**MEMBRANE REACTORS FOR THE DIRECT
CONVERSION OF CO₂ TO DIMETHYL
CARBONATE**

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Membrane reactors for the direct conversion of CO₂ to dimethyl carbonate

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MEMBRANE REACTORS FOR THE DIRECT CONVERSION OF CO₂ TO DIMETHYL CARBONATE

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Summary

Due to the increasing oil prices the chemical industry searches for alternative feedstock for the production of chemicals. CO_2 is considered as an interesting alternative for environmental and economic reasons. However, due to the high thermodynamic stability of CO_2 it is rather difficult to convert it into valuable chemicals. For e.g. the direct conversion of CO_2 and methanol into dimethyl carbonate (DMC) this could be resolved by using membrane reactors. DMC is a frequently used chemical for the production of poly carbonates, as methylation agent, in the use as solvent for lithium ion batteries and potentially as fuel additive. The combination of a reactor and a membrane allows the instant removal of reaction products (e.g. H_2O) from the reaction mixture and as such enhances the conversion of CO_2 . Since the use of membrane reactors for this application is rather unexplored, the aim of this research is to investigate the potential of membrane reactors for the direct conversion of CO_2 into DMC.

Chapter 2 describes a model that compares the performance of a catalytic membrane reactor (CMR) in which locations of reaction and separation coincide, with an inert membrane reactor (IMR) in which locations of reaction and separation do not overlap. For the numerical simulations the Maxwell-Stefan theory is adopted to describe multi-component mass transport and include drift fluxes. The results show that it is essential to apply the Maxwell-Stefan theory as Fick's law does not adequately address the multi-component mass transfer characteristics. Further, the results indicate that the performance of both membrane reactor configurations can be divided in three different regimes, based on the value of the equilibrium constant (K_{eq}). At very low and intermediate K_{eq} , the CMR outperforms the IMR and particular benefits from a high membrane area/reactor volume ratio (A/V), a large residence time, a high water permeance and a sufficiently high mass transfer coefficient over the boundary layer. For high K_{eq} the performance of the IMR is superior to that of the CMR.

For the direct conversion of CO_2 into DMC, the previous chapter proposes the use of catalytic membrane reactors. To further enhance the conversion of the reactor, the water vapor permeability of the membrane should be improved. Therefore **Chapter 3** focuses on the development of highly water vapor permeable membranes, meanwhile retaining the reactant CO_2 . This chapter describes the development of sulfonated poly(ether ether ketone) (SPEEK)/chitosan membranes that are thermally stable up to $220\text{ }^\circ\text{C}$, which make them able to withstand to a certain extent the extreme conditions in membrane reactors. The results show that the addition of a chitosan layer on top of SPEEK enhances the water vapor permeation and simultaneously improves the $\text{H}_2\text{O}/\text{CO}_2$ selectivity, despite the fact that the membranes are thicker. It proves that adding two selective layers on top of each other, not by definition results in a diminishing performance.

In order for SPEEK to withstand the high temperatures in membrane reactors, literature proposes to improve the thermal stability of SPEEK by exchanging the mobile counter ion (usually H^+) of the sulfone moiety in SPEEK. **Chapter 4** investigates how the exchange of mono- (H^+ , Li^+ , Na^+ , K^+), di- (Ca^{2+}) and trivalent (Al^{3+}) counter ions affects the water vapor and CO_2 permeability. In general it can be concluded that replacing the H^+ cation in SPEEK for another cation results in an improved thermal stability up to $450\text{--}500\text{ }^\circ\text{C}$. Further, the results indicate that the water vapor sorption increases with an increasing cation hydration enthalpy, but the water vapor and the CO_2 permeability decrease with increasing cation hydration enthalpy. We hypothesize that the latter is caused by the formation of cation-water cluster that hinder the diffusion of water vapor and CO_2 and the cation-water and cation- CO_2 interactions, that result in a worse desorption and thus a decreasing water vapor and CO_2 permeability. Nevertheless, also other parameters that affect the permeation can play a role, e.g. cation-anion interactions and the formation of ionic crosslinks between the $-\text{SO}_3^-$ group of SPEEK and di- or trivalent charged cations.

Chapter 5 finally describes a techno-economic evaluation using water vapor selective catalytic membrane reactors for the direct conversion of

CO₂ and methanol into DMC. It provides valuable insight and a better understanding of the process limitations. The Aspen simulations show that even at an excess of methanol, the removal of water vapor is insufficient to stimulate the conversion and therefore only a maximum of 1.5 mol% DMC in the reactor effluent is obtained. To purify this to the required specifications, large size equipment and a substantial amount of energy (13.61 kWh/kg DMC) is required, which results in high investment and utility costs. Therefore future research on membrane reactors should focus on the selective removal of DMC (instead of water) to obtain higher DMC concentrations in the reactor effluent.

Samenvatting

Door de toenemende olieprijs zoekt de chemische industrie naar alternatieve grondstoffen voor de productie van chemicaliën. In dit kader is CO_2 een interessant alternatief vanwege economische en milieutechnische redenen. Door de hoge thermodynamische stabiliteit van CO_2 is het echter lastig om deze om te zetten in meer waardevolle chemicaliën. Voor bijvoorbeeld de directe omzetting van CO_2 en methanol naar dimethyl carbonaat (DMC), kunnen membraanreactoren in dergelijke gevallen een oplossing bieden. DMC wordt gebruikt voor de productie van polycarbonaten, voor methylatiereacties, oplosmiddel in lithium-ion batterijen of als potentieel brandstofadditief. Door een membraan en een reactor te combineren kunnen reactieproducten (bijv. H_2O) meteen worden verwijderd van het reactiemengsel en dit verhoogt de conversie. Omdat het gebruik van membraanreactoren voor deze applicatie nog vrij nieuw is, is het doel van dit onderzoek om de potentie van membraanreactoren voor de directe omzetting van CO_2 naar DMC te onderzoeken.

Hoofdstuk 2 beschrijft een model dat de prestaties van een katalytische membraanreactor (CMR), waarin de katalysator en het membraan volledig zijn geïntegreerd, vergelijkt met een inerte membraanreactor (IMR), waarin katalysator en membraan niet zijn geïntegreerd. Voor het modeleren is de Maxwell-Stefan theorie gebruikt, die in de beschrijving multi-componenten massa transport en drift fluxen meeneemt. De modeleerresultaten laten zien dat het toepassen van de Maxwell-Stefan theorie essentieel is, omdat de wet van Fick multi-componenten massa transport niet adequaat beschrijft. Gebaseerd op de evenwichtsconstante (K_{eq}), laten de resultaten verder zien dat de conversie in beide membraanreactoren in drie regimes onderverdeeld kan worden. Bij een lage en gemiddelde K_{eq} presteert de CMR beter dan de IMR en dit komt vooral tot uitdrukking bij hoge membraanoppervlak/reactorvolume ratio's, een lange verblijftijd, een hoge waterpermeabiliteit en een voldoende hoge membraangrenslaag massatransportcoëfficiënt. Daarentegen presteert bij een hoge K_{eq} de IMR beter dan de CMR.

Het vorige hoofdstuk laat zien dat voor de directe omzetting van CO₂ naar DMC een katalytische membraanreactor de voorkeur heeft en om de conversie te stimuleren de waterdamppermeabiliteit van het membraan zo hoog mogelijk moet zijn. Daarom ligt in **Hoofdstuk 3** de nadruk op de ontwikkeling van membranen met een hoge waterdamppermeabiliteit, die tegelijkertijd de reactant CO₂ kunnen tegenhouden. In dit hoofdstuk worden gesulfoneerde poly(ether ether ketone) (SPEEK)/chitosan membranen ontwikkeld die met een thermische stabiliteit tot 220 °C in redelijke mate de extreme condities in membraanreactoren kunnen weerstaan. De resultaten laten zien dat door het aanbrengen van een chitosanlaag bovenop een SPEEK membraan de waterdamppermeabiliteit en de H₂O/CO₂ selectiviteit toenemen, ondanks dat de membranen dikker zijn geworden. Dit geeft duidelijk aan dat het combineren van twee selectieve lagen bovenop elkaar niet direct hoeft te resulteren in slechtere membranen.

Om SPEEK te beschermen tegen de hoge temperatuur die heerst in membraanreactoren, stelt de literatuur voor om het counter ion dat tegenover de sulfongroep in SPEEK zit (normaal H⁺), te vervangen. **Hoofdstuk 4** onderzoekt hoe verschillende mono- (H⁺, Li⁺, Na⁺, K⁺), di- (Ca²⁺) en trivalente (Al³⁺) kationen in SPEEK de waterdamppermeabiliteit en CO₂ permeabiliteit kunnen beïnvloeden. Over het algemeen kan gezegd worden dat de thermische stabiliteit van SPEEK omhoog gaat (450-500 °C) als het H⁺ kation in SPEEK wordt vervangen. Daarnaast laten de resultaten ook zien dat de waterdampsorptie toeneemt met een toenemende kation hydratatie-enthalpie, maar daarentegen de waterdamppermeabiliteit en CO₂ permeabiliteit juist afnemen met een toenemende kation hydratatie-enthalpie. Het vermoeden bestaat dat dit laatste wordt veroorzaakt door enerzijds de vorming van kation-water clusters die de diffusie van water en CO₂ verhinderen en anderzijds door sterkere kation-water en kation-CO₂ interacties, waardoor beide componenten minder makkelijk desorberen, wat resulteert in lagere permeabiliteiten. Desondanks zijn er ook nog andere aspecten die een rol kunnen spelen, zoals de kation-anion interactie of ionische crosslinks die

gevormd kunnen worden tussen de $-\text{SO}_3^-$ groep van SPEEK en de di- of trivalent geladen kationen.

Hoofdstuk 5 beschrijft techno-economische evaluatie van waterdamp selectieve katalytische membraanreactoren voor de directe omzetting van CO_2 en methanol naar DMC. Het doel is om een duidelijk inzicht te krijgen in de mogelijkheden en de beperkingen van dit proces. De simulaties laten duidelijk zien dat zelfs bij een overmaat aan methanol, de verwijdering van waterdamp onvoldoende is om de conversie voldoende te stimuleren. Als resultaat bevat de productstroom uit de membraanreactor maximaal 1.5 mol% DMC. Om dit te zuiveren tot de gewenste specificaties is veel energie (13.61 kWh/kg DMC) en grote apparatuur nodig, wat resulteert in te hoge investeringskosten en hoge kosten voor nutsvoorzieningen. Om dit te voorkomen moet het onderzoek naar membraanreactoren zich richten op de ontwikkeling van DMC selectieve membranen, zodat een hogere DMC concentratie uit de reactor wordt verkregen.

Chapter 1

Introduction

Abstract

An increasing oil price forces the chemical industry to search for alternative feedstock for the production of chemicals. CO_2 is both from an environmental and economic perspective considered as an interesting candidate, but faces the problem that it is thermodynamically very stable and therefore difficult to convert into valuable products. An interesting synthetic route is the direct conversion of CO_2 and methanol to dimethyl carbonate (DMC), an equilibrium limited reaction. The challenge is to prevent equilibrium to establish and enhance the conversion by selectively removing products (H_2O) from the reaction mixture using e.g. membrane reactors. Little is known about the use of membrane reactors for this application and therefor the aim of this chapter is to investigate the potential of membrane reactors for the direct conversion of CO_2 and methanol to DMC.

1.1. CO₂ as feedstock

An increasing worldwide demand for oil and decreasing fossil fuel reserves causes the oil price to raise. In 2010 the price per barrel of oil was \$86 - \$110 and is expected to rise to \$140 per barrel in 2035 [1]. Due to this chemicals produced from oil also become increasingly expensive. To be less dependent on expensive oil, the chemical industry searches for alternative production routes that start from cheap raw feedstock. In this search CO₂ is considered as an economically and environmentally interesting alternative. Using CO₂ as feedstock not only decreases the demand for fossil fuels. It also reduces the anthropogenic CO₂ emission into the atmosphere, it is nontoxic and since it is considered as waste product it is a cheap feedstock. Currently, the CO₂ concentration in the atmosphere is ca. 380 ppm but was ca. 270 ppm before the industrial era [2]. It is not fully proven that we can all attribute this to human activities, however according to the International Energy Agency (IEA) CO₂ emission by human activity accounted in 2010 for 30.4 Gt [1]. This is equal to 4.6% of the earth's total "carbon flow", which further consist out of global fixation by terrestrial plants and microorganisms, exchange between the atmosphere and water basins and underground inorganication [2]. It strongly suggests that human activities influences the CO₂ concentration in the atmosphere. Due to the large distance from safe sequestration sites, the diluted concentration of CO₂ in the emitting gas and the small-medium CO₂ sources, Centi and Perathoner [3] stated that 5-10% of the emitted CO₂ can be used for the production of fuels and chemicals. Much more than the 0.11 Gt (0.4%) [2] that is currently used for the production of e.g. urea [2, 4], inorganic carbonates and pigments [2].

To re-use CO₂ and convert it into valuable products (carbon capture and conversion (CCC) [5]), CO₂ has to be captured. Different sources are available for CCC. However, not all CO₂ sources are commercially interesting. The commercial and transportation sectors are for instance unsuitable since the CO₂ production is individually, small and mobile [6]. Due to the lower costs to capture CO₂ and because CO₂ capture is technically more easy to implement, large stationary CO₂ sources are more interesting [7].

Main stationary CO₂ sources are [6, 7]:

- Fossil-fuel-based power generation
- Natural gas production and upgrading
- Cement and lime production
- Iron and steel industry
- Oil refineries

To capture the CO₂ there are different technologies available, e.g. solvent wet scrubbing using physical or chemical absorbents, solid dry scrubbing using physical adsorbents or chemical absorbents, cryogenic separation and membrane separation [7]. Each technology has its advantages and disadvantages, and it depends on the specific application which technology is favorable. For instance, in postcombustion (CO₂ capture after combustion) CO₂ partial pressure is lower than in precombustion (CO₂ capture before combustion). Other considerations are the amount of CO₂ that needs to be removed, the required purities of the CO₂ product stream, the presence of pollutants in the feed and the location of the capturing technology in the process [7]. A more detailed summary that discusses the different aspects that have to be considered is given by White et al. [7].

According to the earlier mentioned data there is about 1.5-3.0 Gt/y (5-10% of 30 Gt [1, 3]) of CO₂ worldwide available as feedstock of which only 0.11 Gt [2] is used. Still there are numerous potential reactions that can use CO₂ as feed, such as the dry reforming of methane to make syngas [5], the production of methanol from hydrogen [5] or the production of carbonates [4]. Figure 1.1 gives a few examples how CO₂ can be used as feedstock and a more elaborate overview is given by Sakakura et al. [4].

Figure 1.1: Few examples of organic syntheses starting from CO₂ [4].

1.2. Dimethyl carbonate production from CO₂

In the last decades the interest for the production of dimethyl carbonate (DMC) increased. Due to its low toxicity and fast biodegradability, DMC is a promising chemical in the search for the so called “Green Chemistry” chemicals. Major applications for DMC can be found in the production of polycarbonates, as methylation agent, in use as solvent for lithium ion batteries and as fuel additive [4, 8-12]. For the production of polycarbonate, DMC can be used to circumvent the use of the highly toxic phosgene. In this reaction phosgene reacts with A-biphenol, but instead of phosgene diphenylcarbonate (DPC) can be used, which is produced from DMC and phenol [9]. For the future the major application for DMC can be found as fuel additive due to DMCs high blending octane number, reduced CO and NO_x emission and high oxygen content [10, 12]. It is estimated that this will result in a worldwide demand of 1360 t/day of DMC, which is much more than the 170 t/day of DMC that was produced in 1997 (most recent production data) [9, 10].

The conventional method to produce DMC (pre 1980s) is via phosgene that reacts with methanol to form DMC ((CH₃O)₂CO) and hydrochloric acid [4, 9, 10, 12].

However, the high toxicity of phosgene, a colorless gas used as chemical weapon in WOI, and problems associated with the disposal of coproduced hydrochloric acid [4] led to the development of the Enichem process and the UBE process. In the Enichem process, industrialized in 1983, DMC is produced by reacting liquid methanol with oxygen and carbon monoxide [9, 12].

The more recently developed UBE process is a two-step reaction where in the first reaction nitrogen monoxide, methanol and oxygen are converted into methyl nitrite and in the second step this methyl nitrite reacts with carbon monoxide towards DMC and nitrogen monoxide [9, 12].

Although the Enichem process and the UBE process are two phosgene free routes, both processes need carbon mono oxide and oxygen, which increases the risk for explosions. As such alternative process routes are considered aiming to reduce the environmental impact and minimize the risks for human health [12]. Due to environmental and economic reasons the direct conversion of CO_2 into DMC is considered as an interesting alternative [4, 8, 9, 12]. In this reaction methanol reacts with CO_2 to form DMC and water.

The direct conversion of CO_2 into DMC is considered as an interesting alternative for these earlier mentioned processes. Not only because CO_2 is cheap and the use of CO_2 reduces its emission into the atmosphere, but also because it is non-flammable and a safe production route using less hazardous chemicals than e.g. carbon monoxide. However, the main

question using CO₂ as feedstock is how to convert it into valuable products. Table 1.1 shows the Gibbs free energy of different components [5]. It clearly shows that CO₂ is thermodynamically very stable in comparison to other components, restricting the spontaneous conversion ($\Delta G_r < 0$) into other (more valuable) chemicals.

Table 1.1: Gibbs free energy of different components [5].

Component	ΔG^θ [kJ/mol]
H ₂	0.0
N ₂	0.0
CH ₄	-50.7
H ₂ O	-228.4
CO	-137.2
CO ₂	-394.0
CH ₃ OH	-159.2
(CH ₃ O) ₂ CO	-463.2
C ₃ H ₈	-23.5
C ₁₀ H ₂₂	34.4

The equilibrium constant (K_{eq}) of the direct conversion of CO₂ to DMC at 298 K and 1 atm equals:

$$K_{eq} = \exp\left[\frac{-\Delta G_r^\theta}{RT}\right] = 2.54 \cdot 10^{-5} \quad (1.1)$$

Since the equilibrium constant is far below one, equilibrium is much more in favor of CO₂ and it is difficult to directly convert CO₂ and methanol into DMC. Based on the thermodynamic relations deduced by Cai et al. [13], the equilibrium constant could be plotted as function of temperature and pressure, as Figure 1.2 shows. According to this figure a decrease in temperature or an increase in the pressure, increases the equilibrium constant and as such shifts the equilibrium towards DMC. However, to induce the spontaneous conversion of CO₂ into DMC, unrealistically high pressures or extremely low temperatures are needed, which are not cost effective at all and technically infeasible.

Figure 1.2: Equilibrium constant (K_{eq}) of the direct conversion of CO₂ and methanol to DMC as function of the temperature and pressure deduced from the thermodynamic relations given by Cai et al [13].

Cai et al. [13] reasoned that chemical or physical measures are needed to shift the equilibrium towards the product (DMC) side, for example one or more reaction products need to be removed instantly from the reaction mixture. This prevents the equilibrium to establish and by that promotes the conversion of CO₂. To do so, the most obvious component to be selectively removed is water. Literature discusses different chemical and physical dehydrating technologies that Sakakura and Kohno divided into two types [14]:

- Non-recyclable agents
- Recyclable agents

Non-recyclable agents are, as the name suggests, difficult to recycle. Examples are orthoesters [15], dicyclohexyl carbodiimide (DCC) [14] and Mitsunobu's reagent [14]. Due to the difficulty to regenerate these dehydrating agents and also because of their high costs, recyclable agents are considered as more promising. Typical examples of recyclable agents are acetals [14, 16] and molecular sieves [17]. Sakakura and Kohono [14] proposed the use of acetals since it is until now the most successful dehydrating agent. In reaction with water, acetals form ketones and depending on the ketone formed determines the ease of acetal regeneration [14]. Although acetals show promising results, its main drawbacks are that at higher acetals concentrations the DMC yield is

suppressed [16] and also a regeneration step is always required to regain the acetals. This indicates that the use of acetals also has its limitations and other dehydrating agents or dehydrating technologies still need to be considered.

1.3. Membrane reactors

A dehydrating technology that is scarcely considered for the direct conversion of CO_2 into DMC are membrane reactors. Li and Zhong [18] proposed this technology for the direct conversion of CO_2 into DMC, in which a membrane is integrated in a reactor, however with little success. The advantage of membrane reactors in comparison to acetals, is that regeneration is not necessary. Further, due to the integration of a membrane and a reactor, membrane reactors require less space and less operating steps due to the integrated reaction and separation, which results in lower investment costs [19]. The challenge of membrane reactors is to fine-tune the operating conditions of the reaction with the separation ability of the membrane. Other important aspects to be considered are the membrane stability at reactor conditions, a sufficiently high permeability and selectivity of the membrane and the costs [20]. There are three major applications for membrane reactors (Figure 1.3) [20]:

- a. Conversion enhancement of equilibrium limited reactions by selective removal of products to circumvent equilibrium. Examples are esterification reactions [21-23] and dehydrogenation reactions [24-26].
- b. Coupling reactions by selective removal of products formed at the feed side of the membrane, to participate in a second reaction on the permeate side of the membrane. For example the dehydrogenation of cyclohexane (feed) and the hydrogenation of pentadiene (permeate) [25].
- c. Controlled addition of reactants to prevent poisoning of the catalyst or to have a better control (safety) over the reactor. An example is the partial oxidation of methane with oxygen [27].

Figure 1.3: Schematic representation of potential membrane reactor applications [20].

For the direct conversion of CO_2 into DMC membrane reactors are intended to prevent equilibrium to establish by selectively removing products of the reaction (e.g. H_2O) using a membrane, meanwhile retaining CO_2 and methanol. Until now only Li and Zhong [18] considered membrane reactor technology for the direct conversion of CO_2 and methanol into DMC. They investigated three different membranes in a membrane reactor and observed a slightly improved conversion and selectivity towards DMC compared to the use of a conversional catalytic reactor, which was a micro reactor connected to a GC. Due to this limited improvement of the conversion, the use of membrane reactors were not considered successful and therefore not further investigated for this application. However, starting from the research of Li and Zhong [18], there is much potential for improvement. For example it is possible to use more active catalytic materials [28], to operate the membrane reactor at higher pressures [17] or to use a more water vapor permeable and H_2O /reactant selective membrane. The maximum $\text{H}_2\text{O}/\text{CO}_2$ selectivity Zhong and Li [18] measured was 1.54, whereas according to literature much more selective membranes are available [29].

1.4. Membrane material selection

To use membrane reactors to stimulate the conversion of CO_2 and methanol into DMC, the selection of the membrane material is critical. As Zhong and Li [18] showed, a membrane with poor water vapor permeability and low $\text{H}_2\text{O}/\text{CO}_2$ selectivity can suppress the success of membrane reactors for the direct conversion of CO_2 into DMC. For this application the desired membrane material should possess a high water

vapor permeability and a high H_2O /reactant selectivity (e.g. $\text{H}_2\text{O}/\text{CO}_2$). A high water vapor permeability is required such that the produced water is instantly removed from the reaction and equilibrium cannot establish. A high membrane selectivity prevents the application of additional separation steps, saving investment costs.

