

The theoretical evaluation of the relevant mass and heat transfer phenomena at different scales in a packed bed membrane reactor for the $\rm CO_2$ conversion to dimethyl ether.

Can significant mass or heat transfer phenomena be predicted using simplified approaches?

Auth	or H.L. van den Bogaard
Direct supervis	or S. Poto
Supervis	or M.F. Neira d'Angelo
Supervis	or F. Gallucci
External Committee Memb	er I. Roghair
	-

Department of Chemical Engineering and Chemistry

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Abstract

The currently ongoing energy crisis has once again shown the dire need for a circular energy system. Not only for environmental reasons but also for political ones, since the energy supply from classical fossil fuel sources can be unreliable. A promising way to create a part of such a circular energy economy is the production of dimethyl ether (DME) from CO_2 . DME is a clean-burning fuel that can be used in already existing engines with little-to-none adaptations. Currently, the production of DME is durable nor green since it is produced from natural gas. In the benchmark process, DME is produced in three steps. First, natural gas is converted to syngas (i.e. a mixture of H_2 and CO) via steam reforming, this is an extremely energy-intensive process. From syngas, methanol is formed. The methanol is purified and reacted into DME via a dehydrogenation reaction. Overall, this process is very energy-intensive, also considering that it has to take place at high pressures (60-70 bar). The production of DME is a severely thermodynamically limited process, and achieving high conversion and DME selectivity is proven to be difficult, especially if CO_2 is used as a carbon source instead of the conventional syngas. Several studies already pointed out improved reactor performance using a one-step process instead of a two-step process for the production of DME. In this process, methanol is formed and directly reacted to DME using either a bi-functional catalyst or two different catalysts. However, the biggest limiting aspect is the formation of large volumes of water when producing DME from CO_2 and H_2 . Moreover, water is also recognized as a component that can deactivate the catalysts used for the conversion of CO_2 to DME. One of the most promising solutions to this issue which has been proposed in literature is an intensified reactor/process, where hydrophilic membranes are used to remove water from the product stream in-situ.

In literature, these types of packed bed membrane reactors are commonly investigated. However, in most of these studies, mass and heat transfer limitations, such as intra-particle mass or heat transport (mass or heat transport in the catalyst particle), external mass or heat transport (mass or heat transport between the catalyst particle and the bulk of the fluid) and membrane concentration polarization (mass or heat transport between the between the bulk of the fluid and the membrane surface), are always assumed to be negligible. Moreover, these types of reactors are always assumed to be in ideal plug-flow operation, also neglecting effects due to axial dispersion (mixing in the axial direction). This study focuses on giving insights into these mass and heat transfer phenomena in the aforementioned process. Complex (two dimensional) models accounting for various heat or mass transfer phenomena are developed and compared with simpler models, that are not accounting for these phenomena. The process conditions are chosen such that limiting situations, still no effect of this phenomenon is observed, the effect can be safely neglected. However, if an effect is found, this phenomenon should be accounted for in the overall packed bed membrane reactor model. The models are developed using MATLAB R2019a employing a central-differencing discretization approach and a Newton-Raphson scheme.

Internal heat transfer limitations, external heat transfer limitations and axial dispersion were found to have little effect on the overall reactor performance. If only external mass transfer limitations are considered, it can significantly change the concentration at the surface of the catalyst particle, with respect to the concentration in the bulk of the fluid (with deviations up to 9%). However, if both internal and external mass transfer are considered, external mass transfer effects have little effect on the overall reactor performance. Internal mass transfer limitations and concentration polarization near the membrane were found to significantly influence the reactor performance. Internal mass transfer effects can significantly influence the catalyst efficiency of both the methanol catalyst (dropped to 50%) and DME catalyst (dropped to 5%) if catalyst particle diameters of 10mm and a reaction temperature of 270 °C are used. To model intra-particle diffusion limitations, a complex 2-D model is used, with one dimension in the length of the reactor and one dimension in the radius of the catalyst particles. Simpler, Thiele modulus, approaches are not applicable due to the complexity of the system, consisting of parallel, reversible and consecutive reactions with complex Langmuir-Hinselwood type of kinetics. This is a complex model, that can not easily be implemented, therefore a shortcut method is developed. This short-cut method is based on the already known Thiele modulus approach. The Thiele modulus is modified to also account for thermodynamic equilibrium concentrations in the diffusion term. Using the 2-D model a large data-set of catalyst efficiencies is calculated at various operating conditions and using different kinetic systems. These calculated catalyst efficiencies correlate well with the modified Thiele modulus and a correlation is derived, to link the modified Thiele modulus to the catalyst efficiency. This correlation shows behaviour that is also observed in the literature. Using this correlation, the overall reactor performance can be estimated with a deviation of less than 5% for values of the Thiele Modulus of up to 2.

