mu_G}{k_w} \right)^{1/3} \left(\frac{D_T}{D_o} \right)^{0.53} \quad (7)$$

Table 1. Catalyst, feed, reactor and membrane specifications.

Parameter	Value	Parameter	Value
<i>Catalyst</i>		<i>Reactor</i>	
Catalyst density	1775 kg/m ³	Tot. reactor length	16 m
Catalyst pellet diameter	0.0042 m	Reactor tube I.D.	0.0254 m
Void fraction of bed	0.4	<i>Membrane</i>	
		Tot. memb. area	450 m ²
		Memb. tube O.D.	0.01 m
<i>Feed</i>		Membrane module length	4 m
Stoichiometric number of feed	2	<i>Sweep & Cooling</i>	
CO/CO ₂ ratio in feed	2.75	Sweep gas per MRP tube	1.200 mol/s
Concentration of inert in feed	2 %	Sweep gas per MMP tube	0.450 mol/s
Inlet temperature of feed	513 K	Sweep gas pressure	70 bar
Inlet pressure of feed	80 bar	C.W. temp. TRP	533 K
Fresh feed to each TRP tube	0.170 mol/s	C.W. temp. MRP	513 K
Feed to each MRP tube	0.270 mol/s	C.W. temp. MMP	513, 523, 533K
Feed to each MMP tube	0.390 mol/s		

In the membrane reactor process (MRP) considered here, see Figure 1b, the synthesis gas is not recycled as in the TRP. The synthesis gas is fed to the reactor and permeate from the membrane is sent to the condenser and the synthesis gas from the condenser is used as sweep gas. The retentate from the reactor is purged. The membrane reactor consists of steel tubes, which are filled with catalyst. A zeolite membrane supported on the outer side of an alumina tube is placed in the centre of each steel tube. The reactor is cooled with boiling water on the outer side of the steel tubes generating medium pressure steam. The dimensions and properties of the membrane reactor are listed in Table 1.

The mass and energy balance for the membrane reactor are:

$$\frac{dF_i}{dz} = r_i \rho_B - f_i \Delta P_i a_m \rho_B \quad (8)$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_B \quad (9)$$

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{n_c} F_i C_{pi}} \left(aU(T_a - T) + a_m U_s (T_s - T) + \sum_{i=1}^{n_r} r_i (-\Delta H_i^{rx}) \rho_b \right) \quad (10)$$

$$\frac{dT_s}{dz} = \frac{a_m U_s (T_s - T)}{\sum_{i=1}^{n_c} F_{si} C_{pi}} \quad (11)$$

The boundary conditions for the membrane reactor are:

$$P|_{z=0} = P_0, F_i|_{z=0} = F_{i0}, T|_{z=0} = T_0, F_{si}|_{z=0} = F_{si0}, T_s|_{z=0} = T_{s0} \quad (12)$$

The overall heat transfer coefficient, U_s , between the gas flow on the reaction side and the sweep gas flow on the inside of the membrane tube was estimated in the same way as in Equation 5, where the heat transfer coefficient between the sweep gas and the membrane with support was obtained by the correlation [6]:

$$h_m = 3.66 \frac{k_G}{D_m} \quad (13)$$

The membrane module process (MMP) evaluated in the present work, see Figure 1c, consists of four 4 meter long water-cooled tubular reactors placed in series with membrane modules after each reactor. In each reactor the cooling water temperature is set independently. The membrane modules consist of several membrane tubes that separate methanol and water from the synthesis gas at reaction temperature. Methanol is condensed from the membrane permeate streams and the retentate from the last membrane module is purged. Synthesis gas from the condenser is used as sweep gas in the membrane modules. The membrane module consists of a steel housing that contains zeolite membrane tubes. The sweep gas is fed co-currently in the module while the synthesis gas from the reactor is fed to the centre of each membrane tube. The module tubes consist of 6 equally large sections in which the sweep gas is fresh for each section, while the retentate from each section is sent to the next section. The permeate from each module is sent to the condenser. The dimensions and properties of the membrane module are listed in Table 1.

The mass balance with boundary conditions for the membrane modules are:

$$\frac{dF_i}{dz} = -f_i \Delta P_i a_m \rho_B \quad (14)$$

$$\frac{dF_{si}}{dz} = f_i \Delta P_i a_m \rho_B \quad (15)$$

$$F_i \Big|_{z=0} = F_{i0}, \quad F_{si} \Big|_{z=0} = F_{si0} \quad (16)$$

Methanol formation occurs through two independent reactions, i.e. hydrogenation of carbon dioxide and the reverse water-gas shift reaction. Here, the kinetics for these reactions are described by a Langmuir-Hinselwood Hougen-Watson model [7] by the following equations with constants in Table 2:

$$r_{CH_3OH} = \frac{k_D p_{CO_2} p_{H_2} \left[1 - \frac{p_{H_2O} p_{CH_3OH}}{p_{H_2}^3 p_{CO_2} K_{eq}^1} \right]}{M^3} \quad (17)$$

$$r_{RWGS} = \frac{k_E p_{CO_2} \left[1 - \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2} K_{eq}^2} \right]}{M} \quad (18)$$

$$M = 1 + k_C \left(\frac{p_{H_2O}}{p_{H_2}} \right) + k_A \sqrt{p_{H_2}} + k_B p_{H_2O} \quad (19)$$

Table 2. Kinetic and equilibrium constants [7].