For the selective removal of water vapor from the gaseous DMC reaction mixture, polymeric membranes are very well suited. In comparison to inorganic membranes, the permeability in polymeric membranes is not only driven by the size of the component, but also depends on the solubility of the component into the polymeric material. Due to the small kinetic diameter of water (2.65 Å) and high critical temperature (647 K), the diffusivity and solubility in polymeric membranes are relatively high compared to that of other components [30]. As a consequence the water vapor permeability and membrane selectivity are relatively high. In literature there is a wide range of promising polymeric membranes available for dehydration purposes, such as PEBAX 1074 [31, 32], Matrimid [33], poly(ethylene oxide) based block copolymers [30], poly(aryl ether sulfone) [34] or sulfonated poly(ether ether ketone) (SPEEK) [31]. From these materials Especially SPEEK is promising for the production of DMC due to its chemical, thermal and mechanical robustness, exceptional high water vapor permeability and low CO_2 permeability a promising candidate [31]. Figure 1.4 represents the molecular structure of SPEEK.

Figure 1.4: Molecular structure of sulfonated poly(ether ether ketone) (SPEEK).

To compare the potential of SPEEK with other membrane materials, Figure 1.5 reports the $\text{H}_2\text{O}/\text{N}_2$ selectivity versus the water vapor permeability of a series of membrane materials obtained from Sijbesma et al. [31]. According to Figure 1.5 SPEEK performs better than all other

materials, since it possess one of the highest water vapor permeabilities with a corresponding high $\text{H}_2\text{O}/\text{N}_2$ selectivity. Due to its large dehydration capacity and ability to retain CO_2 [31, 35], the hypothesis is that SPEEK has the potential to be used as membrane material in a membrane reactor for the direct conversion of CO_2 and methanol into DMC.

Figure 1.5: $\text{H}_2\text{O}/\text{N}_2$ selectivity as function of the water vapor permeability for various polymeric membrane materials from Sijbesma et al. [31].

1.5. Scope of this thesis

This thesis investigates the potential of membrane reactors for the direct conversion of CO_2 and methanol into DMC.

For the direct conversion of CO_2 and methanol into DMC, different membrane reactor configurations can be considered. **Chapter 2** compares the potential of a concept where catalyst and membrane are fully integrated (catalytic membrane reactor) and a non-integrated system (inert membrane reactor). It examines how the conversion in both configurations is affected by multi-component mass transfer behavior and how their performance can be optimized via different process and material parameters.

One conclusion from chapter 2 is that a high water vapor permeability can result in much higher conversions for strong equilibrium limited reactions, such as the direct conversion of CO_2 and methanol into DMC. Therefore

the focus in **Chapter 3** is on the development of highly water vapor permeable membranes, meanwhile retaining CO₂ and methanol. In order to do so SPEEK membranes with on top of that a layer of chitosan are developed. These membranes are known to retain methanol [36], but it is unclear whether these membrane are also suitable to be used in membrane reactors and how the addition of a chitosan layer affects the water vapor permeability and H₂O/CO₂ selectivity. This is investigated in more detail in this chapter.

In order to use polymeric membranes in membrane reactors, the polymeric material has to be able to withstand high temperatures due to kinetic limitations and CO₂ activation. **Chapter 4** shows that by exchanging the counter ion in SPEEK the thermal stability of the SPEEK membranes improves. Next to this, Chapter 4 also investigates how this exchange of counter ions affects the dehydration performance and H₂O/CO₂ selectivity.

Chapter 5 discusses the commercial viability of the direct conversion of CO₂ into DMC using a membrane reactor. A detailed process simulation is performed that studies the use of water vapor selective catalytic membrane reactors, but also considers the purification train that is necessary to obtain pure DMC. Based on the economic evaluation the main challenges are discussed and directions for future investigations are presented.

Finally, **Chapter 6** sums up the work that is described in this thesis, evaluates the potential of membrane reactors for the direct conversion of CO₂ into DMC and provides several recommendations for future research.

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Chapter 2

**Multi-component mass transfer behavior in
catalytic membrane reactors**

Abstract

Numerical simulations are presented to compare mass transfer at the bulk fluid-membrane interface of two types of membrane reactors, for arbitrary equilibrium reactions: the Catalytic Membrane Reactor (CMR) in which the location of the reaction and separation coincide, and the Inert Membrane Reactor (IMR) in which locations of reaction and separation are distinct. The Maxwell-Stefan theory is adopted to describe this multi-component mass transport and to take friction between the species in the reaction mixture into account. Simulation results are presented that aid selection of the most appropriate reactor configuration for different reaction equilibrium characteristics. Effects of process conditions, membrane properties, and possibilities to optimize reactor design are discussed.

Three regimes can be distinguished, based on the value of reaction equilibrium constant (K_{eq}). At very low K_{eq} , the CMR outperforms the IMR, and in particular a high membrane area/reactor volume ratio (A/V), a high product permeance, and a large residence time are required. At moderate K_{eq} , the CMR potentially outperforms the IMR, and conversion benefits in particular from a high A/V ratio and sufficiently high mass transfer. For high K_{eq} the performance of the IMR is superior as compared to the CMR.

The simulation results indicate that, in particular for the CMR, a mass transport description that can properly address multi-component mass transport characteristics is vital. The results predicted based on the Maxwell-Stefan theory will not be captured adequately by a model based on, for instance, the law of Fick.

2.1. Introduction

Process intensification combining two or more unit operations may reduce investment costs and increase energy efficiency. Examples include membrane reactors in which chemical reaction and membrane separation are united. A prospective major application of membrane reactors is the selective in-situ removal of one or more components from the reactor aiding a shift in the equilibrium of thermodynamically limited reactions to the product side. Typical examples of such reactions are dehydrogenation processes such as that of light alkanes to alkenes [1] or cyclohexane to benzene [2, 3]. In these two reactions, the selective removal of hydrogen from the reaction mixture using palladium membranes enhanced the reaction rate and conversion exceeded thermodynamic equilibrium. Additionally, the removed hydrogen could be coupled to a hydrogenation reaction at the permeate side of the membrane in a so-called coupling reaction as Gryaznov [2] showed for the hydrogenation of pentadiene. Over the years, many more examples on the use of membrane reactors enhancing equilibrium limited reactions are reported, such as the water-gas-shift reaction [4, 5] and esterification reactions [6-9]. Different review articles are available that summarize the extensive work done in the field of membrane reactors [10-17].

Sanchez and Tsotsis [13] distinguish six different membrane reactor configurations, each having its own characteristics. In this work we focus on two configurations that address the difference in multi-component mass transfer behavior the most:

- Catalytic Membrane Reactor (CMR): In this reactor the membrane exhibits catalytic activity, causing the location of reaction and separation to coincide. The catalytic activity of the membrane can be inherent to the membrane material (e.g., zeolites [6]) or can be achieved by coating the membrane with a catalytically active material [18]. Technical complexity of CMRs will imply relatively high investment costs.

- Inert Membrane Reactor (IMR): In this reactor the membrane does not exhibit catalytic activity. The locations of reaction and molecular separation are distinct and reactants must be transported from the reaction zone (for instance the fluid bulk) to the membrane surface before they can be removed from the reactor. As compared to a CMR, the less complex design of an IMR will imply lower investment costs.

In literature these types of membrane reactors are often compared with more conventional fixed bed reactors (FBR). Typical early work is that of Sun and Khang [19] who investigated if CMRs and IMRs could overcome equilibrium limitations for the dehydrogenation of cyclohexane. But also in more recent work, Bernal et al. [6] evaluated the three earlier mentioned reactor configurations for the esterification of ethanol with acetic acid. They found the highest conversion for the CMR and the lowest for the FBR and attributed this to additional transport resistances in the FBR and the IMR, as compared to the CMR where the reaction occurs at the membrane.

Much work is done on investigating the influence of process and material parameters on the conversion in membrane reactors. For example the effect of space time [19], reaction time/transport ratio, membrane selectivity [20], membrane area and feed ratio [21] is reported.

In addition to this, also membrane reactor design and the influence of the catalyst is subject of research. Yeung et al. [22] concluded that a Dirac delta distribution of the catalyst placed at the feed side outperforms a uniform catalyst distribution. Basically this means that the reaction should take place as close to the membrane as possible, while the remainder of the membrane should operate as a separator [22, 23]. Work of Peters et al. [18] described the mass transfer characteristics inside the catalyst layer of a CMR as a function of the catalyst thickness and compared that with an IMR. They found that CMRs outperform IMRs, but with an increasing catalyst thickness this advantage disappears due to diffusion limitations within the catalyst layer.

Although previous papers often compare the performance of CMRs and IMRs, mass transport towards the membrane is often neglected (e.g. gas phase) or described considering relatively straightforward theories such as Fick's law. Although the use of Fick's law is an elegant, very valuable and relatively easy to apply approach, it is a simplification of reality and the exact inaccuracy is difficult to estimate. Mass transport in CMRs is a complex multi-component process. The removal of one or more species through the membrane results in an overall drift flux, causing concentration polarization of reactants and products. The concentration of species that are retained by the membrane will increase at the catalytic membrane interface, and these species will diffuse back towards the liquid bulk. The concentration of species that permeate through the membrane will be lowered at the membrane interface, resulting in an increased diffusion towards the membrane.

In the present article, we use the Maxwell Stefan theory to describe mass transfer in a membrane reactor. The Maxwell Stefan approach inherently accounts for a drift flux and the friction between each component i and j present in the reaction mixture [24]. We explicitly use this Maxwell Stefan approach to describe mass transfer solely at the interface between fluid bulk and membrane to compare both reactor concepts (IMR and CMR), but we do not intent to provide an advanced mathematical description of an entire membrane reactor.

Simulation results are presented and the impact of different process and material properties the mass transfer is studied. While conclusion from existing literature are usually reaction specific and extrapolation to other reactions is not always straightforward, this work has a generic approach and can be translated towards any equilibrium reaction. As such, it describes mass transfer at the bulk fluid-membrane interface in an IMR and CMR for arbitrary equilibrium reactions, while taking into account the friction between the species in the reaction mixture.

2.2. Theory

2.2.1. Membrane reactor modeling

Two membrane reactor configurations are considered, as schematically depicted in Figure 2.1.

Figure 2.1: Schematic representation of a catalytic membrane reactor (CMR, left) and an inert membrane reactor (IMR, right).

Both reactors are operated in a continuous mode and their bulk is considered ideally stirred. For each component present, the corresponding mass balance over the bulk is given by:

$$0 = (\phi_V x_i c_{tot})_{in} - (\phi_V x_i c_{tot})_{out} + v_i V R_{bulk} - A N_i \quad (2.1)$$

where ϕ_V is the volume flow [m^3/s], x_i is the molar fraction of species i , c_{tot} is the total concentration [mol/m^3], v_i is the stoichiometric coefficient of component i [-], V is reactor volume [m^3], R_{bulk} is the rate of the reaction occurring in the bulk [$mol/m^3 \cdot s$], A is the membrane surface area [m^2] and N_i is the flux of component i through the boundary layer [$mol/m^2 \cdot s$].

Due to the overall molar production or consumption by chemical reaction and removal of components through the membrane, $\phi_{V,out}$ is not necessarily equal to $\phi_{V,in}$. There are nc mass balances, containing $2nc+3$ unknowns ($x_1, \dots, x_{nc}, N_1, \dots, N_{nc}, R, c_{tot}, \phi_{V,out}$); $nc+3$ additional equations are required. One additional equation is the summation of molar fractions in the bulk:

$$\sum_{j=1}^{nc} x_j = 1 \quad (2.2)$$

A second equation relates the total concentration to the composition of the mixture. For reasons of simplicity, in this work the total concentration is assumed constant.

$$c_{\text{tot}} = \frac{P}{RT} = \text{constant} \quad (2.3)$$

The reaction rate R_{bulk} [mol/m³·s] is considered to obey power-law kinetics:

$$R = k_f \left(\prod_j^{\text{reactants}} (c_{\text{tot}} x_j)^{|v_j|} - \frac{1}{K_{\text{eq}}} \prod_j^{\text{products}} (c_{\text{tot}} x_j)^{v_j} \right) \quad (2.4)$$

Here, k_f is the forward reaction rate constant, K_{eq} is the equilibrium constant of the reaction, and the reaction orders are taken identical to the stoichiometric coefficients [18]. For the CMR calculations the reaction in the bulk is neglected as the reaction predominantly takes place at the catalyst on the membrane at the fluid-membrane interface.

The fluxes through the boundary layer are calculated from the $nc-1$ independent Maxwell Stefan equations, assuming ideal thermodynamic behavior [24]:

$$-c_{\text{tot}} \Delta x_i = \sum_{j \neq i} \frac{\bar{x}_j N_i - \bar{x}_i N_j}{k_{ij}} \quad (2.5)$$

Here Δx is the difference in mole fraction between the bulk and the membrane interface [-], $\bar{x}$ is the average mole fraction between the bulk and the membrane interface, and k_{ij} is the Maxwell Stefan mass transfer

coefficient for components i and j [m/s]. The additional value of using the Maxwell Stefan approach in contrast to other mass transport description theories (e.g. Fick) is that it takes the drift flux and friction between different species in the mixture into account. In a multi-component mass transfer system such as in a CMR, this is important since the back diffusing of non-permeating species can make CMRs much less beneficial than predicted by other theories. For more extensive reading on this topic the reader is directed to the book of Wesselingh and Krishna [24].

An additional equation is provided by the summation of molar fractions at the interface:

$$\sum_{j=1}^{nc} x_j^{\text{interface}} = 1 \quad (2.6)$$

The molar fractions at the membrane interface are nc additional unknowns; corresponding required equations are provided by mass balances over the membrane interface:

$$N_i = N_{\text{membrane},i} + v_i R_{\text{interface}} \quad (2.7)$$

The flux through the membrane, $N_{\text{membrane},i}$, is calculated from:

$$N_{\text{membrane},i} = P_i x_i p_{\text{tot}} \quad (2.8)$$

with P the permeance [$\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$] and p_{tot} is the total pressure at the feed side [Pa]. In this, it is assumed that the partial pressure of the permeating components at the permeate side is negligible. This is close to reality as often a vacuum or a sweep gas is used at the permeate side, which removes all permeating species and keeps the partial pressure at the permeate side at the very low range.

The relation for the reaction rate at the interface of the membrane, $R_{\text{interface}}$ [$\text{mol}/\text{m}^3 \cdot \text{s}$], is similar to equation 2.4:

$$R = k_f'' \left(\prod_j^{\text{reactants}} (c_{\text{tot } X_{j,\text{interface}}})^{|v_j|} - \frac{1}{K_{\text{eq}}} \prod_j^{\text{products}} (c_{\text{tot } X_{j,\text{interface}}})^{v_j} \right) \quad (2.9)$$

For comparison between IMR and CMR, the forward reaction rate constant for the interface reaction is calculated from:

$$k_f'' = k_f \frac{V}{A} \quad (2.10)$$

In the absence of transport resistance due the boundary layer, this would cause the performance of the IMR and CMR to be identical, as the model assumes all other resistances to transport than the boundary layer and membrane (e.g., resistance in and toward the catalyst particles) to be negligible.

The above equations are solved using Matlab (version 2010b), see supporting information. Performance of the reactor is compared based on the conversion (ζ) [-], determined as:

$$\zeta = \left(1 - \frac{(X_i \Phi_v)_{\text{out}}}{(X_i \Phi_v)_{\text{in}}} \right) \cdot 100\% \quad (2.11)$$

Or on the difference in conversion ($\Delta\zeta$) [-] :

$$\Delta\zeta = \zeta_{\text{CMR}} - \zeta_{\text{IMR}} \quad (2.12)$$

2.2.2. Base case specifications and conditions

For our simulations we have arbitrarily chosen an equilibrium reaction with 2:1:1:1 stoichiometry

An example of such a reaction is the formation of dimethyl carbonate (DMC) from carbon dioxide and methanol. Since carbon dioxide and methanol are stable molecules, equilibrium is at the reactant side ($K_{eq} \sim 10^{-5}$ at ambient conditions) and it is difficult to obtain high yields towards DMC [25-27].

Unless mentioned otherwise, the following data have been used in the simulations. Reactant A and B enter the CMR or IMR in a molar ratio of 2:1, equal to the stoichiometric ratio of the reactants. The total reactor volume is 1 m^3 and the ratio of the membrane surface over the reactor volume (A/V) is 1000 1/m . This corresponds to a diameter of $\sim 4 \text{ mm}$ for hollow fiber membrane experiments. The membrane is assumed 100% selective towards water, with a permeance of $10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. The permeance value is in the same order as Sijbesma et al. [28] have found for dense polymeric membranes in a mixture of $\text{H}_2\text{O}/\text{N}_2$ and Verkerk et al. [29] for ceramic membranes for the dehydration of alcohols. Although the work of Sijbesma et al. [28] reports values obtained at $30\text{-}70^\circ\text{C}$, the values give a good estimation of the order of magnitude. The residence time in the membrane reactor (τ) is 100 s , such that $\varphi_v/A = 10^{-5} \text{ m/s}$, which is comparable to Peters et al. [18]. The forward reaction rate constant (k_f) is $0.01 \text{ (m}^3\text{)}^2/\text{mol}^2 \cdot \text{s}$, corresponding to 50% conversion if the reaction would be considered first order irreversible. For reasons of simplicity, for all components the value of the mass transfer coefficient (k_{ij}) is 10^{-4} m/s , in between typical values for liquids (10^{-5} m/s) and gases (10^{-2} m/s) [24]. A summary of all data is given in Table 2.1. As supplementary information the source code of the model is supplied with this work, making it possible to adjust the assumptions or modify the source code if desired.

Table 2.1: Feed composition and process and material conditions used in the model.

Parameter	Value	Unit	Parameter	Value	Unit
c_{tot}	100	mol/m ³	A/V	1000	1/m
T	150	°C	k_f	10 ⁻²	(m ³) ² /(mol ² ·s)
$x_{\text{in}, A}$	0.67	-	k_{ij}	10 ⁻⁴	m/s
$x_{\text{in}, B}$	0.33	-	$P_{\text{H}_2\text{O}}$	10 ⁻⁶	mol/(m ² ·s·Pa)
V	1	m ³	$P_A=P_B=P_E$	0	mol/(m ² ·s·Pa)
τ	100	s			

2.3. Results and discussion

2.3.1. Base case

Figure 2.2 depicts base case calculations of the conversion as a function of the equilibrium constant K_{eq} , for both the IMR and the CMR configurations. The range of K_{eq} reflects a realistic series of value for equilibrium reactions. Extreme low equilibrium reactions are represented by reactions such as the direct conversion of CO_2 towards dimethyl carbonate, which has a K_{eq} in the order of 10^{-6} - 10^{-5} [25]. A more moderate equilibrium constant ($K_{eq} = 10^{-1}$ - 10^1) represents esterification reactions often investigated for membrane reactors. Even higher equilibrium constants ($K_{eq} = 10^4$) refer to irreversible reactions and show how H_2O removal effects the conversion in those cases.

Figure 2.2: Conversion of the CMR and the IMR as a function of the equilibrium constant.

In Figure 2.2 three different regimes can be distinguished. For low equilibrium constants (regime 1) the rate of the backward reaction is much higher as compared to the forward reaction, and the conversion is limited. For very low equilibrium constants ($\log(K_{eq}) = -8$) no significant conversion is observed. At slightly higher values for K_{eq} some conversion of reactants is observed. The conversion in the CMR is slightly higher than that in the IMR. This suggests that, for low conversion, removal of water from the CMR is more efficient, allowing for a more pronounced shift in the reaction to the product side.

In regime 3, at very large K_{eq} values, the rate of the backward reaction is negligible. Essentially, the reaction has become irreversible and the conversion reaches an asymptotic value below 100%, due the limited residence time (τ) and limited rate of the forward reaction. A difference in conversion between the CMR and IMR indicates that removal of water has an effect on the conversion, despite the fact that it cannot induce a shift in the equilibrium reaction towards the product side. This can be explained as follows: the selective removal of water results in increased concentrations of the reactants and hence faster reaction kinetics. For the selected base case, the conversion in the pseudo-irreversible regime is slightly higher in the IMR than in the CMR. Here, the removal of water in the IMR is more effective because only transport water from the bulk of the reactor to the membrane surface occurs. In contrast, for the CMR simultaneous mass transport of all components in the boundary layer has to occur, constituting a larger overall transport resistance. It is important to note that the difference in performance of the two reactor configurations is directly related to the multi-component characteristics of mass transport in the boundary layer, which would not have been evident from simulations based on the law of Fick.

For intermediate values of the equilibrium constant, i.e., regime 2, water removal combines the two distinct effects on the conversion. Similar as in regime 1, the removal of water decreases the backward reaction kinetics and shifts equilibrium towards the product side. Comparable to regime 3,

the removal of water results in higher concentrations of reactants and hence faster reaction kinetics.

In Figure 2.3 the difference in conversion between the CMR and IMR is depicted as a function of the equilibrium constant. The same three regimes can be distinguished as in Figure 2.2. At very low K_{eq} values, in regime 1, there is no conversion, and hence no difference in conversion. At high K_{eq} values, in regime 3, the conversion in the IMR is slightly higher. The largest difference in conversion, in favor of the CMR, is observed in regime 2 indicating more efficient removal of water in the CMR at intermediate K_{eq} values. This conclusion is in agreement with Bernal et al. [6]. They also concluded that the mass transport resistance is higher when the reaction is carried out in the bulk (IMR), compared to the situation where the catalyst material is highly integrated with the membrane (comparable to CMR) [6].

Figure 2.3: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant.

The base case simulations in Figure 2.2 and Figure 2.3 indicate that a CMR may be an interesting option for intermediate K_{eq} values, while for higher K_{eq} values the IMR has a small advantage in terms of conversion. For typical equilibrium reactions, e.g., for esterification reactions with K_{eq} in the order of 0.1 [7, 8, 30], the simulations would suggest that a CMR is not the preferred configuration. However, the performance of both membrane reactor concepts is sensitive to the values of the different process and material parameters. In the remainder this is evaluated and the effects of

the most relevant parameters on the difference in conversion are investigated and discussed.

2.3.2. Mass transport coefficient

The main difference between both configurations is related to the transport through the boundary layer of the membrane. In the CMR the reaction occurs at the catalytic membrane surface and multi-component mass transfer occurs; reactants diffuse towards the membrane surface and products diffuse in the opposite direction. In the IMR the reaction occurs in the bulk and only transport of water through the boundary layer occurs. The different mass transport characteristics are evident from Figure 2.4, in which the conversion is depicted as a function of K_{eq} , for different values of k_{ij} .

Figure 2.4: a) Conversion in the CMR as a function of the equilibrium constant for different values of the mass transfer coefficient of the boundary layer of the membrane (k_{ij}). b) Conversion in the IMR as a function of the equilibrium constant for different values of the mass transfer coefficient of the boundary layer of the membrane.

For the CMR the effect of a decrease in mass transfer coefficient on conversion is particularly pronounced in region 3. The asymptotic value of the conversion is reached at more or less the same K_{eq} value ($\sim 10^{-2}$), implying that a larger resistance to transport in the boundary layer does not affect when the reaction attains pseudo-irreversible characteristics. The impeded transport for lower k_{ij} values results in a similar reduction of the forward and backward reaction. The strong reduction in conversion in

region 2 and 3, for decreasing k_{ij} , results from the requirement of simultaneous transport of multiple components through the boundary layer, in order to allow the reaction at the membrane surface to occur.