Membrane concentration polarization also significantly influences the overall reactor performance, reducing the CO_2 conversion with 7% and the DME selectivity with 5% in a limiting situation. Similarly to intraparticle diffusion limitations, a complex 2-D model needs to be developed to access the effect of concentration polarization. A Sherwood-type of correlation is proposed to account for the effect of concentration polarization without having to develop a 2-D model. With the 2-D model, mass transfer coefficients are calculated using various operating conditions. From these mass transfer coefficients, Sherwood numbers are determined. A correlation is again derived, which includes a type of Peclet number, accounting for entrance effects in the reactor. The proposed correlation can accurately predict conversion and selectivity (with a maximum deviation of 2%) in a membrane reactor that is limited by concentration polarization.

In literature, a zeolite catalyst weight fraction of 50% is usually defined. However, due to the fast reaction of the methanol dehydration, a lower zeolite catalyst weight fraction would be beneficial. Better choosing the zeolite weight fraction can double the production of DME in a large-scale reactor with small reductions of CO_2 conversion and DME selectivity. Including the effect of internal mass transfer, increases the optimal zeolite weight fraction.

Preface

This project started off in the later stages of the COVID-pandemic. For me this meant that I was sleeping, working and relaxing more or less in the same 17 m^2 . The moment I noticed that my step-counter reported less than a thousand steps a day, I decided to go for daring changes such as working in the kitchen, living room or even in the corridor instead of my own dorm room. Luckily, the somewhat boring days were met by less boring evenings with eating with roommates and friends, keeping me same during these times. For this, a great deal of graduate has to go to these people. Nevertheless, I learned an important lesson from this, the quality of scientific work (or anything for that matter), is not only dependent on your own quality, but also on the connections and the casual coffee-break discussions with friends or colleagues.

A big thanks, of course, also goes to my supervisor Serena Poto. Your enthusiasm and critical view, made me look further into subjects than I initially would have. I also really liked it when we could switch back from the digital meetings to the meetings in your office. I hope that you get your set-up finally working, but I have no doubt that you will find a way. I wish you the best of luck with finalizing your PhD, and I am sure that you will produce many more interesting results.

I want to thank Fernanda Neira d'Angelo and Fausto Galluci as well. Especially when you made me realize that I was completely wrong, I was grateful to you. These regular progress meetings really improved my work and made me realize that there are more options than one might initially think.

Natuurlijk kan ik geen dankwoord schrijven, zonder mijn grootste sponsoren te benoemen. Pap, Mam, bedankt voor alles. Mijn excuus als jullie weer eens (onvrijwillig) mee moesten doen aan een van mijn experimenten, van gekleurd eten tot doolhoven van kartonnen dozen, jullie hebben van alles langs zien komen. Na vierentwintig jaar is het wel eens tijd dat ik geen kaas, koffiebonen en nog veel meer 'leen' vanuit de keuken. En als het enigszins meezit, hebben jullie over een jaar of wat dat vakantiehuisje.

Beste Frank, ik heb geen idee of je dit leest, maar ik ga voor het zekere voor het onzekere. Ik vind het enorm jammer dat jij hier niet bij kan zijn. Je had het (hopelijk) interessant gevonden. En alhoewel jouw afwezigheid me vast en zeker wat moeilijke vragen zal besparen, had ik het eigenlijk niet willen missen.

Lastly, I want to thank (once again) my friends and colleagues for drinking coffee, for the fun activities and for supporting me altogether. After many times 'thanks', I also would like to express one 'sorry' for making various people check my (poorly-spelt) report. This is not one of my strong suits, so thanks for taking the time to do this.