$k=A\exp(B/RT)$	A	B
$k_A [\text{bar}^{-1/2}]$	0.499	17 197
$k_B [\text{bar}^{-1}]$	6.62e-11	124 199
$k_C [-]$	3 453.38	-
$k_D [\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-2}]^*$	1.07	36 696
$k_E [\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-1}]^*$	1.22e10	-94 765
$K_{eq}=10^{(A/T-B)}$	A	B
$K_{eq}^1 [\text{bar}^{-2}]$	3066	10.592
$K_{eq}^2 [-]$	2073	2.029

*The rate constants k_D and k_E are multiplied with 0.7 in the model to reflect the activity of a used catalyst.

To solve the ordinary differential equations above an implicit Runge-Knutta method was used. Permeation rates depend on the partial pressures, and the composition of the feed to reactor depends on the recycled flow. An iterative method was thus used to determine these variables and MATLAB R2008b (MathWorks, Inc.) was used for numerical solution.

4. Results and discussion

The prepared ZSM-5 membranes, shown in Figure 2, are comprised of well intergrown crystals and the film thickness is about 500 nm.

Fig 2. SEM images of a) the surface and b) the cross section of a ZSM-5 membrane.

The observed permeances for the ZSM-5 membranes in mixture separation experiments at room temperature were 0.3, 1, 12 and $18 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for H_2 , CO_2 , CH_3OH and H_2O , respectively. The methanol permeance is five times higher than for previously reported zeolite membranes [8, 9]. The resulting separation factor α methanol/ H_2 was about 30, and α methanol/ CO_2 was about 9. In the present work, it was assumed that the same membrane performance would be obtained at reaction conditions as that experimentally observed at room temperature and atmospheric pressure. It was also assumed that the CO and N_2 permeances were identical to the H_2 permeance.

Based on the experimental data for membrane performance and literature data for catalyst performance, the processes described in Figure 1 were evaluated, for a production of 70 000 ton methanol per year using a stoichiometric feed with 2% inert (N_2) and a feed pressure of 80 bar. A steady-state model validation against published data on a traditional reactor process (Lurgi low-pressure process) showed that the model prediction was satisfactory [4].

Table 3 shows results from simulations of the modeled processes. The total flow to the condensers is about 1.4 and 1.1 times higher for the MMP and MRP compared to the TRP. A lower total flow to the condensers is an advantage for the TRP due to the lower cost in cooling water. In principle, the sweep gas flow rate can be reduced further to minimize the flow to the condensers. However, for an effective membrane process, the sweep gas flowrate must be sufficiently high, to maintain sufficient driving force for transport through the membrane. For more selective membranes, the flow to the condensers would be reduced further.

Table 3. Comparative data for the different processes.

Specification	TRP	MRP	MMP
Flow to condenser [kmol/h]	3810	4200	5230
Catalyst mass [ton]	11.3	5.9	5.9
Hydrogen loss [kmol/h]	38.0	21.5	178.4
Pressure drop [%]	17.3	1.3	1.0
Recycle ratio [-]	3.8	0	0
Inert concentration [%]	21-23	2-17	2-8
Reactor tubes	1460	810	3020
Membrane tubes	0	810	3180
Length of membrane tubes [m]	0	16	4
CO _x -conversion per pass [%]	26	97	81
CO _x -conversion overall [%]	98	97	81

The membrane processes require 1.9 times less catalyst mass than the TRP due to the selective removal of products, which increases the reaction rate, and due to that no recirculation, which would lead to accumulation of inert, is applied. The hydrogen loss is highest in the MMP due to that some reactants leave through the membrane, which also impede the membrane processes to reach 100% CO_x-conversion, and the lower CO_x-conversion. However, the reactants will leave with the purge and energy could be recovered in a boiler. Obviously, with a more selective ZSM-5 membrane, the hydrogen loss would be reduced and the maximum CO_x-conversion would increase for the MMP.

The pressure drop is quite high in the TRP due to the high flow rate in this reactor, which is caused by the recirculation of synthesis gas, while the pressure drop is almost insignificant in the membrane processes. In addition, a compressor is needed in the TRP to recompress the recycled gas, which is not needed in the membrane processes (MMP and MRP) due to the one pass design.