For the IMR the behavior is distinct. When the resistance to transport in the boundary layer becomes larger, the asymptotic value of conversion is reached at larger values of K_{eq} , and the decrease in the asymptotic value is less pronounced as compared to the CMR. The smaller decline in asymptotic conversion is due to the fact that in the IMR the conversion of the pseudo-irreversible reaction is only affected by a higher concentration of the reactants, and hence faster kinetics, due to removal of water. The observed conversions are relatively low, so not much water is produced and removal of water will only have a limited effect. The shift of the K_{eq} at which the asymptotic behavior is observed (K_{eq} shifts from $\sim 10^{-2}$ m/s to ~ 1 , for k_{ij} is 10^{-4} and 10^{-6} m/s, respectively) implies that the larger resistance to transport in the boundary layer extends the reversible characteristics of the reaction to larger K_{eq} values. For large values of k_{ij} (10^{-2} m/s) most of the water is removed for $K_{eq} \sim 10^{-2}$. For smaller values of k_{ij} (10^{-4} m/s) water removal is less efficient, and the backward reaction remains more pronounced. In region 1 this leads to a delay of the increase in conversion with K_{eq} . This delay is sustained in region 2. For sufficiently high values of K_{eq} the backward reaction is no longer important and asymptotic conversion is reached. The value of the asymptotic conversion is only slightly less than for $k_{ij}=10^{-2}$ m/s, suggesting that again most of the water is removed. Further increasing the transport resistance of water in the boundary layer to $k_{ij}=10^{-6}$ m/s, leads to an even more pronounced delay in the increase in conversion with K_{eq} . The asymptotic value is now significantly lower than for $k_{ij}=10^{-2}$ - 10^{-4} m/s, suggesting that the high resistance to water transport in the boundary layer results in a larger water concentration in the bulk. Again, the asymptotic behavior as function of K_{eq} confirms that the removal of water does not cause a shift in thermodynamic equilibrium. The larger concentration of water results in decreased concentrations of reactants, and hence slower reaction kinetics.

Figure 2.5 represents the difference in conversion between the CMR and the IMR as a function of the equilibrium constant, for different values of k_{ij} . For large values of k_{ij} the boundary layer poses no significant resistance to mass transport. In the absence of a mass transport resistance in the boundary layer the performance of both reactor configurations should be identical and $\Delta\zeta$ should be zero. Indeed, for $k_{ij} \sim 10^{-2}$ m/s only minor differences in performance are observed. When the resistance to mass transfer increases, the performance of the IMR and CMR diverge and the three different regimes are clearly distinguishable. For $k_{ij} = 10^{-4}$ m/s, difference in performance is observed in particular in region 2. Here, the CMR outperforms the IMR by 15%. This is a result of the effective removal of water in the CMR, due to the coincidence of the locations of reaction and water removal. When the resistance to mass transport is further increased, to $k_{ij} = 10^{-6}$ m/s, the diffusion of the reactants and products in the boundary layer is impeded and the superior performance of the CMR ceases. In regime 3 the IMR outperforms the CMR in all cases, in particular when the resistance to transport is significant. This is due to the multi-component mass transport characteristics, i.e., simultaneous diffusion of reactants and products through the boundary layer required in the CMR. Hence, for reactions with large equilibrium constants a proper comparison between the two configurations requires a mass transport description suitable for multi-component diffusion, such as the Maxwell-Stefan theory, rather than Fick's law.

Figure 2.5: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different mass transfer coefficients of the boundary layer of the membrane.

2.3.3. Reaction rate constant

Figure 2.6 shows the effect of an increasing forward reaction rate constant on the conversion in the CMR and the IMR as a function of the equilibrium constant.

Figure 2.6: Conversion in the CMR and the IMR as a function of the equilibrium constant for different values of the forward reaction rate constants (k_f).

For both reactor configurations, in regime 1 no significant influence of k_f on the conversion is observed due to the dominant backward reaction. In regime 2 the conversion increases with k_f . The onset of this increase occurs at lower K_{eq} for the CMR, as compared to the IMR. This is a result of the more effective removal of water in the CMR, as has been discussed in the previous sections. In regime 3 the asymptotic value of the conversion, corresponding to a pseudo-irreversible reaction, occurs. For higher values of k_f this asymptotic value is reached at high values of K_{eq} , indicating that for faster reaction kinetics the reversible characteristics of the reaction extend to larger values of the equilibrium constant. The conversion in regime 3 increases with k_f because of the faster reaction kinetics. For a low reaction rate, the performance of the two reactor configurations is comparable. This is due to the small amount of water that is produced in case of slow reaction kinetics, allowing only a minor increase in the concentration of reactants and hence a minor increase in the reaction rate. For larger values of k_f the conversions are higher and more water is produced. Similar behavior was observed by Peters et al. [18] for the esterification of acetic acid and butanol ($K_{eq} \sim 4$ [31]). In regime 3

the removal of water is more effective in the IMR. In this reactor configuration only water is transported through the boundary layer, whereas for the CMR the transport of all components should be considered.

Figure 2.7 shows the difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different values of the forward reaction rate constant.

Figure 2.7: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different values of the forward reaction rate constant.

Figure 2.7 shows that, at intermediate K_{eq} values, increasing the forward reaction rate constant is in favor of the CMR. The maximum in the difference in conversion increases with k_f and shifts to larger values of K_{eq} . As such, in regime 2 a CMR is preferred over an IMR and the performance of a CMR will strongly benefit from a catalyst that enables faster reaction kinetics.

2.3.4. Permeance

Figure 2.8 shows the effect of the water permeance (P_{H_2O}) of the membrane on the conversion as a function of the equilibrium constant.

Figure 2.8: Conversion in the CMR and the IMR as a function of the equilibrium constant for different values of the H₂O permeance of the membrane (P_{H_2O}).

Figure 2.8 shows that the performance of the IMR is insensitive to the value of the permeance of the membrane. In the IMR the total resistance to transport of water can be considered as two resistances in series: that of the boundary layer and the membrane itself. For the presented simulations, the resistance in the boundary layer is dominant. Hence, further improvement of the permeance of the membrane would not lead to an improved performance. For the CMR the situation is different. Here, for removal of water, the only resistance to transport is the membrane, whereas the boundary layer poses mass transport resistance to the other species present. As a result, in regime 2, increasing the permeance of the membrane has a positive effect on the performance of the CMR. When the membrane allows faster permeation of water, the reversible characteristics of the reaction become less pronounced. As a result, for a given value of K_{eq} higher conversion is observed. For high values of K_{eq} the reaction has become pseudo-irreversible, and performance is dictated by the multi-component mass transfer in the boundary layer. In this regime the conversion is not affected by the water permeance of the membrane. These results imply that, for the pseudo-irreversible regime (e.g. esterification reactions) improving the membrane flux has a minor impact on the conversion compared to other parameters, for the IMR improving the membrane properties has no impact in any of the three regimes.

Contradictory to these observations in Figure 2.8, Peters et al. [18] and Feng and Huang [21] both observed for esterification reactions (high K_{eq}) an increasing conversion with increasing H_2O permeance. Such behavior is observed in Figure 2.9, where the value of the permeance is reduced to values where resistance to transport of the membrane becomes significant with respect to resistance of the boundary layer. Figure 2.9 shows an increasing conversion for high K_{eq} values when P increases from 10^{-8} to 10^{-6} mol/m²·s·Pa. Lowering the H_2O permeance to an extremely (non-realistic) value of 10^{-100} mol/m²·s·Pa yields a limiting value for the conversion. Again, it is important to recognize that at high values of K_{eq} the changes in conversion are not due to a shifted equilibrium, but due to faster kinetics in a less water diluted mixture.

Figure 2.9: Conversion in the CMR and the IMR as a function of the equilibrium constant for different values of the H_2O permeance.

Figure 2.10 shows the difference in the conversion between both the CMR and the IMR as a function of the equilibrium constant, for increasing H_2O permeance.

Figure 2.10: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different H₂O permeances.

Figure 2.10 shows that in regime 2 the CMR outperforms the IMR. The difference in conversion becomes more pronounced for increasing permeance, and the maximum in the difference shifts to lower values of K_{eq} . These results indicate that for reactions with high equilibrium constants improving the membrane properties is not sensible, whereas in regime 1 and 2 the performance of a CMR can be markedly improved when the membrane shows higher permeance.

2.3.5. Residence time

Figure 2.11 shows the conversion of the CMR and the IMR as a function of the equilibrium constant for an increasing residence time (τ).

Figure 2.11: Conversion in the CMR and the IMR as a function of the equilibrium constant for different values of the residence time (τ).

Figure 2.11 shows that for low and intermediate K_{eq} values the conversion in both reactor configurations increases with the residence time. With higher residence times there is more time to convert the reactants and to remove water. As a consequence equilibrium can shift to the product side, resulting in higher conversions in regime 1 and 2. As in regime 1 and 2 the removal of water is more efficient in a CMR, the effect of residence time on the performance is more pronounced for this reactor configuration. In regime 3 the reaction is pseudo-irreversible. The residence time is long, the removal of water is almost complete for both reactor configurations. When the residence time is short, only limited conversion is reached and the corresponding amount of water is only small; only a limited improvement in conversion can be reached by removing this water.

Feng and Huang [21] also found higher conversions with increasing residence time. In their work they investigated an high equilibrium constant (esterification reaction) and depicted the conversion as a function of the residence time. According to their study the conversion increases in time, which indicates that conversion goes up with the residence time, as Figure 2.11 also shows.

Figure 2.12 shows the difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different values of the residence time.

Figure 2.12: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different values of the residence time.

Figure 2.12 shows the maximum in favor of the CMR goes up with increasing residence time, and shifts to lower values of K_{eq} . Hence, for thermodynamically limited reactions with low equilibrium constant, increasing the residence time has a pronounced positive effect on reactor performance.

2.3.6. A/V ratio

Figure 2.13 represents the conversion as a function of the equilibrium constant for an increasing membrane area to reactor volume (A/V) ratio. In the model the reactor volume is kept constant at 1 m³ and the membrane area is changed accordingly.

Figure 2.13: a) Conversion in the CMR as a function of the equilibrium constant for different values of the membrane area : reactor volume (A/V) ratio. b) Conversion in the IMR as a function of the equilibrium constant for different values of the membrane area : reactor volume ratio.

Figure 2.13a and Figure 2.13b show that an increasing A/V ratio (more membrane area in the same volume) has a positive effect on the conversion in both membrane reactor configurations. For the IMR, performance is only affected by the A/V ratio through the rate of removal of water. Increasing the A/V ratio allows faster removal of water and results in all three regimes in higher conversion. The equilibrium shifts more to the product side at low and intermediate K_{eq} values, and less water accumulates in the bulk for regimes 2 and 3. In the CMR, performance is affected by the rate of removal of water, but also by the resistance to mass

transfer of the reactants and products between the reactor bulk and catalytic membrane surface. As a result, the A/V ratio has a much more pronounced effect on reactor performance. The conversion of the CMR increases much more strongly with increasing A/V ratio, as compared to the IMR. This effect is comparable to increasing the k_{ij} values and again requires a description of multi-component mass transport (Maxwell-Stefan) rather than Fick's law

Feng and Huang [21] also investigated the effect of the A/V ratio on the conversion of a similar configuration as the IMR. They support the conclusion that an increasing A/V ratio has a positive effect on the conversion and attribute this to an increase in water removal.

Figure 2.14 shows the difference in conversion between the CMR and the IMR as function of the equilibrium constant for an increasing A/V ratio.

Figure 2.14: Difference in conversion between the CMR and the IMR as a function of the equilibrium constant for different values of the membrane area : reactor volume ratio.

Figure 2.14 shows that a CMR benefits from a large A/V ratio. For low and moderate equilibrium constants a lower A/V ratio reduces the benefit of using the CMR instead the IMR. For large equilibrium constants the superior performance of the IMR becomes more pronounced for lower A/V ratio. These results indicate that for a CMR, a high A/V ratio is crucial.

2.3.7. Model limitations

Various assumptions are underlying the simulations. In particular, two assumptions have been made only to simply minimize the number of parameters in the simulation studies.

The first is the assumption of a single identical value for all k_{ij} . In the model it is not required to have a single value; a symmetric matrix of k_{ij} values can be used. In particular for the CMR configuration, multi-component mass transport in the boundary layer has a pronounced effect on the reactor performance and for a particular system appropriate values for the various k_{ij} will be essential for a proper prediction of the real reactor performance.

The second assumption is that there is no resistance to mass transport other than in the stagnant layer between the bulk and membrane interface. In reality there will also be other resistances. For the CMR a porous catalytic layer on the membrane will have mass transport limitations, as has been extensively investigated by Peters et al. [18]. For the IMR, when the catalyst in the bulk consists of solid particles, a stagnant boundary between the particle surface and fluid bulk will exist. In Figure 2.15 the effect of this additional resistance on performance of the IMR configuration is depicted for base case conditions. The values for k_{ij} in the boundary layer between particles and bulk are chosen identical to those in the boundary layer between membrane and bulk.

Figure 2.15: Conversion in the IMR as a function of the equilibrium constant with and without the boundary layer resistance of the catalyst particle. “Without resistance” refers to the case that there is no resistance to migrate back and forward to the catalyst particles in the IMR. “With resistance” refers to the case that reactants and products have resistance to diffuse to the particle, which is described with Maxwell Stefan.

Figure 2.15 shows that the additional mass transport resistance has only a moderate negative influence on the performance of the IMR. Consequently, the above presented simulation results for the IMR are slightly overestimated.

2.4. Implications

2.4.1. Guidelines

The simulation results indicate that a sensible choice for a membrane reactor configuration, and a good design and operation of the reactor, depends strongly on the value of the equilibrium constant. A few general guidelines can be derived from our simulations. Table 2.2 gives a summary of the presented results.

Table 2.2: Influence of increasing parameter on the conversion in the CMR and IMR for a low, intermediate and high equilibrium constant (++ = large positive effect, + = positive effect, 0 = no effect).

		k_{ij}	k_f	P_{H_2O}	τ	A/V
CMR	Low K_{eq}	+	0	++	++	+
	Intermediate K_{eq}	++	+	+	++	++
	High K_{eq}	++	++	+	++	++
IMR	Low K_{eq}	+	0	0	++	+
	Intermediate K_{eq}	++	+	0	++	+
	High K_{eq}	+	++	0	++	+

The selection of best performing type of membrane reactor, for a specific thermodynamically limited equilibrium reaction, depends on the equilibrium constant of that reaction. For our base case results, the following guidelines can be proposed.

2.4.2. Low K_{eq}

For reactions with low thermodynamic equilibrium conversion, the most appropriate reactor configuration is the CMR. At low K_{eq} values, very efficient removal of the product water is crucial. This can be achieved by having a large A/V ratio, a long residence time and a high H_2O permeance.

2.4.3. Intermediate K_{eq}

At moderate equilibrium constants, the CMR is the best performing membrane reactor configuration: it is more effective in shifting the equilibrium to the product side, and it prevents accumulation of H_2O in the bulk. But CMRs are very sensitive to changing k_{ij} values and to a minor extend to the A/V ratio. A moderate k_{ij} value and a high A/V ratio are beneficial.

2.4.4. High K_{eq}

For high equilibrium constants (e.g. esterification reactions), the CMR and IMR achieve similar conversions. But due to the less complex design of an

IMR investment costs will be lower in that case. H_2O removal does not aid shifting the equilibrium to the product side. Nevertheless, removal of H_2O prevents accumulation of H_2O in the bulk. The higher water concentration lowers the reactant concentrations, resulting in slower reaction kinetics and thus lower the conversion. Increase of conversion can be established via higher residence times and faster reaction kinetics.

2.5. Conclusions

Membrane reactor technology has a large potential for future applications because it can reduce investment costs, increase energy efficiency and has a wide range of operating possibilities to increase conversion in equilibrium limited reactions. This work presented numerical simulations for the conversion of thermodynamically limited reactions in membrane reactors. A comparison is made between two reactor configurations: in one the reaction is catalyzed exactly at the interface of the membrane (CMR), in the other catalysis occurs in the fluid bulk of the reactor (IMR). In particular, performance is evaluated as function of the equilibrium constant (K_{eq}), and the effect of various parameters is investigated.

The simulation results indicate that, in particular for the CMR, mass transport description that can properly address multi-component mass transport characteristics is essential. The results predicted based on the Maxwell-Stefan theory will not be captured adequately by a model based on, for instance, the law of Fick. Adjusting mass transport description towards Maxwell Stefan are simple adjustments in future modeling work and gives a better description of mass transport in membrane reactors.

2.6. Acknowledgments

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2.7. List of symbols

A	membrane area	$[\text{m}^2]$
c_{tot}	total concentration	$[\text{mol}/\text{m}^3]$

K_{eq}	equilibrium constant	[-]
k_b	backward reaction rate constant	[m ³ /mol·s]
k_{ij}	mass transport coefficient boundary layer of the membrane	[m/s]
k_f	forward reaction rate constant	[(m ³) ² /mol ² ·s]
N	flux through the boundary layer of the membrane	[mol/m ² ·s]
$N_{membrane}$	flux through the membrane	[mol/m ² ·s]
P	permeance	[mol/m ² ·s·Pa]
p_{tot}	total pressure	[Pa]
R	reaction rate	[mol/m ³ ·s]
$R_{interface}$	reaction rate at the interface of the membrane	[mol/m ² ·s]
R_{bulk}	reaction rate in the bulk	[mol/m ³ ·s]
T	temperature	[K]
x	molar fraction	[-]
V	reactor volume	[m ³]
Δx	difference in molar fraction between bulk and interface	[-]
$\bar{x}$	average mole fraction between bulk and membrane interface	[-]

Greek symbols

τ	residence time	[s]
ν	stoichiometric ratio of the reaction	[-]
ζ	conversion	[%]
$\Delta\zeta$	difference in conversion	[%]
φ_V	volume flow	[m ³ /s]

subscripts

A	component A
B	component B
bulk	bulk
E	component E
i	component i
in	ingoing stream
interface	interface of the membrane
j	component j
nc	number of components
out	outgoing stream

2.8. References

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Chapter 3

Water vapor selective membranes: Towards the separation of methanol and CO₂ for the production of dimethyl carbonate in catalytic membrane reactors

Abstract

For the direct conversion of CO₂ and methanol into dimethyl carbonate (DMC) membrane reactors are proposed as an interesting technology to avoid thermodynamic limitations and to enhance the conversion. For successful implementation highly water permeable membranes are required that selectively retain the reactants.

This work describes the development of sulfonated poly(ether ether ketone) (SPEEK)/chitosan membranes and their performance in mixed water vapor/CO₂ environments for application in a membrane reactor for the direct conversion of CO₂ and methanol into DMC. The results show that the properties of both individual polymers remain present in the SPEEK/chitosan composite membranes and that these are thermally stable up to 220 °C, which makes them capable to withstand the extreme conditions in membrane reactors. Opposite to what was expected, binary water vapor/CO₂ permeation experiments showed that the addition of an additional chitosan layer on top of a SPEEK membranes enhances water vapor permeation and simultaneously improves the H₂O/CO₂ selectivity, despite the larger membrane thickness. Overall this means that by combining two distinctively different materials in one membrane, we were able to benefit from the advantages of both individual materials while diminishing their disadvantages.

3.1. Introduction

Over the last decades dimethyl carbonate (DMC) caught interest due to its low toxicity and fast biodegradability as fuel additive, methylating agent and carbonylation agent [1-4]. Since for the conventional production of DMC highly toxic phosgene is needed, alternative production routes are investigated [1, 3, 4]. A sustainable interesting route is the direct conversion of CO₂ and methanol to DMC. However, thermodynamic equilibrium limits the conversion. Membrane reactors can overcome this problem by selectively removing products (e.g. H₂O) from the reaction mixture, shifting equilibrium to the product side and increasing conversion. Previous work [5] shows that for extreme equilibrium limited reactions catalytic membrane reactors perform best. One of the major focus points for large scale commercial application is the improvement of the H₂O permeability of the membrane. Wang et al. [6, 7] showed for instance very promising zeolite membranes for the direct conversion of CO₂ into DMC, however they do not exhibit a very high H₂O permeability.

As such the membrane material is critical. According to literature different polymeric membrane materials are available for gas dehydration that exhibit high H₂O permeabilities ($T \leq 70\text{ }^{\circ}\text{C}$), such as PEBAX 1074 [8, 9], Matrimid [10], 6FDA-TMPDA [10], poly(ethylene oxide) based block copolymers [11], poly(aryl ether sulfone) [12] or sulfonated poly(ether ether ketone) (SPEEK) [8]. A more extended overview is given by Bolto et al. [13] and Scholes et al. [14]. Out of these materials SPEEK (Figure 3.1) is one of the most promising materials due to its chemical and mechanical robustness, exceptionally high H₂O permeability and low CO₂ permeability. Sijbesma et al. [8] measured water vapor permeabilities in the order of 10^5 - 10^6 Barrer ($1\text{ Barrer} = 10^{-10}\text{ cm}^3(\text{STP})\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$) and a CO₂ permeability of 0.11 Barrer (H₂O activity = 0) at temperatures ranging from 30 °C to 70 °C.

Figure 3.1: Chemical structure sulfonated poly(ether ether ketone) (SPEEK).

SPEEK is available in different sulfonation degrees (SD) and its properties strongly depend on the percentage of sulfonated groups present in the polymer. According to Fathima et al. [15] SPEEK with a SD > 40% is soluble in DMSO or NMP. Above a SD of 70% it is soluble in methanol and at 100% even in water. As we opt for the direct conversion of CO₂ and methanol into DMC and H₂O (byproduct), it is undesired that the membrane polymer is soluble in methanol or water. Consequently, we are forced to work with low sulfonated SPEEK (e.g. SD = 40%). Nevertheless, even at low sulfonation degrees water vapor permeabilities remain sufficiently high. Silva et al. [16] however showed that under pervaporation conditions at T = 55 °C using a 20 wt% aqueous methanol solution, SPEEK with a SD of 40% exhibits an undesirable high methanol permeability of $2.2 \cdot 10^4$ Barrer.

For applications in direct methanol fuel cells (DMFCs) researchers also aim to reduce methanol cross over in SPEEK. Zhong et al. [17] solved this by introducing a thin layer of chitosan on top of the SPEEK film. They reduced the methanol diffusion coefficient more than a tenfold. This makes SPEEK/chitosan membranes an interesting alternative to use in membrane reactors for the direct conversion of CO₂ and methanol to DMC. However, little information is available regarding the affinity of the other components present in the feed (H₂O and CO₂) towards this composite membrane and it is unclear how an additional chitosan layer affects the dehydration capacity and the H₂O/CO₂ selectivity.

Chitosan (Figure 3.2) is a cheap material gained from crab and shrimp shells and is frequently investigated for pervaporation to dehydrate alcohols such as ethanol and iso-propanol [18-20]. Won et al. [20] investigated the separation of water from methanol and observed that at a very high methanol feed concentration (> 98 wt%) the separation factor is

still in favor of water (separation factor = 4), which proves that chitosan is very well capable to retain methanol. The dehydration capacity of chitosan is rather high. Despond et al. [21] showed H_2O permeabilities up to $0.8 \cdot 10^5$ Barrer (H_2O activity = 1). Meanwhile measuring a maximum CO_2 permeability of 5 Barrer (H_2O activity = 1). Others reported higher, but still reasonably low CO_2 permeabilities up to 100 Barrer [22] at similar conditions.

Figure 3.2: Chemical structure of chitosan.