Contents

A	bstra	nct			iii
P	refac	e			v
Li	st of	Figure	es		ix
Li	st of	Tables	3		xiii
G	lossa	ry			xv
1	Intr	oducti	on		1
	1.1	DME I	Production		1
		1.1.1	Thermodynamics		2
		1.1.2	Catalysts		3
		1.1.3	Reactor Design		3
		1.1.4	Membrane Selection		3
	1.2	Mass a	and Heat Transfer Phenomena		4
		1.2.1	Internal Mass Transfer Limitations		4
		1.2.2	Internal Heat Transfer Limitations		6
		1.2.3	External Mass and Heat Transfer Limitations		6
		1.2.4	Axial Dispersion		7
		1.2.5	Concentration Polarisation		7
	1.3	Goal o	f the Study		8
2	Met	thods			9
	2.1	Numer	rical Methods		9
		2.1.1	Discretization grid		9
		2.1.2	Convective spatial discretization		9
		2.1.3	Dispersion		10
		2.1.4	Discretization boundary conditions		10
		2.1.5	System of algebraic equations		11
		2.1.6	Newton Raphson Scheme		11
		2.1.7	Pressure Drop and Velocity Profiles		12
	2.2	Param	eter selection		13
		2.2.1	Diffusion coefficient		13
		2.2.2	Tortuosity		14
		2.2.3	Thermal conductivity		14
		2.2.4	Specific heat		15
		2.2.5	Heat of reaction		15
		2.2.6	Viscosity		15
		2.2.7	External mass transfer coefficient		15
		2.2.8	External heat transfer coefficient		16
		2.2.9	Axial Dispersion		16
		2.2.10	1D Global Heat Transfer Coefficient		16

		2.2.11 Radial Dispersion
		$2.2.12 \text{ Radial Heat Transfer} \dots \dots$
	2.3	Kinetics
		2.3.1 Permeance
	2.4	Performance Indicators
9	Dam	tiala apola
ა	Par 2 1	Method 21
	0.1	Method
		5.1.1 Governing equations and boundary conditions
		3.1.2 Model implementation
		3.1.3 Grid size analysis $\ldots \ldots \ldots$
	0.0	3.1.4 Verification
	3.2	Results
		3.2.1 Internal Mass Transfer Limitations
		3.2.2 Internal Heat Transfer Limitations
	3.3	Modified Thiele Modulus
	3.4	Conclusions
1	Dor	ticlo-Fluid interphyse
-	4 1	Method 20
	т.1	A 1.1 Coverning equations and Boundary Conditions
		4.1.1 Model Implementation 30
	19	Populta 21
	4.2	4.2.1 External Maga Transfor Limitationa 21
		4.2.1 External Heat Transfer Limitations
	19	4.2.2 External field framsler Limitations
	4.5	
5	Pac	ked Bed Reactor 35
	5.1	Method
		5.1.1 Governing Equations and Boundary Conditions
		5.1.2 Model Implementation
		5.1.3 Grid Size Analysis
		5.1.4 Verification 37
	5.2	Results
		5.2.1 Internal Mass transfer Limitations
		5.2.2 Modified Thiele Modulus 37
		5.2.3 External Heat Transfer Limitations 39
		5.2.4 Axial Mass Dispersion 40
	5.3	Conclusions 41
	0.0	
6	Pac	ked Bed Membrane Reactor 43
	6.1	Method
		6.1.1 Governing Equations and Boundary Conditions
		6.1.2 Model Implementation
		6.1.3 Model Verification
	6.2	Results
		6.2.1 Optimal Zeolite weight fraction
	6.3	Conclusion
7	Two	o Dimensional Reactor 51
	7.1	Methods
		7.1.1 Governing Equations and Boundary Conditions
		7.1.2 Numerical Implementation
		7.1.3 Grid size analysis
		7.1.4 Verification $\ldots \ldots \ldots$

	7.2 Results	53			
	7.2.1 Concentration polarization	53			
	7.2.2 Correlation Concentration Polarization	55			
	7.3 Conclusions	59			
8	Conclusions	61			
	8.1 Recommendations	62			
Bi	ibliography	63			
A	ppendices	67			
A	Particle Schale	69			
в	B Packed bed Reactor				
С	C Packed bed Membrane Reactor 7				
D	Two Dimensional Reactor	79			