Figure 3a shows the temperature along the reactor length for the three processes. The temperature reaches the catalyst sintering temperature after about one meter in the TRP and levels out at the cooling water temperature (533 K) in the last part of this reactor. In the MRP

and the MMP, the reaction rate is higher due to a more concentrated feed, the different cooling water temperatures and the removal of products, which results in more uneven temperature profiles. Due to the high reaction rate in the membrane processes, it was necessary to reduce the tube diameter from 38 (as in the Lurgi process) to 25 mm and to dilute the catalyst 35 % in the first 4 meters of the reactors to limit the maximum catalyst temperature below the sintering temperature. For the sake of simplicity, this reactor tube diameter and catalyst dilution were used in all cases. It was necessary to reduce the cooling water temperature 20 K to 513 K in the MRP to reduce the maximum catalyst temperature below the sintering temperature. In the MMP the cooling water temperature was reduced with 20K to 513K in the first two reactors (to reduce the maximum catalyst temperature and keep it below the sintering temperature), and then increased with 10K and 20K for the two remaining reactors in order to compensate for the decrease in the reaction rate. The temperature in the MRP reaches its maximum after about one meter and is then quickly approaching the cooling water temperature, while in the MMP the the maximum temperatures varies more due to the different conditions in each reactor..

Fig 3. Temperature profiles (a) and methanol concentration profiles (b) for the three processes

Figure 3b shows the methanol concentration along the reactor length of the three processes. The highest methanol concentration is observed for the MMP, which is explained by the more concentrated feed with less inert compared to the TRP and that methanol is not continuously removed as for the MRP. The MMP could be optimized by a more suitable distribution of membrane area in the four membrane modules (larger area in the first module), which may allow complete removal of methanol between each reactor in the MMP. The MMP could also be optimized with respect to the reactor length and since a large part of the catalyst mass operates close to equilibrium in the last two reactors. However, for the sake of simplicity, the feed temperature was set to 513 K for all reactors and the membrane area in each module was set to 1/4 of the total membrane area, which is not optimal for the MMP.

As illustrated by Figure 4, it is possible to reach about 97%, 81% and 26% CO_x -conversion per pass, for a MRP, MMP and TRP, respectively. However, the overall CO_x -conversion is equal the one pass conversion for the membrane processes but for the TRP it is as high as 98%. The high overall CO_x -conversion is due to the recycle of the synthesis gas. Consequently, one pass operation is possible for the membrane processes if the CO_x -conversion for the membrane processes could be as high as for the TRP. Due to CO_x and H_2 loss through the membranes, it is not possible to reach 100% CO_x -conversion using the membrane processes. However, with a more selective ZSM-5 membrane, higher conversion could be achieved using the membrane processes.

Fig 4. CO_x -conversion for the three processes.

5. Conclusions

Provided that the same performance as observed at room temperature and atmospheric pressure is obtained at reaction conditions, the performance of our current ZSM-5 membranes seems sufficient in order to improve the methanol synthesis process. This work shows that the MRP is the best alternative with the highest conversion per pass enabling one pass operation for a stoichiometric feed in commencing biorefineries, and even more selective membranes would of course improve the membrane processes (MRP and MMP) even further. A membrane module configuration (MMP) is better from a practical point of view since catalyst and membrane is separated and by adding more membrane units, the performance of the MMP will approach the MRP. Also, a MRP would have less degrees of freedoms compared to a MMP. However, a similar system to the MMP could be designed by replacing each membrane module by a reactor effluent heat exchanger, a cooler and a condenser. A disadvantage with the latter process would be a higher complexity of the processes and higher flows through the heat exchangers, coolers and condensers. Membrane processes would be more preferable in systems that not only are limited by thermodynamic equilibrium, but also have selectivity issues, such as in the synthesis of higher alcohols from synthesis gas.

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7. References

- [1] G. Barbieri, G. Marigliano, G. Golemme, E. Drioli, *Simulation of CO₂ hydrogenation with CH₃OH removal in a zeolite membrane reactor*, Chem. Eng. J.. 85 (2002) 53-59.
- [2] F. Gallucci, L. Paturzo, A. Basile, *An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor*, Chem. Eng. Proc.. 43 (2004) 1029-1036.
- [3] Hedlund, J.; Sterte, J.; Anthonis, M.; Bons, A. J.; Carstensen, B.; Corcoran, N.; Cox, D.; Deckman, H.; De Gijnst, W.; de Moor, P. P.; Lai, F.; McHenry, J.; Mortier, W.; Reinoso, J., *High-flux MFI membranes*, Micro. Meso. Mat.. 52 (2002) 179-189.
- [4] F. Harting, F.J. Keil, *Large-scale spherical fixed bed reactors: modeling and optimization*, J. Ind. Eng. Chem. Res.. 32 (1993) 424-437.
- [5] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, 1997.
- [6] F. P. Incropera, D. P. DeWitt, *Fundamentals of heat and mass transfer*, Wiley, New York, 2007.
- [7] K.M. Vanden Bussche, G. F. Froment, *A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst*, J. Catal.. 161 (2006) 1-10.
- [8] M.D. Jia, B. Chen, R. D. Noble, and J. L. Falconer, *Ceramic-zeolite composite membranes and their application for separation of vapor/gas mixtures*, J. Memb. Sci.. 90 (1994) 1-10.
- [9] K. Sato, K. Sugimoto, Y. Sekine, M. Takada, M. Matsukata, and T. Nakane, *Application of FAU-type zeolite membranes to vapor/gas separation under high pressure and high temperature up to 5 MPa and 180°C*, Micro. Meso. Mat.. 101 (2007) 312-318.