Based on the previous description, SPEEK/chitosan composite membranes have the potential to be used in membrane reactors to directly convert CO_2 and methanol into DMC. The intention of combining both materials in one membrane is to benefit from the advantages of both individual materials while overcoming their disadvantages. Zhong et al. [17] showed that SPEEK/chitosan membranes are capable in retaining methanol. However, little is known about the interaction of these composite membranes with other components that are present during this reaction and no data are available about the effect of an additional chitosan layer on the water vapor permeation and $\text{H}_2\text{O}/\text{CO}_2$ selectivity. Therefore this work focusses on the development of SPEEK/chitosan membranes and their performance in mixed water vapor/ CO_2 environments for application in a membrane reactor for the direct conversion of CO_2 into DMC. We are especially interested in the dehydration capacity and $\text{H}_2\text{O}/\text{CO}_2$ selectivity of these SPEEK/chitosan membranes and how these are affected by the chitosan layer thickness and the water vapor activity. The results clearly show the unexpected beneficial contribution of an extra chitosan layer on both membrane permeability and selectivity.

3.2. Experimental

3.2.1. Materials

For the preparation of SPEEK membranes, SPEEK polymer granulate (fumion® E-800), IEC 1.25 (DS 40%) was obtained from Fumatech and N-methyl-2-pyrrolidinon (purity 99%) from Acros organics. For the chitosan membranes, chitosan (medium molecular weight) and glutaraldehyde solution for crosslinking (50 wt% in H₂O) were purchased from Sigma-Aldrich, sodium hydroxide (purity ≥ 99%) from VWR, acetic acid (purity ≥ 99.8%), ethanol (purity ≥ 99.9%), acetone (purity ≥ 99.8%) and sulfuric acid (purity 95 – 98%) from Merck. .

3.2.2. Membrane preparation

3.2.2.1. SPEEK membranes

SPEEK membranes were prepared according to the recipe of Potreck et al. [23]. First 15 wt% SPEEK was dissolved in N-methyl-2-pyrrolidone (NMP) at 120 °C. The solution was filtered with 15 µm Bekispor® filter to remove gel particles, cast on a glass plate with a 0.3 mm casting knife and put in a nitrogen box for one week. After most NMP was evaporated, the membranes were removed from the glass plate by immersing them in a milliQ water bath. The membranes were washed for 3 days in milliQ water, dried for 4 days at 60 °C under a nitrogen atmosphere and finally the membranes were put in a vacuum oven at 30 °C for about 10 days to remove last traces of solvent.

3.2.2.2. Chitosan membranes

Chitosan membranes were prepared by making an aqueous solution of 3.0 wt% chitosan, 6.0 wt% acetic acid and 91.0 wt% ultrapure water. The mixture was stirred at 70 °C until most chitosan particles were dissolved. The solution was filtered with a 25 µm Bekispor ® filter, casted on a polyoxymethylene (POM) plate with a 2 mm casting knife and put in an oven at 30 °C. After 24 hr the membranes were removed from the oven and carefully poured from the POM plate. Here after the membranes were treated for 24 hr in a 0.8 M NaOH in 50/50 (v/v) ethanol/ultrapure water

solution to make the membranes insoluble in water. Finally the membranes were washed in ultrapure water for several days and dried under ambient conditions. The acetic acid used for solution preparation protonates the $-\text{NH}_2$ group in the chitosan and solubilizes the polymer. To make the chitosan membranes insoluble in water, the membranes are treated with NaOH, which deprotonates the $-\text{NH}_3^+$ group again [24]. This is the standard procedure for the preparation of chitosan membranes [20]. However, membranes made according to this procedure were only used for preliminary swelling experiments as NaOH treatment did not provide sufficient mechanical stability in the case of the SPEEK-chitosan composite membranes, as will be discussed in the next part.

3.2.2.3. Composite membranes

For the SPEEK/chitosan composite membranes the same SPEEK solution as described earlier was prepared. The SPEEK solution was cast on a glass plate with a 0.3 mm casting knife and placed in a nitrogen box for at least 7 days to evaporate most NMP. Chitosan solution was prepared by dissolving 1.5 wt% chitosan and 3.0 wt% acetic acid in water at 40 °C. After filtering the solution with a 25 μm Bekispor ® filter, the solution was cast with a 2 mm, 1 mm or 0.25 mm casting knife over the SPEEK layer and the samples were put in an oven at 30 °C for 24 hr. Next day, the double layer membrane was cut from the glass plate and crosslinked for 24 hr in an acetone solution containing 3.0 wt% glutaraldehyde solution (containing 50 wt% H_2O) and 0.5 wt% H_2SO_4 (Figure 3.3). After crosslinking, the membranes were washed in milliQ water for several days and then dried under ambient conditions. Here the membranes were treated with glutaraldehyde crosslinking solution instead of with NaOH. SPEEK/chitosan composite membranes treated with NaOH showed no adhesion between the chitosan and the SPEEK film. Consequently, the chitosan layer could easily be removed from the SPEEK film. To solve this we treated the membranes with a glutaraldehyde solution instead [17].

To compare the results of the composites and to omit the effect of glutaraldehyde crosslinking solution, SPEEK and chitosan films were also

treated individually for 24 hr in acetone solution containing 3.0 wt% glutaraldehyde solution (containing 50 wt% H₂O) and 0.5 wt% H₂SO₄. Since glutaraldehyde is a known crosslinker for chitosan making the material insoluble in water, these membranes were not treated with an alkali solution. Figure 3.3 represents the crosslinking mechanism of chitosan by glutaraldehyde in an acidic environment (e.g. H₂SO₄). Chitosan is crosslinked on its amine groups that react with the aldehyde groups of glutaraldehyde to form imine bonds. Since glutaraldehyde is dialdehyde, both ends can react with different amine groups of chitosan forming crosslinked chitosan. These membranes were only used for swelling, FT-IR and TGA measurements, but not for the permeation experiments. In the permeation experiments only SPEEK/chitosan membranes (prepared according to the procedure described above) and SPEEK membranes cast from NMP but without the treatment of the chitosan crosslinking solution were applied.

Figure 3.3: Crosslinking mechanism of chitosan with glutaraldehyde in an acidic environment [25].

3.2.3. SEM

Scanning electron microscope (SEM) type Jeol JSM-6010LA and Jeol JSM-5600LV were deployed to make high magnification images of the membrane. Samples were made by squeezing the membrane sample in a holder, immersing these in liquid nitrogen and then fracturing the protruding part above the holder with tweezers. Before use, the samples were dried at 30 °C for at least 24 hr in a vacuum oven. The samples were not sputtered with gold as they were highly conductive by themselves.

3.2.4. Thermal properties

To determine the thermal stability of the membranes measurements in a PerkinElmer TGA (TGA 4000) were performed. Samples of 5~10 mg were heated in a nitrogen atmosphere from 30 °C to 900 °C with a temperature increment of 20 °C/min.

3.2.5. FTIR

FTIR spectra were taken using a Bruker Alpha FT-IR spectrometer with a diamond crystal. Before the measurement the crystal was cleaned with ethanol, then the membrane was secured in the setup and the measurement was performed.

3.2.6. Swelling measurements

The membrane samples were pre dried for at least 2 days at 30 °C in a vacuum oven to determine the dry weight. Then the samples were immersed in liquid ultrapure water, methanol or DMC and their weight increase over time was measured. This was done by carefully drying the sample on both sides with tissue paper before measuring the weight. The swellings degree was determined according to the following formula:

$$SwD = \left(\frac{M_{\infty} - M_{\text{polymer,dry}}}{M_{\text{polymer,dry}}} \right) \cdot 100\% \quad (3.1)$$

Where M_{∞} [g] is the equilibrium mass of the polymer sample and the absorbed solution and $M_{\text{polymer,dry}}$ [g] is the dry weight of the membrane.

3.2.7. Dehydration measurements

Dehydration measurements were performed in the setup described earlier by Metz et al. [26] and Sijbesma et al. [8] with the modifications of Potreck et al. [9] and Reijerkerk et al. [11]. In this setup H_2O and CO_2 permeabilities of membranes can simultaneously be detected for different water vapor activities and temperatures. In this setup CO_2 is humidified to the desired water vapor activity by mixing a dry CO_2 stream (activity = 0) with a wet CO_2 stream (activity = 1) in the desired ratios. Before entering the membrane cell, the humidified CO_2 stream passes a dew point mirror (Mitchell instruments) to determine the water vapor activity of the feed. Entering the cell CO_2 and H_2O partly diffuse through the polymeric membrane, the rest leaves the cell as retentate through a bubble flow meter to determine the flow. Permeated H_2O and CO_2 are swept with helium (30 ml/min, 1 bar), pass again a dew point meter and leave the setup via a gas chromatograph and bubble flow meter. The measured H_2O permeabilities were corrected for the effect of cell design and concentration polarization described in more detail by Sijbesma et al. [8] and Metz et al. [26]. Table 3.1 gives the operating conditions of the dehydration experiments.

Table 3.1: Operating conditions dehydration setup.

Parameter	Value	Unit
Temperature	50	°C
H_2O activity	0.5-0.85	-
Feed flow CO_2	300	ml/min
Feed pressures	2.5	bar
Sweep flow He	30	ml/min
Permeate pressure	1	bar

Both SPEEK membranes cast from the solvent NMP and SPEEK membranes with a chitosan layer on top of that (three different thicknesses) were measured. The membranes were prepared according to the procedure described above, however, in contrast to the

SPEEK/chitosan membranes, the SPEEK membranes were not treated with the glutaraldehyde/H₂SO₄/acetone solution that is used for crosslinking of the chitosan layer.

3.3. Results and discussion

3.3.1. SEM

Figure 3.4 represents the cross section of the composite membrane with on the left hand side the chitosan layer and on the right hand side the SPEEK layer. There seems to be a third layer on top of the SPEEK layer. However, this is an artifact due to the edge effect and caused by charging of the material which can occur when the material is not gold sputtered. Evident from the picture is the successful preparation of a double layer SPEEK/chitosan membrane with a good adhesion between both layers. For this adhesion the crosslinking step is crucial. Figure 3.5 represents the result of a composite treated with only NaOH solution instead of treating it with the glutaraldehyde crosslinking solution. This figure shows that the adhesion between SPEEK and chitosan is poor. For the alkali treated composite, the chitosan layer swells substantially more in water than the SPEEK layer. When the membrane is dry, one can easily pull off the chitosan layer. For the composite treated with crosslinking solution we do not observe this behavior. Instead the material seems to swell uniformly in water.

The difference in adhesion depends on two factors: electrostatic interaction between both polymers and interpenetration of chitosan in SPEEK. The electrostatic interaction between SPEEK and chitosan is caused by interaction of the $-\text{SO}_3^-$ groups of SPEEK and the $-\text{NH}_3^+$ groups in chitosan. The negatively charged $-\text{SO}_3^-$ group interacts with the positively charged $-\text{NH}_3^+$ group due to their opposite charge, forming an electrostatic interaction and enforcing the binding between SPEEK and chitosan. This electrostatic interaction does not occur when treating the composite with an alkali solution. During the preparation of the chitosan solution, the polymer dissolves in an aqueous acetic acid solution. Acetic acid protonates the $-\text{NH}_2$ group of chitosan, making chitosan soluble in water. When treating the composite with an alkali solution (e.g. NaOH),

chitosan is regained by deprotonating the amine again. However, treating the composite with a crosslinking solution, $-\text{NH}_3^+$ groups are still present in the chitosan layer. As a result chitosan and SPEEK can only show electrostatic interaction with each other when treating the composite with the crosslinking solution. The interpenetration of chitosan in SPEEK occurs when chitosan solution is cast on top of the SPEEK film. Since chitosan is dissolved in water, chitosan will partly penetrate into the SPEEK layer upon swelling of SPEEK while in contact with the chitosan solution. Treating the composite with a glutaraldehyde crosslink solution results in the formation of crosslinks between penetrated chitosan and free chitosan, resulting in an improved adhesion between SPEEK and the chitosan layer. Both theories are supported by Wang et al. [27], who proofed that chitosan can form interpenetrating networks with other polymers and also showed that the $-\text{NH}_3^+$ group of chitosan can form electrostatic interactions with negative side groups of the opposing polymers.

Figure 3.4: SEM images of the cross section of glutaraldehyde treated composite (M32) (magnification: 900 x).

Figure 3.5: SEM images of the cross section of NaOH treated composite (magnification: 1400x).

Table 3.2 shows that the theoretical thicknesses for SPEEK and chitosan are in good agreement with the experimental thicknesses. The experimental thickness in Table 3.2 is the thickness as determined using the SEM and equals the dry thickness of the composite membrane. According to Zhong et al. [17] manipulating the chitosan thickness affects the methanol diffusion such that a thicker chitosan layer results in a lower methanol diffusion. So in principle, a thicker chitosan layer would be preferred, but the question rises how this affects the dehydration performance of the membrane. Therefore we vary the chitosan layer thickness such that there is a clear distinction between the layer thicknesses of chitosan in the SPEEK/chitosan composite membranes.

Table 3.2: Thickness of the casting knife used, the theoretical membrane thickness calculated based on solution concentrations and the final dry thickness of the ultimate SPEEK layer and chitosan layer in the composite membranes based on SEM images. Membranes are named after the chitosan thickness in the composite.

Membrane	SPEEK			Chitosan		
	$l_{\text{casting knife}}$ [μm]	$l_{\text{theoretical}}$ [μm]	$l_{\text{experimental}}$ [μm]	$l_{\text{casting knife}}$ [μm]	$l_{\text{theoretical}}$ [μm]	$l_{\text{experimental}}$ [μm]
M4	300	45	39 ± 4	250	4	4 ± 0
M17	300	45	37 ± 5	1000	15	17 ± 3
M32	300	45	39 ± 6	2000	30	32 ± 6

3.3.2. FTIR

Figure 3.6 shows the FTIR results of the composite membrane. It indicates a clear difference between both sides of the film. The bottom side (SPEEK side) is in good agreement with that of glutaraldehyde treated SPEEK as its spectrum exactly matches that of SPEEK. Peaks at 1077 cm^{-1} and 1021 cm^{-1} are assigned to the sulfonic acid groups characteristic for SPEEK and the absorbance at 1489 cm^{-1} is related to the aromatic C-C bond of PEEK [28, 29]. The top side of the composite (chitosan side) corresponds with that of crosslinked chitosan. A peak at 1632 cm^{-1} assigned to --C=N-- is evident proof that the top layer in the composite is indeed crosslinked chitosan [30]. This bond is a product of the reaction between the --C=O group of glutaraldehyde and the --NH_2 group of chitosan [25, 31]. In the case of non-crosslinked chitosan an overlapping peak appears at 1643 cm^{-1} , but this is related to the --NH_2 group [30].

FTIR distinguishes the presence of two different layers in the composite, one corresponding with glutaraldehyde treated SPEEK and the other with crosslinked chitosan. Based on these results and the results from the SEM images, we conclude that SPEEK and chitosan are intact in the composite as a separate layer and we successfully developed a double layer SPEEK/chitosan composite membrane.

Figure 3.6: FTIR of the composite membrane (bottom and top side) and the glutaraldehyde treated SPEEK and crosslinked chitosan films.

3.3.3. TGA

In order to use these membranes in a membrane reactor a high thermal stability ($> 200\text{ }^{\circ}\text{C}$) is desired due to the imposed reaction conditions. For instance, Aresta et al. [32] and Hofmann et al. [33] found a maximum CO_2 conversion towards DMC for a CeO_2 catalyst at temperatures between $135\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. In order to use polymeric membranes in membrane reactors the membrane should therefore be stable up to at least $200\text{ }^{\circ}\text{C}$.

Figure 3.7 shows the thermal degradation of the composite membranes SPEEK and crosslinked chitosan. The figure shows that the composite membranes are thermally stable up to $220\text{--}230\text{ }^{\circ}\text{C}$ and are therefore well suited to be used in membrane reactors. The start of the degradation is independent of the chitosan thickness and coincides with the degradation of crosslinked chitosan. The thermal degradation profile of the composite membranes predominantly follows that of glutaraldehyde treated SPEEK since it is most present in all three samples. The first degradation ($250\text{--}400\text{ }^{\circ}\text{C}$) is dedicated to the splitting-off of sulfonic groups of SPEEK and the second degradation ($400\text{--}600\text{ }^{\circ}\text{C}$) is due to the decomposition of the main chain of PEEK [28, 34]. However, between $200\text{--}400\text{ }^{\circ}\text{C}$, the composite membranes lose relatively more mass than glutaraldehyde treated SPEEK. This relates to the thermal decomposition of the backbone of crosslinked chitosan that according to Figure 3.7 starts to decompose around $220\text{--}230\text{ }^{\circ}\text{C}$. Also the thicker the chitosan layer becomes, the more the degradation profile corresponds to that of crosslinked chitosan. Since M32 contains a relatively higher fraction of chitosan than M4, the effect of the decomposition of chitosan becomes more pronounced. Based on these observations the thermal degradation of the composite membrane is the product of both SPEEK and chitosan. However, thermal degradation starts when the least thermally stable material (crosslinked chitosan) starts to decompose, which is still at high enough temperatures to allow the use in a membrane reactor for the direct conversion of CO_2 into DMC.

Figure 3.7: Thermal degradation profiles of the composite membranes and glutaraldehyde treated SPEEK and crosslinked chitosan films.

3.3.4. Swelling measurements

Figure 3.8 shows the swelling degree in water, methanol and DMC of the different membranes. An increasing chitosan layer thickness on top of the SPEEK layer results in an increasing degree in water swelling, whereas the swelling degree in methanol and DMC stays constant. Compared to a pure SPEEK film, the composite membranes show increased water and DMC swelling, while the methanol swelling remains constant or even shows a slight decrease. Zhong et al. [17] also measured the water swelling for SPEEK/chitosan composites and also observed an increasing water uptake upon the addition of a layer of chitosan. However, due to the use of a higher degree of sulfonated SPEEK ($SD = 78\%$), the water swelling was already relatively high and the effect of the additional chitosan layer was less pronounced compared to our results. For the methanol uptake Zhong et al. [17] noticed a decreasing trend when the chitosan layer thickness increased, whereas we observe a constant swelling degree. Since Zhong et al. [17] worked with SPEEK with a sulfonation degree of 78% , methanol uptake is higher ($48.2 \text{ wt}\%$). As Figure 3.8 shows methanol uptake in chitosan is around $30 \text{ wt}\%$, and consequently in the case of Zhong et al. [17] an additional chitosan layer will decrease the methanol uptake resulting in a decreasing trend with increasing thickness.

The DMC swelling in the composite membranes is more comparable to that of crosslinked chitosan than to that of SPEEK. Remarkably, all

glutaraldehyde treated membranes show an enhanced DMC swelling in comparison to the membranes that are not treated with a glutaraldehyde solution. This suggests that glutaraldehyde affects the swelling behavior for DMC. Wang et al. [35] observed for glutaraldehyde crosslinked PVA membranes an increased methanol/DMC swelling when they increased the glutaraldehyde content. They suggested that the unreacted aldehyde groups from glutaraldehyde promote the swelling. Rather surprising is the increased water swelling of crosslinked chitosan compared to non-crosslinked chitosan. One would expect a decreasing water uptake after crosslinking [36]. However, it is not uncommon to observe an increasing water swelling when crosslinking a polymer with glutaraldehyde [25, 37, 38]. In our results we devote the increasing water swelling to the fact that chitosan is treated with an alkali solution and crosslinked chitosan is not. Therefore in chitosan the $-\text{NH}_3^+$ group is deprotonated to $-\text{NH}_2$, but in crosslinked chitosan the $-\text{NH}_3^+$ group can still be present. Due to this $-\text{NH}_3^+$ group, crosslinked chitosan attracts more water resulting in an increased water swelling.

Figure 3.8: Swelling degree in H₂O, methanol and DMC of SPEEK, glutaraldehyde treated SPEEK, chitosan, crosslinked chitosan and the composite membranes M4, M17 and M32.

3.3.5. Dehydration experiments

Dehydration measurements with the developed membranes were performed. In contrast to the SPEEK/chitosan membranes, pure SPEEK membranes were used as obtained after casting from NMP and subsequent drying and washing with water. In contrast to the SPEEK/chitosan membranes, these pure SPEEK membranes were thus not treated with the glutaraldehyde/H₂SO₄/acetone solution used for crosslinking of the chitosan layer in the SPEEK/chitosan membranes. Although at first sight this may look as not appropriate, this approach was chosen for practical reasons. The SPEEK membranes are cast using NMP as solvent. Some residual NMP will remain in the membrane, even after very thorough washing (see next chapter). The N-atom in the solvent can carry a slightly positive charge and interact with the negatively charged SO₃⁻-entity in SPEEK. This decreases the degree of sulfonation by shielding the SO₃⁻-moiety resulting in a lower effective degree of sulfonation. This residual NMP can be removed by a thorough wash with a strong acidic solution. Although the solution used for crosslinking of the chitosan layer contains only 0.5 wt.% H₂SO₄, it is slightly acidic. In the case of chitosan, this acid is used for the crosslinking reaction, and to a little extent this may also be present for possible exchange of NMP. In case also pure SPEEK would be treated with this crosslinking solution, the situation would be different. As no crosslinking occurs in that case, all acid would be available for NMP exchange, which could lead to a difference in the effective degree of sulfonation of SPEEK in the pure SPEEK membrane and that in the SPEEK/chitosan membrane. This would not allow a fair comparison. Therefore we decided not to treat the pure SPEEK membrane with the crosslink solution. To support the chosen approach and validate the effect of the crosslinking procedure on the degree of sulfonation in the samples, the effective degree of sulfonation of pure SPEEK and SPEEK with a 4 μm chitosan layer crosslinked in acidic glutaraldehyde was determined. In both cases equal effective degrees of sulfonation of both the pure SPEEK membrane and the SPEEK in the SPEEK/chitosan membrane were found. In other words, the crosslinking procedure did not change the degree of sulfonation of the SPEEK layer significantly and it allows fair comparison of the permeation data of all samples.

Figure 3.9 shows the H_2O vapor permeability as a function of the water vapor activity for SPEEK and the composite membranes with increasing chitosan layer thickness. Pure chitosan measurements could not be performed due to the tremendous swelling in water, these membranes are mechanically not strong enough for the dehydration experiments. Total membrane thicknesses (SPEEK+chitosan layer together) to calculate the permeability are measured using a screw micrometer. These measurements are done prior to the dehydration experiments, when the membranes are air dried. The H_2O vapor permeability is relatively high for both SPEEK and the composite membranes, due to the high hydrophilicity of the material, and the high solubility (high critical temperature) and high diffusivity (small kinetic diameter) of water [11]. In comparison to SPEEK with higher degrees of sulfonation ($\text{SD} = 60\%$), the obtained permeabilities are relatively low [8], which we devote to the lower degree of sulfonation leading to lower swelling degrees. SPEEK shows increasing water vapor permeability with water vapor activity. A detailed analysis performed by Potreck et al. [23] showed that this can be devoted to an increase in solubility and diffusivity. For the composite membranes we observe similar behavior as for SPEEK and therefore we expect a similar effect occurring in the composite membranes especially due to the large fraction of SPEEK present in the composite.

Figure 3.9: H_2O vapor permeability of native SPEEK and the composite membranes with different chitosan layer thicknesses as a function of the water vapor activity at $50\text{ }^\circ\text{C}$ and 2.5 bar in a $\text{H}_2\text{O}/\text{CO}_2$ mixture. Values normalized for total membrane thickness ($1\text{ Barrer} = 10^{-10}\text{ cm}^3(\text{STP})\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$).