List of Figures

$\begin{array}{c} 1.1 \\ 1.2 \end{array}$	Concentration profiles for a particle with internal and external mass transfer limitations Concentration profiles in the radial direction in the case of significant concentration polarization	$\frac{5}{8}$
3.1	The concentration of the reactants in the catalyst particles $(T_{surf} = 270 \text{ °C}, P = 40 \text{ bar}, d_{part} = 10 \text{ mm})$	23
3.2	The concentration of the products in the catalyst particles $(T_{surf} = 270 \text{ °C}, P = 40 \text{ bar}, d_{part} = 10 \text{ mm})$	24
3.3	The concentration of reactants in the catalyst particles ($T_{surf} = 270$ °C, P = 40 bar, $d_{part} = 10$ mm)	24
3.4	The catalyst efficiency as function of the generalised Thiele modulus for systems with varying pressures, temperatures, particle diameters and surface compositions ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ har $d_{res} = 0.1-20$ mm)	25
3.5	The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions (T_R = 200.270 °C, $R_{\rm eff}$ = 20.40 have $d_{\rm eff}$ = 0.1.20 mm)	20
3.6	The catalyst efficiency from the rigorous model and the correlation for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions (T_R	20
	= 200-270 °C, $P_{R,in}$ = 30-40 bar, d_{part} = 0.1-20 mm)	28
4.1	The normalised surface concentration for different super facial velocities ($T_{bulk} = 270$ °C, $P_R = 40$ bar, $d_{part} = 10$ mm)	31
4.2	The normalised surface concentration for different super facial velocities for a model including internal mass transfer ($T_{bulk} = 270$ °C, $P_R = 40$ bar, $d_{part} = 10$ mm)	32
4.3	The relative difference between surface and bulk concentration for different superficial veloci- ties, temperatures and particle sizes ($T_{bulk} = 200-250$ °C, $P_R = 30-40$ bar, $d_{part} = 1-20$ mm	22
4.4	$v_{SF} = 0.001$ -1 m/s)	32
4.5	40 bar, $d_{part} = 10 \text{ mm}$) The normalised surface temperature for different superficial velocities for a system with a	33
	lowered thermal conductivity of hydrogen ($T_{bulk} = 270$ °C, $P_R = 40$ bar, $d_{part} = 10$ mm)	33
5.1	Conversion of CO ₂ and the selectivity of CO, MeOH and DME for varying particle diameters. $(T_R = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, \text{ GHSV} = 500 \text{ 1/hr } C_{H2}/C_{CO2} = 3, d_{part} = 0.1\text{-}20 \text{ mm}, L_R = 10 \text{ cm}, D_R = 2.6 \text{ cm}, D_{cat} = 0.33, w_{vol cat1} = 0.5) \dots \dots$	38
5.2	Conversion of CO ₂ and the selectivity of CO, MeOH and DME for varying operating temper- atures. ($T_R = 200-270$ °C, $P_{Rin} = 40$ bar, GHSV = 500 1/hr, $C_{H2}/C_{CO2} = 3, d_{part} = 10$	
5.3	mm, $L_R = 10$ cm, $D_R = 2.6$ cm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$)	38
	The solid line is a model without internal mass transfer, the astrixes is a model with internal mass transfer and the circles is the alternative Thiele modulus model. ($T_R = 270$ °C, $P_{R,in} = 40$ bar, GHSV = 500 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{nort} = 0.1-20$ mm, $L_R = 10$ cm, $D_R = 2.6$ cm.	
	$D_{cat} = 0.33, w_{vol,cat1} = 0.5)$	39

6.1 Conversion of CO_2 and the selectivity of DME for varying particle diameters. The solid line is a model without internal mass transfer and the astrixes is a model with internal mass transfer (Reactor conditions are reported in Table 6.1, $d_{part} = 0.25$ -10 mm, $T_w = 153$ -178 °C) 46 6.2 Catalyst Efficiency for the methanol and DME catalyst over the length of the membrane

- bar, GHSV = 1000 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{part} = 0.1$ -10 mm, $L_R = 1$ m, $D_R = 2.8$ cm, $D_{cat} = 0.33$, SW = 1, $D_{mem} = 10$ mm, $\Delta p_{mem} = 5$ bar) $\ldots \ldots 49$ 6.7 The conversion of CO₂, the selectivity of DME and the productivity of DME in a PBMR for various DME catalyst weight fractions Table 6.1, $d_{part} = 3.1$ mm, $T_w = 158$ -178 °C,
- $X_{wt,DMEcat} = 0.1-50\%$
- 7.1 Radial concentration profiles in the 2D packed bed membrane reactor in the middle of the column. ($T_R = 270$ °C, $P_{R,in} = 40$ bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{part} = 0.25$ mm, $L_R = 0.5$ m, $D_R = 10$ cm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$, $D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0) 54
- 7.3 The Sherwood number determined from the 2D model and the Sherwood number calculated from a correlation using two different correlations ($T_R = 200-250$ °C, $P_{R,in} = 35-40$ bar, GHSV $= 200-2000 \text{ 1/hr}, C_{H2}/C_{CO2} = 2-3, d_{part} = 0.25-5 \text{ mm}, L_R = 0.1-10 \text{ m}, D_R = 5-200 \text{ cm}, D_{cat}$ $= 0.25-0.5, w_{vol,cat1} = 0.25-0.75, D_M = 5-20 \text{ mm}, P_M = 35-40 \text{ bar}, \text{SW} = 0.5-2.0) \dots 56$