The addition of a layer of chitosan promotes the water vapor permeability tremendously and the composite membranes show significantly higher water vapor permeabilities than the native SPEEK membranes. Increasing the chitosan layer thickness even slightly improves the dehydration capacity further. This is predominantly due to the thickness normalization to calculate permeabilities to allow a fair comparison as the composite membranes are thicker than the native SPEEK films due to the additional chitosan layer. As the chitosan layer thickness increases the relative contribution of chitosan to the overall permeability of the composite membrane increases. Figure 3.8 clearly shows that chitosan has an exceptionally high water swelling degree, much higher than SPEEK. This will translate into the permeability and as such the water vapor permeability increases with increasing chitosan layer thickness. Figure 3.10 eliminates the normalization and expresses the flux in terms of the permeance.

Figure 3.10: H₂O vapor permeance (1 GPU = 10⁻⁶ cm³(STP)/(cm²·s·cmHg)) as a function of the water vapor activity at 50 °C and 2.5 bar in a H₂O/CO₂ mixture of native SPEEK and composite membranes with different chitosan layer thicknesses.

Kurek et al. [39] observed a similar effect for a chitosan layer coated on polyethylene (PE) films. Pure PE films were impermeable for water vapor. When a chitosan layer was applied on top of the same PE film, especially at higher water vapor activities, significant water vapor permeation through the composite films was observed. Kurek et al. related this to the

fact that the hygroscopic chitosan layer acts as a so-called water reservoir. They consider it likely that this increases the amount of water (driving force) at the interface of the PE layer, thus increasing the permeability of water vapor through the PE film. The same effect can play a role here. In addition another effect may play a role. Figure 3.10 shows that also in terms of the water vapor permeance the composite membranes still outperform the SPEEK film with a thickness of 40 μm (40 μm is the thickness of the SPEEK layer of the composite membrane, see Table 3.2). Figure 3.10 indicates that the dehydration capacity of the composite membranes is more comparable to that of thinner SPEEK films. As discussed before the composite membranes consist of a chitosan and a SPEEK layer. At the interface between both layers, both layers will interfere and as a consequence of the preparation method, chitosan will predominantly diffuse into the SPEEK layer. This results in a mixed chitosan/SPEEK layer at the interface between both layers. This interpenetration of chitosan in SPEEK results in higher water vapor permeances of this layer compared to SPEEK. In addition, the actual pure SPEEK thickness decreases, thus decreasing its resistance to mass transfer. We hypothesize that the higher dehydration capacity of the composite membrane is because of the lower mass transfer resistance of chitosan compared to that of SPEEK. The fact that for the composite membranes an increasing chitosan layer thickness has only very little influence on the water vapor permeation (Figure 3.10) supports this hypothesis.

Figure 3.11 shows the CO_2 permeability as a function of the water vapor activity for SPEEK and the composite membranes with various chitosan thicknesses. The CO_2 permeability is much lower than the water vapor permeability and in the order of 0.2~2.2 Barrer. The trends observed in the permeability are also visible in the permeance data, indicating that also for CO_2 the mass transfer rate of the SPEEK layer predominantly determines the CO_2 transport through the composite membranes. Differences in the permeability are rather small, but a small effect of the chitosan layer is visible as lower permeabilities are measured for thicker chitosan layers. Despond et al. [21] showed already that the CO_2 permeability of chitosan is very low in humid conditions, an order 10 ~ 20

lower than we measured for SPEEK. This supports our observation that adding a layer of chitosan decreases the CO₂ permeability. The measured CO₂ permeabilities are in good agreement based on what could be expected for gas permeation through SPEEK membranes under humid conditions [8, 40].

For all membranes we observe an increasing CO₂ permeability with water vapor activity. An increase in gas permeation with increasing water activity is observed by others as well and can be attributed to water vapor induced relaxation and plasticization phenomena [8, 14, 23, 41].

Figure 3.11: CO₂ permeability of dry native SPEEK and composite membranes with different chitosan layer thicknesses as a function of the water vapor activity at 50 °C and 2.5 bar in a H₂O/CO₂ mixture. Permeabilities normalized for total dry membrane thickness.

Figure 3.12 shows the H₂O/CO₂ selectivity as function of the water vapor activity for SPEEK and the composite membranes. The composite membranes are significantly more selective towards water vapor permeation than native SPEEK, sometimes even almost an order of magnitude. This is due to the higher water vapor permeability and also lower CO₂ permeability of the SPEEK/chitosan composites. Since the CO₂ permeability is already low, a small decrease in the permeability results into much higher selectivities. Increasing the water vapor activity has a strong negative effect on the composite membrane selectivity due to the stronger increase in CO₂ permeability than in water vapor permeability, caused by water vapor induced relaxation and plasticization phenomena [8,

14, 23, 41]. Nevertheless the selectivity of the composite membranes still exceeds that of SPEEK.

According to Figure 3.12 a thicker chitosan layer on top of SPEEK is much more beneficial for the selectivity, which is not that evident from our earlier results. This is due to the decrease CO_2 permeability of the composite membranes with increasing chitosan thickness (Figure 3.11). Although the absolute values of this decrease are small at such low permeabilities, this effect is reflected in the selectivity.

Figure 3.12: $\text{H}_2\text{O}/\text{CO}_2$ selectivity as function of the water vapor activity for SPEEK and the composite membranes with increasing chitosan thickness.

Overall this work shows that the addition of a layer on top of a selective membrane material does not have to have a negative effect on the permeability of in our case water vapor. This approach allows reducing the permeation of undesired components (in our case CO_2), while at the same time increasing the permeability of the desired component. With this work, where we developed SPEEK/chitosan composite membranes, we showed this concept. Due to the interpenetration of chitosan in SPEEK we enhance the dehydration capacity. Meanwhile, we show that we can decrease the CO_2 permeability and others [17] proved the same accounts for the methanol cross over. Overall this means that we have created a promising membrane that has desired properties required for the use in a membrane reactor for the direct conversion of CO_2 and methanol into DMC and H_2O .

3.4. Conclusions

In this work we developed a double layer SPEEK/chitosan composite membrane for use in a catalytic membrane reactor for the direct conversion of CO₂ and methanol into dimethyl carbonate (DMC). To shift the reaction equilibrium to the product side, the membrane should have a very high water vapor permeability and correspondingly high H₂O/CO₂ selectivity. We designed a double layer SPEEK/chitosan composite membrane and tailored its properties towards this application. The results show that the properties of both individual polymers remain present in the composite. The thermal stability measurements show that the material is stable up to 220 °C and consequently should be capable to withstand the extreme conditions in membrane reactors.

Binary water vapor/CO₂ permeation experiments show that the addition of a layer of chitosan on top of SPEEK reduces CO₂ to permeate meanwhile promoting water vapor permeation. These changed permeabilities as a consequence of the addition of the chitosan layer results in much higher H₂O/CO₂ selectivities compared to native SPEEK. It shows that by introducing a different selective layer on top of another selective material we can play with the properties of the final membrane. Here we show that by introducing chitosan on top of SPEEK we can improve the water vapor permeability meanwhile decreasing the CO₂ permeability. Overall this means we designed a membrane that has all the promising properties for use in a membrane reactor for the direct conversion of CO₂ and methanol into DMC.

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Chapter 4

The effect of the type of counter ion on the dehydration performance of sulfonated poly(ether ether ketone)

Abstract

Sulfonated poly(ether ether ketone) (SPEEK) is sulfonated high performance polymer with a negatively charged SO_3^- -moiety attached to its backbone. This charge is compensated by a mobile counter ion, usually a proton. SPEEK is a promising membrane material for dehydration applications in e.g. membrane reactors. Membrane reactors are beneficial for equilibrium limited reactions and the selective removal of reaction products, e.g. water vapor, from the reaction mixture can enhance the conversion. Many membrane reactor applications operate at high temperatures. To improve the thermal stability of SPEEK, literature proposes the exchange of the proton as counter ion by other counter ions.

This work describes the influence of different mono- (H^+ , Li^+ , Na^+ , K^+), di- (Ca^{2+}) and trivalent (Al^{3+}) counter ions in SPEEK on the thermal stability, dehydration capacity and $\text{H}_2\text{O}/\text{CO}_2$ selectivity of the membrane. This work shows that in general the exchange of the counter ion by cations other than protons results in thermal stabilities up to 450-500 °C. The water vapor sorption increases with increasing cation hydration enthalpy. Further, the water vapor and CO_2 permeability increase with increasing water vapor activity, but decrease with increasing cation hydration enthalpy. We hypothesize that the latter can be devoted to the increase in the formation of cation-water clusters that hinder the permeation of water vapor and CO_2 and the strong water-cation and CO_2 -cation interactions, which result in a worse desorption and thus decreasing permeability of both components. Nevertheless, also other parameters that affect the permeation do play a role, e.g. cation-anion interactions and the formation of ionic crosslinks between the $-\text{SO}_3^-$ group of SPEEK and di- or trivalent charged cations.

4.1. Introduction

Sulfonated poly(ether ether ketone) (SPEEK) (Figure 4.1) is a widely investigated polymer in the field of membranes and has potential applications in nanofiltration [1, 2], proton exchange membrane (PEM) fuel cells [3], gas separation [4] and flue gas dehydration [5, 6].

Figure 4.1: Structural formula of sulfonated poly(ether ether ketone) (SPEEK) with 1-x the degree of sulfonation.

SPEEK is a polymer with high application potential, but its use in high temperature applications is restricted by its limited thermal stability (during thermo-gravimetric analysis the material starts to seriously deteriorate at ~ 250 °C [3]). Nevertheless, there are several high temperature applications for which SPEEK could be used, such as high temperature fuel cells [7] or membrane reactors [8]. As Figure 4.1 indicates, SPEEK is a negatively charged material due the presence of $-\text{SO}_3^-$ groups. Consequently, it contains positively charged counter ions, usually protons (H^+), for electro-neutrality reasons. To improve the thermal stability of SPEEK, literature suggests replacing the H^+ counter ion of the $-\text{SO}_3^-$ group in SPEEK by another cation. For Nafion [9], sulfonated poly (styrene-isobutylene-styrene) (SIBS) [10], sulfonated poly(ether ketone ketone) (SPEKK) [11] and SPEEK [12-14] this proofed to increase the thermal stability of the polymer during thermo-gravimetric analysis (TGA). For SPEEK the exchange of H^+ for Na^+ resulted in an improved thermal stability as determined during TGA from 275 °C up to 500 °C [12]. Koziara et al. [12] and Zaidi et al. [15] proofed that for SPEEK with H^+ as counter ion the thermal degradation during TGA starts with the degradation of the $-\text{SO}_3^-$ group present in SPEEK (desulfonation). Koziara et al. [12] showed that by replacing H^+ by Na^+ the degradation of the $-\text{SO}_3^-$ group shifts to higher temperatures (~ 500 °C) and coincides with the degradation of the PEEK backbone. They explain the observed difference in degradation for H^+ and Na^+ containing SPEEK by the possible replacement of the $-\text{SO}_3^-$ group by

H^+ , leading to the creation of an intermediate when $-\text{SO}_3^-$ leaves the aromatic ring. Due to the formation of this intermediate when H^+ is present as counter ion, the desulfonation of SPEEK can occur at lower temperatures. Since other counter ions (e.g. Na^+) cannot insert into the aromatic ring to create an intermediate, the desulfonation for materials containing these counter ions is shifted to higher temperatures, making SPEEK more thermally resistant [12].

Due to the hydrophilic nature of SPEEK, this polymer is a very promising dehydration material for e.g. flue gas dehydration [6] or for membrane reactors for which permeation of hydrophilic reaction products (such as water and alcohols) helps to prevent an equilibrium to establish [8]. Especially when equilibrium limited reactions are considered, the use of membrane reactors can improve the yield [16], for example the direct conversion of CO_2 into dimethyl carbonate (DMC) [8]. The combination of the reactor and the membrane in one unit operation allows the immediate selective removal of (at least) one reaction product (e.g. H_2O), thus shifting the reaction to the product side. Often, such membrane reactors are operated at higher temperatures. When SPEEK membranes with their hydrophilic character and high water vapor permeability are applied under these challenging conditions, not only the catalyst, but these membranes need to be able to withstand these higher temperatures as well. To enhance the thermal stability of SPEEK towards reactor conditions, the exchange of H^+ for other counter ions is an interesting approach. However, the effect of the type of counter ion on the water vapor sorption and water vapor permeability of SPEEK is unknown. Although some studies [5, 17] have shown that other counter ions (e.g. Na^+) improve the water vapor permeability in SPEEK (to be discussed in detail in the next chapter), no elaborate study has been performed that investigates in detail how the water vapor permeation in SPEEK is affected by the nature of the counter ion. Therefore the aim of this work is to perform an elaborate study that systematically examines and discusses the effect of different mono- (H^+ , Li^+ , Na^+ , K^+) di- (Ca^{2+}) and trivalent (Al^{3+}) counter ions on the thermal stability, the water vapor sorption capacity and the dehydration performance of SPEEK. Additionally, the effect of the counter ion on the

CO₂ permeability is obtained, since one of the potential applications of SPEEK is in the membrane reactor based production of dimethyl carbonate from CO₂.

4.2. Theory

The effect of the nature of the counter ion on water vapor mass transport through SPEEK films has been studied by different investigators. Jia et al. [5] and Wang et al. [17] showed that the exchange of counter ions has a large effect on the dehydration capacity of SPEEK. Jia et al. [5] showed that the water vapor permeability decreases in the order $\text{Na}^+ > \text{H}^+ > \text{Fe}^{3+} > \text{Cu}^{2+}$. They argue that SPEEK with Cu^{2+} or Fe^{3+} as counter ion has a lower dehydration capacity because these cations form ionic crosslinks with the sulfone group ($-\text{SO}_3\sim\text{Cu}\sim\text{SO}_3-$) that hinder water diffusion. Meanwhile, for the N₂ permeability they observed the opposite trend ($\text{Fe}^{3+} > \text{Cu}^{2+} > \text{H}^+ > \text{Na}^+$), which is according to Jia et al. [5] caused by the presence of more free volume created by the more voluminous counter ions (Cu^{2+} , Fe^{3+}) [5]. Both Jia et al. [5] and Wang et al. [17] measured an increased dehydration capacity when exchanging H^+ for Na^+ , suggesting that the exchange of counter ions can also improve the dehydration performance. The reason for this observation was not discussed. Furthermore, the effect of other counter ions was not investigated.

Khan et al. [4] performed a more elaborate study on the effect of the type of counter ion on the CO₂, CH₄ and N₂ permeability in SPEEK. However, this study was done under dry conditions in the absence of water. This study provides a better insight in the effect of counter ions during the transport of gasses through SPEEK for gas separation purposes, but does not necessarily provide any fundamental insight in the effect of counter ions on the behavior of SPEEK in membrane reactors in which water is produced or in gas dehumidification. Khan et al. [4] found that the gas permeability decreases with increasing atomic radius of the counter ion, caused by the increased steric hindrance, and increasing charge of the counter ions, due to the formation of ionic crosslinks with $-\text{SO}_3^-$ [4]. Interestingly, this observed trend is opposite to the trend reported by Jia et al. [5] for N₂ permeability. This suggests that humid conditions do affect

the effect of the type of counter ion on mass transfer in SPEEK. Quezado et al. [18] also showed this for Nafion and discussed that water can influence the cation-anion interaction in two ways:

- Water can insert between the $-\text{SO}_3^-$ group (anion) and the cation.
- Water can attach to the cation/anion without disrupting the cation-anion bond.

They noticed that when the water content increases, water inserts itself more and more between the $-\text{SO}_3^-$ group and the cation, dissociating the cation from the $-\text{SO}_3^-$ group [18]. This shows that the addition of water has a large influence on the anion-cation interactions, and as such, the presence of water directly influences the mass transfer properties, thus explaining the different behavior observed by Khan et al. [4] and Jia et al. [5].

Jalani and Datta [19] investigated how the nature of the counter ion affects the water vapor sorption in Nafion. Similar to Jia et al. [5] and Khan et al. [4] they concluded that, among others, the radius of the counter ions plays an important role, but also its charge density, the water hydration number and the hydration enthalpy. They observed that the smaller the cation, the higher the hydration energy and the water hydration number, and thus the more water Nafion can absorb. This suggests that the water vapor permeability is also influenced by similar parameters. Table 4.1 gives an overview of the ion radius, the surface charge density, the hydration enthalpy and the water hydration number of different counter ions. The surface charge density is a measure how eager the cations are to attract an electron. The hydration enthalpy ($\Delta H_{\text{hydration}}$) is the energy released when the cations bind water and the hydration number ($n_{\text{hydration}}$) is the amount of water molecules the cation can bind. Table 4.1 shows that for monovalent cations there is a strong correlation between the ion radius, the surface charge density, the hydration enthalpy and the water hydration number.

Table 4.1: Ion radius (r) [20], surface charge density, hydration enthalpy ($\Delta H_{\text{hydration}}$) [21] and water hydration number ($n_{\text{hydration}}$) [22] in pure water.

Ion	r	Surface charge density ^a	$-\Delta H_{\text{hydration}}$	$n_{\text{hydration}}$
	[Å]	[charge/ Å ²]	[kJ/mol]	[-]
Al ³⁺	0.53	0.85	4665	20.4
Ca ²⁺	1.00	0.16	1577	7.2
H ⁺			1091	2.7
Li ⁺	0.74	0.15	519	5.2
Na ⁺	1.02	0.08	409	3.5
K ⁺	1.38	0.04	322	2.6

^a The surface charge density equals the charge (z) of the cation divided by the spherical surface of the cation ($z/4\pi r^2$) [23].

4.3. Experimental

4.3.1. Materials

For the preparation of SPEEK membranes, SPEEK polymer granulate (fumion® E-800), IEC 1.25 (sulfonation degree = 40%), was obtained from Fumatech. N-methyl-2-pyrrolidinon (purity 99%), lithium chloride (purity 99%) and sodium chloride (purity 99.5%) were obtained from Acros organics. Calcium chloride (purity 97%) and aluminum nitrate (purity 98%) are purchased from Sigma Aldrich. Potassium chloride (purity 99.5%) was obtained from Fluka and hydrochloric acid (37 wt%) from Merck.

4.3.2. Preparation SPEEK membranes

SPEEK membranes were made according to the procedure of Potreck et al. [24]. First 15 wt% of SPEEK was dissolved overnight in N-methyl-2-pyrrolidinon (NMP) at 120 °C. The solution was filtered using a 15 µm Bekispor® filter. Subsequently, the solution was cast on a glass plate with a 0.3 mm casting knife and the plate was put under nitrogen flow for one week. After most NMP had evaporated, the membranes were removed from the glass plate by immersing them in a milliQ water bath. The membranes were washed for 3 days in milliQ water at room temperature and subsequently dried for 4 days at 60 °C under a nitrogen atmosphere.

Preliminary TGA measurements showed an additional decrease in weight for the membranes that were used as prepared (without any ion exchange step) compared to those that were treated with salt solutions to guarantee full exchange of the counter ion. We attribute this additional loss in weight to the loss of residual NMP (used as solvent for membrane preparation). To allow a fair comparison, all membranes were therefore treated with a salt solution to remove any residual solvent and assure the exchange of the counter ion by the desired one. To replace the counter ion, the SPEEK membranes were immersed in a 1L aqueous solution of 1M HCl (H^+), LiCl (Li^+), NaCl (Na^+), KCl (K^+), CaCl_2 (Ca^{2+}), or $\text{Al}(\text{NO}_3)_3$ (Al^{3+}) respectively for 24 hr. The solutions with the SPEEK films were put on a roller bench. After 24 hr the SPEEK membranes were removed from the exchange solution and extensively rinsed with milliQ water. Finally the SPEEK membranes were dried and stored at ambient conditions. The membranes are named after the counter ion that is present in SPEEK.

4.3.3. Thermo-gravimetric analysis (TGA)

To determine the thermal stability of the membranes, TGA measurements were performed using a PerkinElmer TGA 4000. Samples of 5~10 mg were heated in a nitrogen atmosphere from 30 °C to 900 °C with a temperature increment of 20 °C/min. It should be realized that this provides information on the thermal stability at dry conditions.

4.3.4. Sorption experiments

Water vapor sorption experiments were carried out using a gravimetric sorption balance (SGA-100 symmetric vapor sorption analyzer from VTI) as described by Potreck et al. [24]. Prior to the measurements the samples were put in a vacuum oven at 30 °C for at least 2 days. Before starting the measurement a sample (10-20 mg, ~30 μm thick) was placed in the sorption balance and additionally dried with nitrogen at 30 °C for 10 hr to remove any residual water. Finally, the dry weight of the sample was determined. Following this procedure, the samples were exposed to a fixed water vapor activity of 0.4, 0.6 or 0.8 ($T = 30\text{ }^\circ\text{C}$) and the mass uptake was measured over time. The water vapor concentration in the film (water

vapor cm³ STP/cm³ polymer) was calculated according to the following formula:

$$c_{\text{H}_2\text{O}} = \frac{(M_{\infty} - M_{\text{dry polymer}}) \cdot V_{\text{H}_2\text{O}}}{M_{\text{w,H}_2\text{O}} \cdot V_{\text{dry polymer}}} \quad (4.1)$$

Where M_{∞} [g] is the equilibrium mass of dry film with absorbed water at a certain water vapor activity, $M_{\text{dry polymer}}$ [g] is the initial dry weight of the film, $V_{\text{dry polymer}}$ [cm³] is the volume of the film in the dry state, $M_{\text{w,H}_2\text{O}}$ [18 g/mole] is the molar mass of H₂O and $V_{\text{H}_2\text{O}}$ (22,418 cm³) is the volume of 1 mole H₂O in the gas phase at 273.15 K and 1.013 bar.

4.3.5. Dehydration performance

Dehydration measurements were performed in the setup earlier described by Metz et al. [25] and Sijbesma et al. [6] with the modifications of Potreck et al. [26] and Reijerkerk et al. [27]. In this setup H₂O and CO₂ permeabilities of membranes as function of the water vapor activity and temperature can simultaneously be measured. In this setup, CO₂ is humidified to the desired water vapor activity by mixing a dry CO₂ stream (activity = 0) with a wet CO₂ stream (activity = 1) in the desired ratio. Before entering the membrane cell, the humidified CO₂ stream passes a dew point mirror (Mitchell instruments) to determine the water vapor activity of the feed. Upon entering the membrane cell CO₂ and H₂O partly dissolve in and diffuse through the polymeric membrane. The remaining CO₂ and water vapor leave the cell as retentate. Both the flow of the permeate and the retentate are determined using a soap bubble meter. The amount of permeated water vapor is measured using a dew point mirror. The CO₂ concentration was determined with an in line GC measurement. A water vapor stage cut between 1-5% was applied. Permeated H₂O and CO₂ were swept with helium (30 ml/min, 1 bar). The measured H₂O permeabilities were corrected for the effect of concentration polarization as described in more detail by Metz et al. [25] and Sijbesma et al. [6] to determine the actual membrane permeabilities and exclude the effect of cell geometry. For all counter ion exchanged membranes at least two

different membranes were measured. Table 4.2 summarizes the operating conditions during the dehydration experiments.

Table 4.2: Operating conditions of the dehydration setup.

Parameter	Value	Unit
Temperature	50	°C
H ₂ O activity	0.4-0.8	
Feed flow CO ₂	300	ml/min
Feed pressures	2.5	bar
Sweep flow He	30	ml/min
Permeate pressure	1	bar

4.4. Results and discussion

4.4.1. TGA experiments

Figure 4.2 shows the mass loss as function of the temperature of SPEEK with the different counter ions. Table 4.3 shows the degradation temperature when the membrane samples lost 5 wt% and 10 wt% of their initial weight.

Figure 4.2: Thermal degradation of SPEEK as received and SPEEK H⁺, Li⁺, Na⁺, K⁺, Ca²⁺ and Al³⁺.

Table 4.3: Thermal degradation temperature when the samples lost 5 wt% (T5%) and 10 wt% (T10%) of their initial weight.

Membrane	T5%	T10%
	[°C]	[°C]
SPEEK Al ³⁺	327	386
SPEEK H ⁺	346	366
SPEEK Ca ²⁺	467	535
SPEEK Li ⁺	471	534
SPEEK Na ⁺	473	522
SPEEK K ⁺	486	510

Figure 4.2 shows that the nature of the counter ion has a strong effect on the thermal stability of the polymer material. To guarantee a fair comparison, the SPEEK membranes as prepared using NMP as solvent were treated with the mentioned salt solutions to remove any residual solvent and to assure full exchange towards the desired counter ion. Except for SPEEK H⁺ and SPEEK Al³⁺ the exchange results in enhanced thermal stabilities up to 450-500 °C (Table 4.3). These results are in good agreement with previous observations [12-14]. SPEEK H⁺ (treated with HCl) shows a typical two step degradation profile, of which the first step is devoted to the loss of the -SO₃⁻ group (desulfonation) [12, 15] and the second step to the degradation of the PEEK backbone [3]. Compared to H⁺, other counter ions do not show a desulfonation step, which is according to Koziara et al. [12] caused by the fact that only H⁺ can replace the leaving sulfone group in the aromatic ring and create a stable intermediate. Since other cations cannot insert in the aromatic ring and form a stable intermediate, the sulfone group remains attached to the aromatic ring and the desulfonation is postponed to higher temperatures, resulting in a higher thermal stability [12].

The thermal degradation profile of SPEEK Al³⁺ deviates from all other counter ions. Remarkable is that SPEEK Al³⁺ does not show a typical desulfonation step, instead the mass loss decreases gradually. For Nafion Al³⁺ literature reports that Al³⁺ also decreases the thermal stability of the polymer [28, 29]. Sun and Thrasher [28] proofed that aluminum as strong Lewis acid catalyzes the reaction, thus breaking the ether bonds in Nafion,

forming a series of small fluorocarbon molecules. We hypothesize that Al^{3+} has a similar effect on SPEEK and catalyzes the degradation of the polymer, resulting in a lower thermal stability compared to the other cations.

4.4.2. Water vapor sorption

Figure 4.3 shows the water vapor sorption as function of the hydration enthalpy (Table 4.1) for SPEEK with various counter ions at different water vapor activities obtained at 30 °C. SPEEKs sorption is plotted as the amount of water vapor (cm^3) at standard temperature (273.15 K) and pressure (1 atm) that is absorbed per cm^3 polymer.

Figure 4.3: Water vapor sorption at 30 °C as function of the hydration enthalpy (Table 4.1) for water vapor activities of 0.4, 0.6 and 0.8.

Figure 4.3 shows there is a correlation between the water vapor sorption and the hydration enthalpy of the different cations. The higher the hydration enthalpy, the more water is absorbed in the SPEEK films. With increasing hydration enthalpy it becomes thermodynamically more favorable for a cation to absorb water, resulting in an increasing water vapor sorption. These results are in line with the observations of Jalani and Datta [19] for monovalent cations in Nafion. Jalani and Datta [19] state that their experimental results show an increased water vapor sorption in the order $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{H}^+$ as counter ion, which is true for water vapor activities of 0.6 and higher. For water vapor activities of 0.4 and lower, the water vapor sorption reported for Nafion with counter ions Cs^+ , K^+ and Na^+ is very low and practically independent of the cation

present, while water vapor sorptions for Li^+ and H^+ containing Nafion are still higher. For Nafion the water vapor sorption increased with increasing water vapor activity over the entire water vapor activity range, independent of the counter ion present. Jalani and Datta [19] reasoned that the smaller the cation, the higher its hydration enthalpy and the more water is absorbed in the polymer film. Figure 4.3 also shows that the water vapor sorption increases with the water vapor activity. SPEEK absorbs more water at higher activities, which is in line with the results reported for Nafion as well [19]. This behavior is in good agreement with what Potreck et al. [24] observed for SPEEK with a sulfonation degree of 59% and 75%. They found that the water vapor sorption increases for SPEEK over the full range of water vapor activities. At low water vapor activities (<0.5) the sorption isotherm obeyed the Dual mode sorption model, whereas at higher water vapor activities (>0.5) it follows the Flory-Huggins sorption model [24]. The water vapor sorptions presented in Figure 4.3 are slightly lower than those obtained by Potreck et al. [24], which can be attributed to the lower degree of sulfonation in the present work resulting in a lower concentration of sulfone groups.

4.4.3. Water vapor permeability

Figure 4.4 shows the water vapor permeability, CO_2 permeability and $\text{H}_2\text{O}/\text{CO}_2$ selectivity as function of the water vapor activity for SPEEK with different counter ions.

Figure 4.4: Water vapor permeability (a), CO₂ permeability (b) and H₂O/CO₂ selectivity (c) as function of the water vapor activity for SPEEK with different counter ions measured in a H₂O/CO₂ mixture at 50 °C and 2.5 bar.

Figure 4.4a shows that the water vapor permeabilities for SPEEK containing either Na⁺, H⁺, or K⁺ are similar (within the accuracy range of

the experiments). SPEEK membranes containing Al^{3+} or Li^+ show similar water vapor permeabilities as well, with SPEEK Al^{3+} showing slightly higher water vapor permeability than SPEEK Li^+ , but lower than the water vapor permeabilities obtained for the SPEEK membranes containing Na^+ , H^+ , or K^+ . Only at a high water vapor activity SPEEK Li^+ shows a water vapor permeability more in line with the SPEEK membranes containing other monovalent cations and thus higher than for SPEEK Al^{3+} . For all membranes the water vapor permeability increases with increasing water vapor activity irrespective of the nature of the counter ion. For SPEEK Ca^{2+} the increase in water vapor permeability with water vapor activity is less steep than for the other membranes. The type of counter ions also influences the CO_2 permeability (Figure 4.4b). In general there is a decreasing CO_2 permeability in the order of $\text{H}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ \approx \text{Al}^{3+} \approx \text{Ca}^{2+}$, although for a low water vapor activity differences in CO_2 permeability are minor and close to the experimental error. Like the water vapor permeability, the CO_2 permeability increases with the water vapor activity, mostly because of the higher swelling degree of SPEEK at higher water vapor activities (as concluded from the water vapor sorption experiments) and possible associated relaxation and plasticization phenomena. Only SPEEK Ca^{2+} shows minor increase in CO_2 permeability with increasing water vapor activity, similar to the trend observed for water vapor permeability. The $\text{H}_2\text{O}/\text{CO}_2$ selectivity (Figure 4.4c) for SPEEK Ca^{2+} is higher than for the other cations, since SPEEK Ca^{2+} has a high water vapor permeability combined with a low CO_2 permeability. SPEEK Na^+ , K^+ and H^+ also show high water vapor permeabilities, but a correspondingly high CO_2 permeability. As a consequence, the $\text{H}_2\text{O}/\text{CO}_2$ selectivity is lower than for SPEEK Ca^{2+} , which shows selectivities over 18,000. The $\text{H}_2\text{O}/\text{CO}_2$ selectivity of SPEEK Al^{3+} and Na^+ are comparable, taking error margins into account and higher than for SPEEK containing H^+ , Li^+ and K^+ for most water vapor activities. For SPEEK H^+ , Li^+ and K^+ the $\text{H}_2\text{O}/\text{CO}_2$ selectivities are comparable at activities of 0.4 and 0.6, whereas at a water vapor activity of 0.8 Li^+ is more selective than K^+ , while H^+ is the least selective at this high water vapor activity as a consequence of the very high CO_2 permeability at this condition.

The exact physical mechanisms explaining the overall trends as we observed in Figure 4.4 are rather complex as multiple aspects contribute to and determine the overall transport behavior. Khan et al. [4] showed that at dry conditions gas permeation in SPEEK for different cations depends on the atomic radius of the cations and the ionic crosslinks formed between the $-\text{SO}_3^-$ groups of SPEEK and the di- and trivalent charged cations. However, the results in Figure 4.4 show no trend with the radius of the counter ions at all. Quezado et al. [18] showed that the presence of clear water changes the anion-cation interactions within SPEEK. As a consequence the mass transfer behavior changes with the presence of water, explaining why we do not see a direct correlation with the atomic radius as Khan et al. [4] did. However, we do observe a strong correlation for the water vapor permeability and the CO_2 permeability as function of the hydration enthalpy (Figure 4.5), as suggested by Jalani and Datta [19].

Figure 4.5: Water vapor permeability (a) and CO_2 permeability (b) as function of the water hydration enthalpy (Table 4.1) for water vapor activities of 0.4, 0.6 and 0.8.

Figure 4.5 shows that both the water vapor permeability and the CO_2 permeability decrease with increasing hydration enthalpy. However, the hydration enthalpy is determined for an ideal system, only taking into account water and the specific cation and does not consider other interactions. In our case, considering SPEEK other interactions do play a role as well. For example the anion-cation interaction between the $-\text{SO}_3^-$ group of SPEEK and the counter ion, the formation of ionic crosslinks between the $-\text{SO}_3^-$ group and the di- and trivalent cations or the formation

of hydrogen bridges between water and the $-\text{SO}_3^-$ group. Overall, these interactions also reduce the effective hydration number of the cation and the amount of water compared to a purely water-cation system. These effects superimpose and it is not possible to distinguish between the individual contributions of each, but could be responsible for the deviations we observe in Figure 4.5, especially for SPEEK H^+ . Nevertheless, Figure 4.5a shows decreasing water vapor permeability with an increasing hydration enthalpy. We hypothesize that at high hydration enthalpies (e.g. Al^{3+}) water is more easily adsorbed by the cation. In contrast, this also implies water desorption is more difficult, resulting in a decreased water vapor diffusivity and consequently decreasing water vapor permeability. At low hydration enthalpies the interaction between water and the cation (e.g. K^+) is less strong, resulting in higher diffusivities and permeabilities. Additionally, also the formation of cation-water clusters within SPEEK can play a role. With an increasing hydration enthalpy the hydration number also increases (Table 4.1), which means more water molecules are bound to the cation and bigger cation-water clusters are formed. This may hinder the diffusion of other species (free H_2O , CO_2) through SPEEK, thus decreasing the water vapor and CO_2 permeability. In the case of CO_2 , also the surface charge density can play a role. The surface charge density shows similar trend as the hydration enthalpy (Table 4.1) and we hypothesize that at higher charge densities the negative oxygen atom of CO_2 is stronger attracted by the cation. Again, this results in a more difficult desorption and a decreasing diffusivity and permeability.

The trend of Figure 4.5a is also in line with what Jia et al. [5] observed for SPEEK. They found for SPEEK with H^+ and Na^+ as counter ion a higher water vapor permeability than when Cu^{2+} or Fe^{3+} were used as counter ion. Since Cu^{2+} and Fe^{3+} possess a higher hydration enthalpy [21], the water vapor permeability of SPEEK with Cu^{2+} and Fe^{3+} is expected to be lower than for SPEEK with H^+ or Na^+ as counter ion. For the N_2 permeability their results are not in line with our results (Figure 4.5b), since they observed that SPEEK Cu^{2+} and SPEEK Fe^{3+} are more permeable than the Na^+ and H^+ forms. However, N_2 and CO_2 are not directly comparable as N_2 is considered to be more inert than CO_2 (having a far lower quadrupole

moment as outlined by Khan et al. [4]), making it far less susceptible to attraction by surface charges). Furthermore, the measured permeabilities for N₂ are rather low (< 0.1 Barrer), making it more difficult to determine a clear trend.

4.5. Conclusions

Sulfonated poly(ether ether) ketone (SPEEK) is proposed as membrane material for multiple membrane applications, especially concerning the selective permeation of water vapor in e.g. flue gas treatment or membrane reactors. SPEEK contains a negatively charged -SO₃⁻ moiety and usually carries a proton (H⁺) as counter ion. However, the nature of the counter ion in SPEEK does influence the thermal stability, the sorption behavior and the gas and vapor permeability of the material.

This work shows that in general the exchange of the counter ion in SPEEK for other cations than protons results in thermal stabilities up to 450-500 °C. The water vapor sorption increases with increasing hydration enthalpy of the cation. Further, the water vapor and CO₂ permeability increase with increasing water vapor activity, but show a decrease with increasing cation hydration enthalpy. For the latter there are two possible phenomena that contribute to this, i.e. the formation of cation-water clusters that hinder the permeation of water vapor and CO₂ and the strong water-cation and CO₂-cation interactions, resulting in a worse desorption and thus decreasing the permeability of both components. Nevertheless, also other parameters that affect the permeation do play a role, e.g. cation-anion interactions and the formation of ionic crosslinks between the -SO₃⁻ group of SPEEK and di- or trivalent charged cations.

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4.7. References

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Chapter 5

Techno-economic evaluation of the direct conversion of CO₂ to dimethyl carbonate using catalytic membrane reactors

Abstract

The production of dimethyl carbonate (DMC) caught more interest in the last decades due to its versatile use (e.g. as fuel additive), low toxicity and fast biodegradability. Different 'green' production routes are being developed to replace the conventional and rather toxic production of DMC via phosgene. An environmental and economically interesting production route is the direct conversion of CO_2 and methanol towards DMC.

This work describes the process design of the direct conversion of CO_2 to dimethyl carbonate, providing a valuable insight and a better understanding of the process limitations. In this design, membrane reactors are used for continuous removal of water by-product, in order to overcome the equilibrium limitations. The rigorous Aspen Plus simulations show that even when using an excess of methanol, the attainable conversion is low and the DMC concentration in the reactor effluent is less than 1.5 mol%. Purifying this diluted stream to the desired concentrations demands large size equipment and a substantial amount of energy (13.61 kWh/kg DMC) resulting in high investment and utility costs, thus making the process not profitable. The focus for new membrane reactors could be on the instant removal of DMC (instead of water) from the reaction area to allow for a more concentrated DMC stream.

5.1. Introduction

In the search for so called “Green Chemistry”, dimethyl carbonate (DMC) caught interest because of its low toxicity and fast biodegradability [1-5]. DMC is considered as an important building block for different organic syntheses [1-5] within 1997 a worldwide production capacity of 45 kt/a [3, 5]. Because of its environmental-friendly nature it can replace hazardous chemicals such as phosgene and dimethyl sulfate [5] and is also considered as a potential fuel additive [2, 3, 5].

Formerly, DMC was produced via phosgenation. However, its high toxicity led to alternative processes such as the oxidative carbonylation of methanol (Enichem process) or the carbonylation of methylnitrite (UBE process) [1-4]. As even more sustainable, future alternative, the direct synthesis from the conversion of CO₂ is promising [1, 2]:

The use of CO₂ as building block for DMC is economically and environmentally interesting. It reduces the CO₂ emission into the atmosphere, decreases the demand for fossil fuels, and since CO₂ is considered as waste product, it is (still) a cheap feedstock.

However, the Gibbs free energy of the reaction (R5.1) at ambient conditions is > 0 [6], resulting in an equilibrium constant in the order of 10^{-5} . The spontaneous conversion of CO₂ towards DMC only occurs at technically infeasible high pressures [6]. Selective removal of reaction products e.g. the use of dehydrating agents, however, shifts the equilibrium to the product side, resulting in higher conversions. Sakakura and Kohno [7] categorized two types of dehydrating agents: recyclable agents such as acetals [7, 8], butylene oxide [9] or molecular sieves [10] and difficult-to-recycle agents such as orthoesters [11] or dicyclohexyl carbodiimide (DCC) [7]. Due to high costs and the difficulty to regenerate this last group, acetals are preferred. Acetals convert water into a ketone. The ketone structure formed determines the ease of acetal regeneration [7]. However, at

higher acetal concentrations DMC yield is suppressed due to the formation of side products [8].

An sustainable alternative is the use of a membrane in a membrane reactor. By combining the reaction with a membrane separation, one can instantly and continuously remove products from the reaction mixture. Li and Zhong [12] considered this approach for the direct conversion of CO_2 towards DMC. They investigated three types of membranes in a membrane reactor and observed an improved methanol conversion compared to the use of a conventional catalytic reactor. The use of more selective membranes [10] [12], an increase in pressure [12] and a better integration of membrane and reactor [13] will enhance the conversion further.

Another challenge is the formation of azeotropes between DMC/methanol [14] and DMC/water [15]. This requires non-standard separation techniques to obtain pure DMC, such as membranes [16], pressure-swing distillation [17] or extractive distillation [17]. Won et al. [16] showed that pervaporation using chitosan membranes, circumvents DMC/methanol azeotrope formation. Wang et al. [17] compared the performance of pressure swing distillation (based on the change of azeotropic composition with pressure) with extractive distillation (uses the difference in solubility in a newly introduced solvent (extractant)). Although both technologies can break the DMC/methanol azeotrope, extractive distillation consumes 71% less energy compared to pressure-swing distillation.

The challenges discussed above set the boundaries for commercial operation. Therefore this work focuses on the design of a DMC process plant for the direct conversion of CO_2 and methanol to DMC. It provides a techno- and economic evaluation of the process and shows the implications of the technical limitations of the process on the technical and economical operation. Further we analyze the influence of the most important parameters that future investigators can consider to enhance the

profitability of the process. The approach followed is based on the systematic design procedure of Douglas [18] and Seider et al. [19].

5.2. Conceptual process design

We consider the direct conversion of CO_2 and methanol to DMC with a DMC production capacity of 20 kton/year and > 99 wt.% purity. The production capacity is an average size of a DMC production facility [20] and the purity is a commonly used industrial grade [21]. We follow the design procedure described by Douglas [18] and Seider et al. [19]. Starting from black box calculations, the process is step-wise designed, followed by a conceptual design and finally a detailed design with heat integration where possible. For the conversion of CO_2 to DMC, this systematic approach finally led to the process presented in Figure 5.1 and shortly discussed here. In the next part we will discuss in more detail the individual elements, the reason for their selection and the specific process conditions. However, for clarity, the total process scheme is presented here already.

Figure 5.1: Schematic overview of the process design for the direct conversion of CO_2 to DMC.

The feed (stream #1, consisting of methanol and CO_2) is mixed with the vapor and liquid recycles to obtain a methanol/ CO_2 feed ratio of 4. This

stream enters the membrane reactor at 50 atm and 135 °C and the reactants are converted with 100% selectivity to DMC. Water, methanol and traces of CO₂ and DMC selectively permeate through the membrane. The product stream (retentate - #2) with DMC leaves the reactor and enters a flash drum where the gaseous components (CO₂) are removed from the liquid components (DMC, water and methanol). To assure that only CO₂ is in the gaseous phase, the temperature in front of the flash drum is decreased to 25 °C. Meanwhile the pressure in the flash drum decreases to 1.5 atm. To minimize CO₂ losses, the obtained CO₂ is compressed to 50 atm and recycled to the membrane reactor.

The liquid product stream leaving the flash drum (#3) is distilled in the pre-distillation column (Dist-01). Water and most of the methanol are removed and the DMC product stream is concentrated. The product stream leaves the condenser of Dist-01 as a liquid at the top in a DMC/methanol azeotropic ratio and CO₂ leaves the top of the column as a vapor. Water and most methanol are removed via the bottom of the column. To minimize the loss, the CO₂ stream and water/methanol stream are both recycled back to the membrane reactor.

The DMC/methanol mixture is separated in an extractive distillation column (Dist-02) by dissolving DMC in an extractant. DMC is together with the extractant obtained at the bottom (#5) of the column. Last traces of CO₂ (vapor phase) and most methanol (liquid phase) are obtained at the top and recycled back to the membrane reactor. Finally, in the third distillation column (Dist-03), DMC is recovered from the extractant and obtained at the top (#6) at a purity of > 99 wt.%. The recovered extractant is obtained as the bottom product and recycled back to Dist-02. Any extractant losses are compensated for by the supply of fresh extractant to the extractive distillation column (#7).

In the membrane reactor water, methanol and small traces of CO₂ and DMC permeate through the membrane. To minimize the methanol loss, this stream is recycled back to the reactor. However, to prevent that also water is recycled methanol is first separated from the water using the

fourth distillation column (Dist-04). To prevent accumulation of extractant, a purge is applied at the bottom product stream of Dist-01.

5.3. Process modeling and simulation

5.3.1. VLE data

DMC forms azeotropes with both methanol [14] and water [15]. In order to describe the interaction between the different components depending on the composition of the mixture, different property models are considered. The Soave-Redlich-Kwong (SRK) property model best describes the VLE data available in literature for DMC/methanol and DMC/water mixtures (Figure 5.2 and Figure 5.3). A reliable property model is required for trustworthy simulation results.

Figure 5.2: Experimental vapor-liquid-equilibrium (VLE) data of DMC/methanol at 1 atm. of Luo [14] and modeling data of the Soave-Redlich-Kwong (SRK) property model.

Figure 5.3: Experimental vapor-liquid-equilibrium (VLE) data of DMC/water at 1 atm. of Camy et al. [15] and modeling data of the Soave-Redlich-Kwong (SRK) property model.

5.3.2. Membrane reactor

The simulation of the process is performed in Aspen plus V8.0. As Aspen plus does not include a membrane reactor, it is simulated as a cascade of reactor and separator combinations as presented in Figure 5.4. In the reactor, the reaction proceeds until equilibrium is reached (equilibrium composition depending on the set temperature and pressure). Subsequently in the separator, the components are separated. The product outflow of the separator enters the reactor of the next block, followed by the next separator, etc.

Figure 5.4: Schematic representation of the membrane reactor simulation and de input and output parameters.

In the reactor, CO₂ and methanol are with the aid of a catalyst, converted into DMC and water. The equilibrium constant of the reaction (K_{eq}) is given by:

$$K_{eq} = \frac{[H_2O][DMC]}{[CO_2][MeOH]^2} \quad (5.1)$$

At set temperature and pressure, the equilibrium constant has a constant value.

At low temperatures (<125 °C), CO₂ activation is problematic and higher temperatures and pressures are desired due to kinetics and thermodynamic limitations [22]. The separator requires membranes with high water/gas selectivity. Polymer membranes based on sulfonated poly (ether ether ketone) (SPEEK) showed excellent dehydrating performances [23]. We slightly extended this to an operating temperature of 135 °C and a corresponding pressure of 50 atm. This is in agreement with the experimental conditions Aresta et al. [24] investigated for a CeO₂, an

effective catalyst for the direct synthesis of DMC from CO₂. For the catalyst, a 100% selectivity towards DMC is assumed [25].