7.5	Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) and a 1D model with the proposed correlation (circles) for various temperatures. ($T_R = 200-270$ °C, $P_{R,in} = 40$ bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{part} =$ 0.25 mm, $L_R = 0.5$ m, $D_R = 10$ cm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$, $D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)	57
7.6	Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) and a 1D model with the proposed correlation (circles) for various temperatures. ($T_R = 200-270$ °C, $P_{R,in} = 40$ bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{part} =$ 0.25 mm, $L_R = 0.5$ m, $D_R = 10$ cm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$, $D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)	58
7.7	The difference of CO ₂ conversion and DME, CO and MeOH selectivity between a model accounting for CP and a model not accounting for CP ($T_R = 270$ °C, $P_{R,in} = 40$ bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3$, $d_{part} = 0.25$ mm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$, $D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)	59
A.1	The error as function of the number of grid points in the catalyst particle radial direction. $(T_{in} = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, d_{part} = 10 \text{ mm}) \dots \dots$	69
A.2	The numerical solution and analytical solution for a simple first order reaction in the catalyst particles $(k_1 = 1 \text{ mol/s/m3}, k_2 = 2 \text{ mol/s/m3}, P_B = 40 \text{ bar}, d_{nart} = 10 \text{ mm}, D_{eff} = 10^{-5})$.	69
A.3	The catalyst efficiency as function of the modified Thiele modulus for systems with vary- ing pressures, temperatures, particle diameters, particle geometries and surface compositions including CO $(T_{eq} = 200, 270)^{\circ}$ C $P_{eq} = -20.40$ has $d_{eq} = -0.120$ mm	70
A.4	The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Bussche & Froment [40] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$	70
A.5	mm)	70
A.6	the kinetics of Graaf [18] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm) The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for	71
A.7	the kinetics of Heckel [22] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm) The catalyst efficiency as function of the modified Thiele modulus for systems with varying	71
	pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Park [32] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm)	72
B.1	The error as function of the number of grid points in the column. $(L_R = 10 \text{ m}, D_R = 2 \text{ m}, T_{in} = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, GHSV_{R,in} = 50 \text{ 1/hr}, d_{part} = 0.25 \text{ mm}, D_cat = 3 m_{sol}^3/m_{cat}^3, w \mapsto 0.5 m^3 \dots (m^3 \text{ m})$	73
B.2	The numerical solution (solid line) and analytical solution (asterisks) for a first order reaction in the column without internal mass transfer and dispersion ($k_1 = 1 \text{ mol/s/m3}$, $P_R = 40 \text{ bar}$,	- 4
B.3	$v_{in} = 0.1 \text{ m/s})$ The numerical solution and analytical solution for a first order reaction in the column without	74
B.4	dispersion ($k_1 = 1 \text{ mol/s/m3}$, $P_R = 40 \text{ bar}$, $v_{in} = 0.1 \text{ m/s}$, $d_{part} = 10 \text{ mm}$, $D_{eff} = 10^{-5}$) The numerical solution and analytical solution for a first order reaction in the column without internal mass transfer ($k_1 = 1 \text{ mol/s/m3}$, $P_R = 40 \text{ bar}$, $v_{in} = 0.1 \text{ m/s}$, $D_{ax} = 10^{-3}$)	74 75
C.1	The normalised mass flow over the lenght of the column. $(T_R = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, C_{H2}/C_{CO2} = 3, d_{part} = 10 \text{ mm}, L_R = 10 \text{ cm}, D_R = 2.6 \text{ cm}, D_{cat} = 0.33, w_{vol,cat1} = 0.5)$.	77
C.2	The normalized mass flow in the industrial scale membrane reactor (Reactor conditions are reported in Table 6.1)	78
C.3	The temperature over the length of the industrial scale membrane reactor. (Reactor conditions are reported in Table 6.1, $d_p = 3.1 \text{ mm}$, $T_w = 176 \text{ °C}$)	78