For an equilibrium-limited reaction, a Gibbs reactor is most suited for the simulations, as it calculates the reaction equilibrium based on the Gibbs energy of the components. However, such a reactor cannot properly solve the thermodynamic equilibrium for a gas-liquid mixture, as for the components in the liquid state, the dependency of the Gibbs energy on the temperature and pressure is not properly calculated. Therefore an equilibrium reactor is considered and an expression for the equilibrium constant (K_{eq}) is incorporated to simulate equilibrium:

$$\ln[K_{eq}] = A + B \cdot T \quad (5.2)$$

With A and B are constants and T is the temperature [K]. Constants A (-6.12) and B (-0.016) are varied such that the equation agrees with the experimental results of Aresta et al. [24] and Hofmann et al. [26] (Figure 5.5).

Figure 5.5: Modeled CO₂ conversion as function of the temperature for different MeOH/CO₂ feed ratios (lines) in comparison with literature data (markers) of Aresta [24] and Hofmann [26].

Figure 5.5 shows a decrease in CO₂ conversion with increasing temperature, as expected based on thermodynamic data and the work of

Cai et al. [6]. The positive effect of increasing feed ratio on the CO₂ conversion is caused by the fact that a higher methanol concentration results into a shift in the equilibrium composition.

According to Figure 5.5 the experimental data of Aresta et al. [24] fit well with the modeled data. The data of Hofmann et al. [26] show a small deviation, but the simulated results are still in good agreement. Consequently, in our work, we use this expression for the equilibrium constant to predict the CO₂ conversion in the reactor of each cascade.

In the separator (Figure 5.4) we assume that the membrane removes 98% of the produced water. How this removal fraction is reached, depends on the amount of cascades used. To solve the membrane reactor module, a maximum of 23 cascades could be considered, due to the limited calculation capacity of Aspen Plus. After N=23 cascades the conversion eventually reaches a maximum conversion. However, this is dependent on the water removal fraction (F_{H_2O}). At a low water removal fraction (e.g. $F_{H_2O} = 0.25$), the maximum conversion is reached already in the first cascade and additional cascades have no further effect on the conversion. At high water removal fractions ($F_{H_2O} > 0.98$), the removal of water in the 23rd cascade is still substantial, indicating that the conversion determined in the simulation is still slightly lower than it is in the membrane reactor.

To account for the removal of other components, membrane selectivity towards methanol, DMC and CO₂ is included as well. A H₂O/methanol selectivity of 25 is assumed and a value of 1000 for H₂O/CO₂ selectivity is selected. For the H₂O/CO₂ selectivity a minimum selectivity is chosen. Based on the work of Sijbesma et al. [23] we can assume even higher H₂O/CO₂ selectivities. Instead we compared different literature sources. Sijbesma et al. [23] measured water permeabilities of 10,000 - 20,000 Barrer at low water vapor activities, while Khan et al. [27] observed for SPEEK CO₂ permeabilities in the order of 10 - 20 Barrer, resulting in a H₂O/CO₂ selectivity of 1000. Although Silva et al. [28] and Sijbesma et al. [23] report values at 50-55 °C, while the membrane reactor operates at 135 °C, selectivities are expected to be in the same order of magnitude. For

polymer membranes only limited information is available in literature regarding the separation of H₂O and DMC. Won et al. [16] investigated the use of chitosan membranes for the separation of a water/DMC/methanol mixture and determined the methanol/DMC and water/methanol selectivity, but did not determine the water/DMC selectivity. Instead, we took the product of their methanol/DMC selectivity (~50) and multiplied this with the water/methanol selectivity (~5), which results into a water/DMC selectivity of 250.

An alternative for water selective membranes is the use of DMC selective membranes to selectively remove DMC in order to shift equilibrium to the product side and increase the conversion. This concentrates the DMC product stream and could possibly break the DMC/methanol and DMC/H₂O azeotropes. This would eventually reduce the recovery train and by that the investment costs. However, as we opt for a commercial process in the long run and such membranes do not exist and research on these membranes is extremely limited yet, we selected membranes that allow the selective transport of water. Literature shows much more data and developments on such membranes.

The percentage of water permeating through the membrane per cascade ($X_{\text{H}_2\text{O-permeate}})_n$ can be determined using the following equation:

$$\left(X_{\text{H}_2\text{O-permeate}}\right)_n = \frac{F_{\text{H}_2\text{O}} \left(\phi_{\text{H}_2\text{O-produced}}\right)_n}{\left(\phi_{\text{H}_2\text{O-reactor out}}\right)_n} \quad (5.3)$$

With $F_{\text{H}_2\text{O}}$ the removal fraction of water, $\left(\phi_{\text{H}_2\text{O-produced}}\right)_n$ the amount of water produced in the reactor of cascade n [kmol/hr] and $\left(\phi_{\text{H}_2\text{O-reactor out}}\right)_n$ the total amount of water leaving the reactor and entering the separation unit of cascade n [kmol/hr]. This stream also contains water that is not removed in the previous cascades.

To determine the fraction of DMC permeating through the membrane, $(X_{\text{DMC-permeate}})_n$, the removal fraction of H_2O ($F_{\text{H}_2\text{O}}$) is divided by the water/DMC selectivity ($S_{\text{H}_2\text{O}/\text{DMC}}$).

$$(X_{\text{DMC-permeate}})_n = \frac{\frac{F_{\text{H}_2\text{O}}}{S_{\text{H}_2\text{O}/\text{DMC}}} (\phi_{\text{H}_2\text{O-produced}})_n}{(\phi_{\text{DMC-reactor out}})_n} \quad (5.4)$$

Since the reactants are already present before entering the membrane reactor, their overall permeation (not per cascade, but over the complete reactor) is determined:

$$x_{\text{reactants-permeate}} = \frac{F_{\text{H}_2\text{O}}}{S_{\text{H}_2\text{O}/j}} \left(1 - \left[n_j \zeta_{\text{CO}_2} \frac{\phi_{\text{CO}_2}}{\phi_j} \right] \right) \quad (5.5)$$

Here n_j is the stoichiometric ratio of the reaction [-], ζ_{CO_2} is the conversion of CO_2 [-], ϕ_{CO_2} is the amount of CO_2 fed to the reactor [kmol/hr] and ϕ_j is the amount of j fed to the reactor [kmol/hr]. If j is CO_2 , $\phi_{\text{CO}_2}/\phi_j$ equals 1. If j is methanol, $\phi_{\text{CO}_2}/\phi_j$ equals 1/4. Due to the excess of methanol, the total methanol conversion is lower than the CO_2 conversion. This is taken into account by multiplying the conversion with $\phi_{\text{CO}_2}/\phi_j$ in equation 5.5. Finally, to determine the amount of reactants that permeates through the membrane per cascade $((x_{\text{reactant-permeate}})_n)$, we calculate the fraction of water that is removed per cascade relative to the total amount of water that is removed in the membrane reactor module and multiply this with $x_{\text{reactants-permeate}}$.

Figure 5.6 shows the calculated CO_2 conversion as function of the water removal fraction ($F_{\text{H}_2\text{O}}$) for different methanol/ CO_2 feed ratios.

Figure 5.6: CO₂ conversion as a function of the water removal fraction for different methanol /CO₂ feed ratios.

Figure 5.6 shows a strong increase in CO₂ conversion especially at higher water removal fractions, due to the shift in equilibrium. This effect is more pronounced at higher methanol/CO₂ feed ratio. Both effects stem from the equilibrium constant (Equation 5.1), which shows a quadratic dependency on the methanol concentration.

Figure 5.6 suggests that it is beneficial to operate the process at higher methanol/CO₂ feed ratios. However, an excess of methanol decreases the DMC concentration in the reactor effluent due to dilution. This will result into a higher energy consumption to purify the product.

To find the optimum feed ratio, we focus on the DMC outlet concentration of the membrane reactor instead of on the conversion. Figure 5.7 shows the DMC concentration in the retentate as function of the methanol/CO₂ feed ratio. The maximum DMC concentration is obtained at a feed ratio of approx. 3.5 ~ 4. Below this feed ratio, conversion is low; above this ratio, dilution by methanol is dominant. Consequently, we assume a feed ratio of 4 in the simulations, since this gives the highest DMC concentration.

Figure 5.7: DMC concentration in retentate as function of the methanol/CO₂ feed ratio.

Table 5.1 summarizes the selected operating conditions of the membrane reactor module as discussed above. The approach described earlier to simulate the membrane reactor can be very well used to model the conversion of CO₂ and methanol to DMC and H₂O. Nevertheless it is a simplified version and does not take e.g. membrane permeabilities, driving forces or sweep gases into account. It only determines the effect of removing components from a reaction mixture. As such it also offers the possibility to assume any other separation technology, making the results more widely applicable. Eventually the aim of this work is to determine the critical process parameters and the window of operation to make this process economically interesting.

Table 5.1: Summary of the membrane reactor (MR) specifications

Parameter	MR conditions	Membrane	Reference
T_{reactor}	135 °C	-	Aresta et al. [24]
P_{reactor}	50 atm	-	Aresta et al. [24]
Methanol/ CO_2 feed ratio	4	-	-
Removal fraction H_2O ($F_{\text{H}_2\text{O}}$)	98%	-	-
$S_{\text{H}_2\text{O}}/\text{DMC}$	250	Chitosan	Won et al. [16]
$S_{\text{H}_2\text{O}}/\text{MeOH}$	25	SPEEK	Silva et al. [28]
$S_{\text{H}_2\text{O}}/\text{CO}_2$	1000	SPEEK	Sijbesma et al. [23], Kahn et al. [27]

5.3.3. Flash recovery and pre-distillation column (Dist-01)

After the membrane reactor a simple gas-liquid flash separation is performed to separate the CO_2 (gas) from the other components. The liquid stream outlet from the flash has to be pre-distilled due to the low DMC concentration attainable at the outlet of the membrane reactor. By pre-distillation, the excess of methanol and remaining water are separated from DMC. The concentrated DMC stream is further concentrated by extractive distillation. This separation sequence resembles a bio-processes, such as bioethanol production [29], where a pre-distillation column is followed by extractive distillation and solvent recovery.

The top distillate of Dist-01 has a near-azetropic composition of DMC/methanol. Figure 5.8 illustrates the dependence of the azeotropic composition of DMC/methanol on pressure. The fraction of methanol increases with pressure and thus in order to concentrate DMC, Dist-01 should operate at low pressure. To maintain a certain driving force over the process (> 1 atm) while minimizing the amount of methanol leaving together with DMC, the column pressure is set at 1.5 atm

Figure 5.8: DMC/methanol azeotropic composition as function of the pressure [30, 31]

Before the flash vessel the reactor effluent is cooled from 135 °C to 25 °C, as a further decrease in temperature leads to an economic penalty due to cooling agent requirements, while at higher temperatures more DMC is lost in the vapor phase and recycled together with CO₂ to the membrane reactor, thus being detrimental to the equilibrium reaction. Optimally, the flash vessel operates at low pressures to achieve high CO₂ recovery, but lower pressures also increase the amount of DMC lost with CO₂ into the vapor phase. However, at higher pressures more CO₂ enters Dist-01 and leaves the column as vapor distillate, taking also a part of DMC with it.

Figure 5.9: Percentage DMC recycled in the flash drum and Dist-01 as a function of the flash vessel pressure (calculated by simulations at a fixed column pressure of 1.5 atm in Dist-01).

Figure 5.9 shows the amount of DMC recycled via the flash drum and Dist-01 as a function of the operating pressure of the flash vessel as determined by simulations, considering a fixed pressure of 1.5 atm in Dist-01. Clearly, a significant amount of DMC is recycled via the flash vessel and Dist-01. In order to minimize the loss, the optimal flash vessel pressure is 1.3~1.5 atm. As Dist-01 operates at 1.5 atm, the flash vessel is also set to this pressure.

5.3.4. Extractive distillation (Dist-02) and solvent recovery (Dist-03)

The concentrated DMC product stream from Dist-01 enters Dist-02, which is the extractive distillation column. Due to the formation of an azeotrope between DMC and methanol (Figure 5.2) it is not possible to obtain pure DMC by conventional distillation. Several technologies are available to purify DMC, such as membranes [16], pressure-swing distillation (PSD) [17] and extractive distillation (ED) [17]. Due to the limited information available regarding membranes for DMC separation, this separation technology was discarded. Wang et al. [17] compared the use of PSD and ED to break the DMC/methanol azeotrope and showed that ED uses 71% less energy as compared to PSD, thus making it an obvious choice to use for DMC/methanol.

Several entrainers are available for ED, e.g. dimethyl oxalate [3], phenol [17], 2-ethoxyethanol and 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK) [32]. The last two were investigated in more detail by Matsuda et al. [32] who observed that MIBK is more selective to DMC. However, the drawback of MIBK is that it is more difficult to separate MIBK again from DMC, as compared to 2-ethoxyethanol. Nevertheless, considering that a less expensive entrainer is preferred over a lower reboiler duty in the solvent recovery step, MIBK was selected as entrainer for the extractive distillation.

The ED column was optimized by plotting the DMC recovery in Dist-02 as function of the MIBK/Feed ratio, as shown in Figure 5.10. We selected a MIBK/Feed ratio of 0.8, leading to a recovery of ~99.5% DMC. At

lower solvent to feed ratios a relative large amount of DMC is lost, while at higher ratios an excessive amount of MIBK is needed to recover the last DMC traces – leading to an economic penalty in the solvent recovery column.

The energy efficiency can be improved by heat integration of the condenser of Dist-02 with the reboiler of Dist-01. Since a minimum temperature difference of 15-20 K is required to drive heat transfer [19, 33] and considering that the reboiler of Dist-01 operates at 76 °C, the temperature of the condenser of Dist-02 is set to 100 °C, resulting in a corresponding pressure of 3.85 atm. This is equal to the boiling point of the mainly methanol containing mixture.

Figure 5.10: DMC recovery after the solvent recovery step from the extractive distillation as function of the MIBK/feed ratio determined by Aspen Plus simulations.

As shown in Figure 5.11, at these conditions most methanol is recovered in the vapor phase of the distillate along with the last traces of CO₂, which is undesired. By increasing the column pressure, the boiling point of methanol increases and more methanol is retained in the liquid distillate while less methanol is lost in the vapor distillate. Consequently, the column pressure in Dist-02 is set at 7 atm, after which a further increase in pressure has only minimum effect on the recovery.

Figure 5.11: Methanol recovery in the vapor distillate of Dist-02 as a function of the column pressure determined via Aspen Plus simulations.

In the solvent recovery column (Dist-03), DMC is separated from MIBK, which is recycled back to Dist-02. A conventional distillation column is used, being designed with the specification that > 99 wt% DMC is recovered at a purity of > 99 wt% DMC. Higher DMC recoveries result in higher energy requirements in Dist-02, as it becomes practically impossible then to prevent methanol from going along with DMC and MIBK to Dist-03.

Again, the condenser of Dist-03 is heat integrated with the reboiler of Dist-01 in order to increase the energy efficiency. The required condenser temperature in Dist-03 is minimum $100\text{ }^{\circ}\text{C}$, giving a temperature difference of $15\text{--}20\text{ }^{\circ}\text{C}$ [19, 33]. Figure 5.12 shows the Dist-03 condenser temperature as function of the column pressure. It shows that a pressure of 1.5 atm is sufficient to reach the minimum condenser temperature of $100\text{ }^{\circ}\text{C}$. Therefore, the pressure of Dist-03 column is set at 1.5 atm .

Figure 5.12: Condenser temperature of Dist-03 as function of the column pressure determined by Aspen Plus simulations.

5.3.5. Methanol recovery (Dist-04)

The permeate flow of the membrane reactor consists mainly of water and methanol with traces of DMC and CO_2 . To recover the products, this stream is separated in a distillation column, which is, based on the relative volatility of methanol/water and the feed composition, the standard technology to separate methanol from water. Alternative separation technologies (e.g. molecular sieves) become economically interesting when the water concentration of the feed is below 15 wt% [34]. This critical water concentration in the permeate is only reached at a water over methanol membrane selectivity < 20 . Since the selectivity selected in this work is 25, distillation is best suited to perform this separation.

The distillation column Dist-04 operates at 1 atm to achieve > 99 wt% methanol recovery with a purity > 98.5 wt% at the top of the column and a water recovery of > 99.5 wt%. The methanol recovery at the top and the water recovery at the bottom of Dist-04 are based on the optimum energy efficiency in Dist-04. Higher recoveries require much higher energy inputs, which is economically not interesting. Except for some small traces of water, the other 1.5 wt% is CO_2 and DMC that are also removed at the top of Dist-04.

Table 5.2 provides a complete overview of the different input variables for the flash drum and the distillation columns. These input data are set in Aspen Plus and the process is optimized to produce 20 kton/a of DMC with a purity of 99 wt%.

Table 5.2: Input variables for the flash drums and the distillation columns.

Unit	Parameter	Condition
Flash drum	P	1.5 atm
Dist-01	P	1.5 atm
Dist-02	T _{condenser}	>100 °C
	P	7.0 atm
Dist-03	MIBK/Feed ratio	0.8 mol/mol
	T _{condenser}	>100 °C
	P	1.5 atm
Dist-04	P	1.0 atm

5.4. Process performance evaluation

Table 5.3 provides the overall mass balance of the process. Notably, the membrane reactor module reaches a CO₂ conversion of 6.3% towards DMC. Overall, 84.9 kmol/hr of reactants enter the process in a ratio of 2:1 methanol/CO₂. This ratio is higher than the stoichiometric requirements and is caused by the methanol loss via the product stream and the purge, while all CO₂ is recycled.

The retentate stream (#2), which contains only 1.5 mol% of DMC, is purified via different steps to eventually obtain 97.7 mol% DMC (equal to > 99 wt%) as main product (#6). The key reason for the low DMC concentration is the low conversion and the excess of methanol used in the process. Due to the low DMC concentrations, it is very energy intensive to purify the outlet stream to the desired DMC purity.

Table 5.3: Calculated compositions and properties of the different streams in the process as calculated in Aspen Plus simulations.

	#1	#2	#3	#4	#5	#6	#7	#8
DMC [mol%]	-	1.5	1.7	11.5	12.6	97.7	-	0.2
Water [mol%]	-	0.0	0.0	0.0	0.0	0.0	-	29.5
CO ₂ [mol%]	32.4	19.8	5.5	4.6	0.0	0.0	-	0.4
Methanol [mol%]	67.6	78.6	92.7	83.8	0.3	2.1	-	69.9
MIBK [mol%]	-	0.1	0.1	0.0	87.1	0.2	100	0.0
F [kmol/hr]	84.9	2071.5	1749.3	239.3	219.8	28.1	0.05	93.4
E [MW]	-6.6	-153.5	-126.5	-19.4	-19.7	-4.6	0.0	-6.6
T [°C]	135	135	3.4	20	192.6	102.9	90	58.8
P [atm]	50	50	1.5	1.5	7	1.5	7	1

Table 5.4 gives an overview of the energy use throughout the process. Remarkable, Dist-01 and Dist-02 use 70% of the total heat required in the process, in both cases mainly to separate methanol from DMC. Especially the large energy demand of Dist-01 is caused by the low DMC concentration in the feed stream. Furthermore, due to the DMC/methanol azeotrope, a maximum DMC purity of 11.5 mol-% is attainable in the liquid distillate. The rest is mainly methanol that is removed over the top of the column along with DMC, according to the azeotropic composition. Evaporation of methanol causes the high energy demand in Dist-01.

Table 5.4: Overview energy use through the process, as calculated by Aspen Plus simulations.

Equipment	Energy [MW]
Distillation columns	
Dist-01	14.12
Dist-02	5.78
Dist-03	2.23
Dist-04	2.61
Pumps	0.16
Compressors	1.56
Heat exchangers	
Cooling	-10.63
Heating	3.82

Cooling also demands a substantial amount of energy and 74% of this energy is used to cool down the retentate stream (#2) from 135 °C to 25 °C prior to the flash drum. This stream contains mainly unreacted CO₂ and methanol and cooling prevents that DMC is lost in the vapor phase and recycled to the membrane reactor. Also the heating consumes a significant amount of energy: 79% of the heating duty being used to heat up the recycled liquid stream from the bottom of Dist-01 to the desired membrane reactor temperature of 135 °C.

Overall, the energy consumption of the process is relatively high compared to the amount of DMC actually produced, mainly due to the low conversion and the excess of methanol present in the process. This process is simulated at an optimal methanol/CO₂ ratio entering the membrane reactor of 4, such that the DMC concentration in the retentate is the highest. At higher membrane reactor feed ratios conversion is higher, but more methanol is present as well. This results in a lower DMC concentration and will cost more energy to purify. At lower membrane reactor feed ratios conversion is too low. Overall a feed ratio of 4 is optimal for the process. Nevertheless the conversion towards DMC is still low.

The conversion in the membrane reactor depends not only on the temperature and pressure, but also on the methanol/CO₂ feed ratio, removal fraction of water (F_{H_2O}), and the selectivity of the membrane. The influence of the H₂O/methanol membrane selectivity ($S_{H_2O/MeOH}$) is limited, as increasing this selectivity from 5 to 1000 results in an increase of the conversion of only 0.76%, of which 0.61% is already gained by increasing the selectivity up to 25.

Preventing the permeation of methanol causes the methanol concentration in the retentate to increase. This in principle shifts the equilibrium towards the conversion of DMC. However, as the effect on the conversion is minimal it is little important to have highly selective membranes to improve the conversion. Nevertheless, more selective membranes have a positive effect on concentrating the water stream in the permeate, as a minimal

water concentration of 15 wt.% is needed for distillation to become interesting. Figure 5.13 shows the water concentration in the permeate as function of the water/methanol membrane selectivity. According to this figure the water concentration exceeds 15 wt.% at a membrane selectivity $S_{\text{H}_2\text{O}/\text{MeOH}} > 20$. Higher $S_{\text{H}_2\text{O}/\text{MeOH}}$ does not increase the conversion much, but reduces the reboiler duty of Dist-04 as less methanol has to evaporate. At higher selectivities, more methanol remains in the retentate and this eventually demands more energy in the subsequent purification steps. However, this energy demand is less than the energy that can be saved in Dist-04 when membranes with high water/methanol membrane selectivity are used. The optimal $S_{\text{H}_2\text{O}/\text{MeOH}}$ will be around 200-400, where Figure 5.13 shows a flattening of the water concentration in the permeate. More selective membranes have only very small effect on the water concentration.

Figure 5.13: Water concentration in the permeate as function of the water/methanol selectivity as determined via Aspen Plus simulations.

5.5. Economic evaluation

A cost analysis was performed to determine profitability the process. Table 5.5 provides the investment costs of all major equipment units in the process. These investment costs were determined using the overall factor method [19]. Price estimation of most equipment is done via the correlations in Peters, Timmerhaus and West [35] and the equipment sizing results obtained from Aspen Plus. These prices are corrected to current prices with a Chemical Engineering Plant Cost Index (CEPCI) of

586 (2014) and multiplied with a Lang factor of 6 to take into account installation, piping, electrical etc. [36].

Table 5.5: Investment costs.

Equipment type	Costs [35]	Costs corrected for 2014	Total costs including installation etc.
	[M\$]	[M\$]	[M\$]
Membrane reactor	-	1.7	10.1
Flash vessels	0.2	0.3	1.8
Distillation columns	1.3	2.0	11.7
Compressors	1.1	1.5	9.2
Pumps	0.1	0.1	0.8
Heat exchangers	-	2.0 ^a	11.9
Total investment cost	2.7	7.6	45.5

^a prices from Matche [40].

For the membrane reactor the amount of membrane area (m^2) is determined by estimating the driving force over the membrane. The feed concentration of water is a product of the average molar fraction of water in the membrane reactor multiplied by the partial vapor pressure of water at 135 °C. The permeate water concentration is assumed to be zero, achievable for example by using a sweeping stream at the permeate side (sweep gas not taken into consideration in the simulations and cost estimates). The average driving force over the membrane is multiplied by a water permeability ($P_{\text{H}_2\text{O}}$) of 15,000 Barrer (1 Barrer = $10^{-10} \text{ cm}^3(\text{STP})\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$) [23]. Assuming a 0.5 μm thick dense membrane on a support leads to a total membrane area of 3235 m^2 . For the membrane reactor design we assume a catalytic membrane reactor, which is best suited for extreme equilibrium limited reactions [13]. A unitary cost of 45 $\text{\$/ft}^2$ was assumed for the membrane, based on Seader et al. [36] for gas separation membrane modules. For the catalyst layer on top of the membrane, a 100 μm thick CeO_2 layer was considered, which is reasonable according to Peters et al. [37]. The catalyst price considered is 50 $\text{\$/kg}$ [38]. The total price for the membrane reactor is then multiplied with a Lang factor of 6 to include the installation.

The process needs two lines of compressors to bring CO₂ back to the reactor pressure of 50 atm: one for the recovered CO₂ from the flash drum combined with the vapor distillate of Dist-01, and another one for the vapor distillate of Dist-02. The flash drum and Dist-01 operate at 1.5 atm and according to industrial information [39] a mainly CO₂ containing stream needs 4 compression stages (centrifugal) to reach 50 atm. As Dist-02 operates at 7 atm, it needs 3 compression stages (reciprocating, due to the small gas flow) to reach reactor specifications. This information is based on centrifugal compressors but is also valid for reciprocating compressors.

For heat exchangers, the main investment costs (75%) are attributed to the reboilers and condensers of the distillation columns. The condensers of Dist-02 and Dist-03 are heat-integrated with the reboiler of Dist-01 to reduce the costs of utilities. Other major costs for the heat exchangers (12%) are the heat exchangers that cool the reactor effluent from 135 °C to 25 °C and heat the bottom product of Dist-01 to reactor specifications.

According to the information in Table 5.5, a total investment of 45.5 M\$ is needed to build this DMC plant. Notably, the total investment costs are relatively equally divided over the membrane reactor, the distillation columns, the compressors and the heat exchangers.

Table 5.6 gives an overview of the operating costs and the revenues for the production of 20 kton/year of DMC. The main conclusion is that the DMC process is not profitable under the current conditions. The main values of the operating costs are based on the factors given by Seider, Seader and Lewin [19]. For the raw materials CO₂ is not taken into account, while the methanol price was estimated at 445 \$/ton [41] and the DMC sale price at 1000 \$/ton [21]. For typical chemical processes, the costs of raw materials account for 50% or more of the total costs. However, in this DMC process the cost of raw materials is only 28%. This is caused by the high costs for utilities, maintenance and depreciation - of which the last two are both related to the high investment costs.

Table 5.6: Operating costs.

	Costs [M\$/year]	Costs [M\$/year]
Raw materials		6.63
Utilities		4.18
Electricity (0.06 \$/kWh)	0.83	
Chilled water (4 \$/GJ)	0.77	
Cooling water (0.05 \$/m ³)	0.40	
Hot water – 95 °C (0.05 \$/m ³)	0.004	
Steam – 2 bar (5 \$/ton)	0.60	
Steam – 5 bar (7 \$/ton)	0.54	
Steam – 20 bar (12 \$/ton)	1.05	
Operations (labor related)		1.32
Maintenance		3.66
Operation overhead		0.74
Property taxes		0.91
Depreciation		4.07
Depreciation (8%)	3.50	
Membrane life time (3 years [42])	0.56	
Cost of manufacture		21.51
General expenses		2.31
Total production cost		23.82
Sales (DMC)		20.00
Revenue		-3.82

The breakdown of the costs of utilities shows that 52% of the costs stem from the steam used in reboilers and heaters, 20% from electricity used in compressors, and 18% from the chilled water. Dist-02 and Dist-03 are heat integrated with the reboiler of Dist-01, hence all steam (20 bar) is practically required for the reboiler of Dist-02. The alternative is that the Dist-01 reboiler is heated with 2 bar steam and that the condensers are not heat integrated, such that Dist-02 and Dist-03 can operate at lower temperatures and use cheaper steam. However, simple calculations reveal that this approach will not save much. Further heat integration is still possible by the integration of the cooler that cools the reactor effluent (#2) from 135 °C to 25 °C, with the heater that heats the bottom product of Dist-01 (mainly methanol) from 77 °C to 135 °C. This integration could

reduce the amount of utilities required in the best-case scenario by another 8%. Since further integration of other heating and cooling equipment only has a minimal effect on the total utility costs, this is not further considered for this design.

The high electricity demand is due to the large amount of CO₂ recycled to the reactor, which requires a high compressor duty as a consequence of the low CO₂ conversion to DMC. The chilled water is needed to cool the last part of the retentate flow (#2) from 45 °C to 25 °C and to operate the condenser in Dist-01 at 20 °C. In both cases, this is necessary to assure that only a minimal amount of DMC is lost with CO₂ towards the gas phase and that most of it is recycled back to the membrane reactor.

Maintenance and depreciation are both related to the investment costs and these costs are high due to the low conversion and large excess of methanol present in the process. Lower excess of methanol will result into smaller distillation columns since less methanol needs to be heated or less MIBK is needed to remove DMC from methanol. Nevertheless, at a lower reactant ratio, less DMC is produced resulting in lower conversions and low DMC concentrations at the reactor outlet. The bottom line is that the DMC concentration in the reactor effluent is practically too low to make this process profitable.

To investigate the profitability of the process, the return on investment (ROI) is plotted as function of the DMC price in Figure 5.14. Also the cases when the investment costs would decrease by 50 or 75% relative to the current investment costs are considered.

Figure 5.14: Return on investment (ROI) as a function of the DMC price for different fractions of investment costs.

For the base case (100%), Figure 5.14 shows that the process reaches its break-even point at a DMC price of 1215 \$/ton. To reach a ROI > 0.2, the DMC price has to go up to 1730 \$/ton, which means that the DMC price has to increase by 73%, before this process becomes economically interesting. According to Figure 5.14 there is a strong relation between the DMC price and the investment costs. In the hypothetical situation that the investment costs could be reduced by 50%, the current price of DMC of 1000 \$/ton is not economically interesting still, being barely sufficient to make the process profitable.

5.6. Key performance indicators

Table 5.7 shows the energy consumption and the CO₂ emissions of the process. According to these numbers the specific energy requirements per kg DMC are high and the process actually generates more CO₂ than it consumes. To have zero CO₂ emission, the energy demand has to decrease by 61%. Table 5.7 clearly addresses that this process cannot be considered as green, in spite of the green chemical reaction. Low conversion and an excess of methanol result in high investment and utility costs. To make this process economically viable, the conversion towards DMC needs to be significantly enhanced. An outgoing reactor effluent with a DMC concentration close to the DMC/methanol azeotropic composition prevents the use of the energy demanding pre-distillation column. To

reach high DMC concentrations, conversion has to increase by 6-7 times. At the current status the reactor effluent contains 0.03 mol% of water. Further dehydration using a membrane reactor to increase the conversion 6-7 times seems therefore unrealistic.

Table 5.7: Energy requirements and net CO₂ emission of the DMC production from the direct conversion of CO₂ ^{a,b}.

	Energy usage	Net CO ₂ emission based on fossil fuels	Net CO ₂ emission based on renewables ^c
	[kWh/kg _{DMC}]	[kg _{CO2} /hr]	[kg _{CO2} /hr]
No heat integration	16.15	3505.4	2783.9
Heat integration	13.61	2619.5	1898.0

^a 1 MW = 139.84 kg_{CO2}/hr [43]

^b $E_{\text{thermal}} = 3 \cdot E_{\text{electrical}}$

^c No CO₂ emission is accounted for electrical energy produced by renewables

5.7. Conclusions

A novel process design for the direct conversion of CO₂ to dimethyl carbonate (DMC) was successfully developed in this study. It uses a membrane reactor to remove the water by-product and thus overcome the equilibrium limitations. The results described here allow a valuable insight in the limitations of this newly proposed process and provide some potential solutions to overcome the envisaged problems.

The results of the rigorous Aspen Plus simulations show that even when using an excess of methanol, only low CO₂ conversion is achieved resulting in a membrane reactor effluent with a low DMC concentration, less than 1.5 mol%. Purifying this diluted reactor outlet stream to the desired product concentrations demands large separation units and a significant amount of energy (specific energy use of 13.61 kWh/kg DMC). This leads to high investment and utility costs, which make this process design not profitable. In order to make this process economically interesting, the focus for new membrane reactors could be on the instant removal of DMC (instead of water) from the reaction area. Ending up with

a concentrated DMC product stream could reduce significantly the costs of the separation process.

5.8. Acknowledgements

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5.9. List of symbols

A	Constant	[-]
B	Constant	[-]
$[CO_2]$	Concentration of CO_2	[mol/m ³]
$[DMC]$	Concentration of DMC	[mol/m ³]
F	Molar flow	[kmol/hr]
F_{H_2O}	Removal fraction of water	[-]
$[H_2O]$	Concentration of water	[mol/m ³]
K_{eq}	Equilibrium constant	[-]
$[MeOH]$	Concentration of methanol	[mol/m ³]
n_j	Stoichiometric ratio of the reaction	[-]
P	Pressure	[atm]
P_{H_2O}	Water permeability	[Barrer]
S_{H_2O/CO_2}	Water/ CO_2 membrane selectivity	[-]
$S_{H_2O/DMC}$	Water/DMC membrane selectivity	[-]
$S_{H_2O/j}$	Water/component j membrane selectivity	[-]
$S_{H_2O/MeOH}$	Water/methanol membrane selectivity	[-]
T	Temperature	[K] or [°C]
$(x_{DMC-permeate})_n$	Fraction DMC permeation through the membrane per cascade	[-]
$(x_{H_2O-permeate})_n$	Fraction water permeation through the membrane per cascade	[-]
$x_{reactants-permeate}$	Fraction reactants permeating through the membrane reactor	[-]

Greek symbols

ΔG_r^0	Gibbs free reaction energy at 298 K and 1 atm	[kJ/mol]
ζ_{CO_2}	CO ₂ conversion	[%]
ϕ_{CO_2}	Amount of CO ₂ fed to the reactor	[kmol/hr]
ϕ_j	Amount of j fed to the reactor	[kmol/hr]
$(\phi_{\text{H}_2\text{O-produced}})_n$	Amount of water produced in reactor at cascade n	[kmol/hr]
$(\phi_{\text{H}_2\text{O-reactor out}})_n$	Amount of water leaving the reactor at cascade n	[kmol/hr]
$(\phi_{\text{DMC-reactor out}})_n$	Amount of DMC leaving the reactor at cascade n	[kmol/hr]

Subscript

n	Number of cascades	[-]
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5.10. References

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Chapter 6

Conclusions & recommendations

Abstract

This research investigated the feasibility of membrane reactors to enhance the conversion of CO₂ and methanol towards dimethyl carbonate (DMC). Due to the selective removal of products (e.g. H₂O) from the reaction mixture using a membrane reactor, thermodynamic equilibrium cannot establish and as such the conversion is enhanced. This chapter summarizes the main conclusions of the work and provides recommendations for further research.

6.1. Conclusions

Membrane reactor technology is a promising technology that combines a reactor and a membrane. This allows the selective removal of components from a reaction mixture and as such can shift the equilibrium of chemical equilibrium reactions to the product side. This results in an increase in conversion. It reduces the amount of unit operations and space and can also be used to selectively add reactants to control the reaction [1]. In this work we studied in detail how membrane reactors can be implemented for the direct conversion of CO_2 and methanol into dimethyl carbonate (DMC). By selectively removing water from the reaction mixture, thermodynamic limitations can be minimized and the conversion will be improved.

6.1.1. Catalytic membrane reactor versus inert membrane reactor

Chapter 2 proves that to select the optimal membrane reactor configuration, it is essential to describe multi-component mass transfer and drift fluxes adequately. Catalytic membrane reactors (CMRs) are often assumed to be the best choice due to the high integration of catalyst and membrane. Due to this integration, water can instantly be removed from the reaction mixture in CMRs, whereas in inert membrane reactors (IMRs) water has to diffuse additionally through the boundary layer of the membrane, reducing the water removal rate. This work shows that CMRs only perform better than IMRs at low equilibrium constants ($K_{\text{eq}} < 1$) because water is more effectively removed. However, for e.g. esterification reactions ($K_{\text{eq}} \approx 1$) IMRs are more suitable since the removal of water is less critical and they are easier to implement. Besides, the performance of CMRs are highly sensitive to multi-component mass transfer behavior, while IMRs are not. This means that even at low equilibrium constants ($K_{\text{eq}} < 1$) CMRs are not always preferred over IMRs when the process parameters and the material properties change.

6.1.2. Membranes for the production of dimethyl carbonate using membrane reactors

According to **Chapter 2** catalytic membrane reactors are most suited for highly thermodynamically unfavorable reactions such as the conversion of CO₂ and methanol into DMC. To stimulate the conversion, one of the recommendations is to improve the water vapor permeability of the membrane. Therefore **Chapter 3** focusses on the development of double layer sulfonated poly(ether ether ketone) (SPEEK)/chitosan membranes and reports experimental results to evaluate the suitability of such membranes for the use in membrane reactors for the direct conversion of CO₂ into DMC. This work shows that for SPEEK/chitosan composite membranes the properties of both individual polymers stay intact and the composite membrane is stable up to 220 °C, which makes it capable to withstand the extreme conditions in membrane reactors to a certain extend. Further, these membranes show in comparison to SPEEK an increased water vapor permeability and H₂O/CO₂ selectivity. The introduction of a different selective layer on top of another selective material can be used to tune the properties of the final membrane. In this case the combination of a chitosan layer and a SPEEK layer improves the water vapor permeability, meanwhile decreasing the CO₂ permeability and methanol cross over.

6.1.3. How counter ions affect the permeation behavior in SPEEK

Chapter 4 also focusses on the development of SPEEK membranes to improve the water vapor permeability and H₂O/CO₂ selectivity. It discusses the effect of the counter ion in SPEEK on the performance. The exchange of the cation (usually H⁺) by e.g. Li⁺, Na⁺ or Ca²⁺, results in a significant increase of the thermal stability. In addition the nature of the counter ion in SPEEK has also a significant effect on the water vapor and CO₂ permeability. Both permeabilities decrease with increasing cation hydration enthalpy. We hypothesize this is devoted to the formation of cation-water clusters that hinder the permeation of water vapor and CO₂ and the strong cation-water and cation-CO₂ interactions, resulting in a worse desorption and thus in a decreasing permeability of both components. Nevertheless, also other parameters that affect the

permeation can play a role, e.g. cation-anion interactions and the formation of ionic crosslinks between the -SO_3^- group of SPEEK and di- or trivalent charged cations.

6.1.4. Membrane reactors for the production of dimethyl carbonate

In **Chapter 5** a techno-economic evaluation is made of the direct conversion of CO_2 and methanol into DMC using water vapor selective membrane reactors. This chapter evaluates the hurdles that have to be taken to make this process potentially commercially interesting. The Aspen simulations show that even at an excess of methanol, the conversion is low and the DMC concentration in the reactor effluent does not exceed 1.5 mol%. Via pre-distillation and extractive distillation eventually an industrial grade of DMC can be obtained. However, this requires large sizes of equipment and a substantial amount of energy (13.61 kWh/kg DMC). This leads to high investment and utility costs, which make this process not profitable. The key point is that the removal of water in the membrane reactor is not sufficient to increase the conversion. Therefore an alternative approach is proposed to make this process commercially interesting, i.e. selectively removing DMC in the membrane reactor. This results in a shift of the equilibrium and if the selectivities can be sufficiently high even the pre-distillation step can be avoided, which will result in a substantial decrease of the investment and utility costs.

6.2. Recommendations

An important conclusion from this thesis is that the selective removal of water vapor using commercially available or the developed membranes, is not sufficient to stimulate the conversion of CO_2 towards DMC using membrane reactors. The first priority therefore is to perform calculations and investigate the potential of the process in case DMC or DMC and water selective membranes could be applied. A similar investigation as described in Chapter 5 is needed with the aim to find the minimal DMC/reactant membrane selectivity when the process becomes profitable. However, if the selective removal of DMC or DMC/water is not sufficient to make this process profitable or unrealistically high membrane selectivities are required, alternative technologies should be

considered to stimulate the conversion of CO_2 towards DMC. To perform this analysis the same approach as described in Chapter 5 can be used, but the purification train needs to be adjusted since the focus is to purify the permeate stream instead of the retentate. Further modifications depend on the membrane selectivity, however a higher DMC concentration in the reactor effluent can be expected compared to the 1.5 mol% in Chapter 5. This could result in avoiding the energy consuming pre-distillation step, which will have a significant impact on the investment and utility costs.

Assuming that the selective removal of DMC is sufficient to make this process profitable, the next step for membrane research is to focus on the development of membrane materials that are selective towards DMC and retain methanol and CO_2 . Only recently researchers [2, 3] started focusing on the removal of DMC from methanol using pervaporation. This approach is considered as less energy intensive than removing large amounts of methanol from DMC, since the azeotropic point is around 15 mol% of DMC [4]. Wang et al. [2] proposed to use polydimethylsiloxane (PDMS) membranes for this application due to the hydrophobic nature of PDMS. They showed DMC/methanol separation factors in the order of 8-9 and that increase with decreasing DMC feed concentration. Besides being selective towards DMC, PDMS membranes also show reasonable water vapor permeabilities (40,000 Barrer [5]), which is advantageous since the combined removal of water and DMC has more effect to prevent equilibrium to establish and such stimulates the conversion more. However, PDMS is also highly permeable for CO_2 , literature report values between 2700 - 3800 Barrer [6-8]. Although the addition of water suppresses the CO_2 permeability [9], it should be taken into account when considering the use of PDMS membranes for membrane reactors.

The model described in Chapter 2 mainly focused on the multi-component mass transfer through the membrane interface and how this affects the performance of two membrane reactor configurations. Interesting is that this model suggests that the removal of water also promotes the conversion of irreversible reactions (high K_{eq}). The removal of water results in an increase in reactant concentration, which results in higher

conversions. It would be interesting to investigate this behavior for a real application and to find out if the conversion of irreversible reactions could be promoted when operated in a membrane reactor and selectively remove the products.

Related to this, the model of Chapter 2 could also be expanded to describe the mass transport in the catalytic layer of the CMR using the Maxwell-Stefan equation. Currently, the model only assumes multi-component mass transfer behavior and drift fluxes in the boundary layer of the membrane. Peters et al. [10] showed already that the thickness of the catalytic layer in CMRs has a strong influence on the performance. However, the use of Fick's law as Peters et al. [10] did does not take into account multi-component mass transfer behavior and drift fluxes. Therefore the recommendation is to expand the model of Chapter 2 and describe the mass transfer in the catalytic layer of the CMR with Maxwell-Stefan as well. To have a fair comparison between the performance of the CMR and the IMR, mass transport in the heterogeneous catalyst particles of the IMR should also be described with Maxwell-Stefan. Overall this will give a better description of mass transport of both membrane reactor configurations. This adjusted model will result in lower conversions, since water is less effectively removed due to the additional resistance within the catalyst. However, it is unclear to what extent both membrane reactor configurations are affected.

Chapter 4 showed that the nature of the counter ion in SPEEK has a significant impact on the membrane permeability and selectivity. Via a simple counter ion exchange procedure, the water vapor permeability and selectivity of SPEEK can improve. Therefore a recommendation based on that work is to test these membranes for the dehydration of flue gas. Sijbesma et al. [11] showed that although the majority of aggressive gasses (e.g. NO_2 , SO_2) are retained using SPEEK membranes to dehydrate flue gasses, the water quality is insufficient to be directly used in the steam cycle. The introduction of Ca^{2+} or Al^{3+} in SPEEK showed that SPEEK becomes more selective towards gaseous components (CO_2) and therefore SPEEK Ca^{2+} or Al^{3+} are possibly better able to retain these aggressive

gasses, producing higher quality water. An alternative is to introduce an additional selective layer on top of SPEEK, as done in Chapter 3 with chitosan. The introduction of an additional selective layer does not instantly result in a decreasing water vapor permeability, meanwhile it could reduce the permeation of other components such as NO₂ and SO₂.

For Chapter 4 additional research is required to explain the detailed mechanism behind this improved dehydration performance when varying the counter ions within SPEEK. At first the observed trend between the performance and the cation hydration enthalpy needs to be validated by performing additional dehydration measurements, especially for SPEEK with other di- and trivalently charged cations (for example Mg²⁺, Cu²⁺, Zn²⁺) with a cation hydration enthalpy between 2000 - 4000 kJ/mol [12]. Also additional experiments are needed that investigate the different hypotheses stated in this chapter. For example, for the different cations next to the water vapor sorption, also the CO₂ sorption could be determined. This would give a better understanding on how CO₂ interacts with the different cations. Further, a more detailed analysis is needed how the counter ion interacts with the -SO₃⁻ group of SPEEK, as done by Quezado et al. for Nafion [13].

Instead of using SPEEK for the direct conversion of CO₂ into DMC, SPEEK could be very promising for the direct conversion of CO₂ and H₂ into methanol using membrane reactors [14]:

At ambient conditions the equilibrium constant is around 0.3 and therefore the conversion towards methanol is thermodynamically limited. When a membrane reactor is used, products can selectively be removed from the reactants, preventing equilibrium to establish and exceed the equilibrium conversion. As Chapter 3 stated, the main drawback for SPEEK is its high affinity for methanol. However, for the direct conversion of CO₂ into methanol this is an advantage, since in this reaction methanol and water can be removed from the reaction mixture to

overcome thermodynamic limitations. The present work showed that proper membrane design can promote water vapor permeation in SPEEK, meanwhile retaining CO₂. Regarding methanol permeation, Silva et al. [15] measured in a pervaporation setup a methanol permeability of $2.2 \cdot 10^4$ Barrer at 55 °C (SPEEK SD = 42%), meanwhile Orme et al. [16] found a H₂ permeability of 96 Barrer at 300 °C (SPEEK SD = 79%). Overall, this suggests that SPEEK is capable to retain the reactants (CO₂ and H₂) and promote the permeation of the products (methanol and water).

Since the permeation of methanol should be promoted, SPEEK with a higher sulfonation degree compared to this thesis should be used (SD = 40%). Sijbesma et al. [11] showed already much higher water vapor permeabilities for SPEEK with a SD of 60%. Since the methanol uptake increases with the sulfonation degree [17], it is expected that the methanol permeability will also increase with the sulfonation degree. However, since SPEEK is soluble in methanol above a sulfonation degree of ~70% [18], the optimal sulfonation degree for SPEEK for the direct conversion of CO₂ into methanol will be around 60%. Preferably, however SPEEK with a sulfonation degree exceeding 70% is used, but this is only possible when SPEEK is crosslinked to avoid dissolution in methanol. In case of crosslinking it is preferred to crosslink the PEEK backbone as suggested by Li et al. [19], keeping the -SO₃⁻ group available, since the SO₃⁻ moiety is responsible for the high water vapor permeation.

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Dankwoord

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