- D.1 The error as function of the number of grid points in the radial direction in the column. $(L_R = 1 \text{ m}, D_R = 10 \text{ cm}, T_{in} = 220 \text{ °C}, P_{R,in} = 40 \text{ bar}, GHSV_{R,in} = 50 \text{ 1/hr}, d_{part} = 0.25 \text{ mm}, D_cat = 3 m_{sol}^3/m_{cat}^3, w_{cat,1} 0.5 m_{cat,1}^3/m_{cat}^3, D_{mem} = 10 \text{ mm}, \text{SW} = 1, P_{mem} = 35 \text{ bar}) \dots$ 79
- D.2 The normalized mass flow in the 2D membrane packed bed reactor model ($L_R = 1 \text{ m}, D_R = 10 \text{ cm}, T_{in} = 220 \text{ °C}, P_{R,in} = 40 \text{ bar}, GHSV_{R,in} = 50 \text{ 1/hr}, d_{part} = 0.25 \text{ mm}, D_cat = 3 m_{sol}^3/m_{cat}^3, w_{cat,1} 0.5 m_{cat,1}^3/m_{cat}^3, D_{mem} = 10 \text{ mm}, \text{SW} = 1, P_{mem} = 35 \text{ bar}) \dots \dots \dots 80$
- D.3 The radial concentration profile for various reactor lengths (k = 1 mol/s/m3, $C_{in} = C_{wall} = 100 \text{ mol/m3}$, $v_{in} = 0.1 \text{ m/s}$, $D_{rad} = 10^{-5}$, $L_R = 1 \text{ m}$, $D_R = 0.2 \text{m}$, $D_M = 10 \text{ mm}$) 80

List of Tables

1.1	Reactions involved in the CO_2 hydrogenation to DME $\ldots \ldots \ldots$	2
$2.1 \\ 2.2$	The kinetic constants used in this work	19 19
3.1	The dependency of a on effective diffusivities	27
$6.1 \\ 6.2$	The reactor properties for an industrial packed bed reactor and a packed bed membrane reactor The reactor Performance for an industrial packed bed reactor and a packed bed membrane reactor with and without INMT	45 45
7.1	The fitted values for Equation 7.11	57

Glossary

Nomenclat	ure	\mathbf{Sc}
А	Area	\mathbf{Sh}
$a_h eat$	Cooling are per reactor volume	Т
a_M	Membrane are per membrane	U
	volume	
a_{mem}	Membrane area per reactor vol-	v
	ume	
\mathbf{b}_{conv}	Constant convective contribu-	V
	tion	
\mathbf{b}_{disp}	Constant dispersion contribution	$v_{c,i}$
C_i	Concentration of i	X_C
$C_{i,surf}$	Concentration at surface	x_{vol}
$C_{p,i}$	Specific heat of i	X_{w}
Ca	Carberry number/Mears number	Y_i
$D_{ax,i}$	Axial Dispersion coefficient of i	\mathbf{Z}
D_{cat}	Catalyst dilution factor	Abl
$D_{eff,i}$	Effective diffusivity of i	CC
d_h	Hydraulic diameter	CC
$D_{k,i}$	Knudsen diffusion coefficient of i	CP
D_M	Outer diameter of the reactor	DM
$D_{m,i}$	Molecular diffusion coefficient of	EX
	i	
D_{mem}	Membrane diameter	EX
d_{part}	Particle diameter	GH
$\hat{d_{pore}}$	catalyst pore diameter	INF
D_R	Reactor diameter	INN
D_{rad}	radial dispersion coefficient	Me
Ent	Dimensionless entrance parame-	MT
	ter	
F	Molar flow	PB
\mathbf{f}_{conv}	Vector containing the convective	PB
	contribution	
\mathbf{f}_{disp}	Vector containing the dispersion	rW
•	contribution	
\mathbf{f}_{react}	Vector containing the reaction	\mathbf{SM}
	contributions	
Gz	Greatz number	SW
h_{int}	Internal heat transfer coefficient	WG
h_M	Membrane heat transfer coeffi-	Gre
	cient	
\mathbf{J}_{conv}	Jacobean containing the convec-	β
	tive contribution	

${ m Sc} { m Sh} { m T} { m U}$	Schmidt number Sherwood number Temperature Overall heat transfer coefficient	
v	Velocity	
V	Volume	
$v_{c,i}$	Diffusion volume of i	
X_{CO2}	Conversion of CO_2	
$x_{vol,i}$	Volume fraction of catalyst i	
X_{wt}	Weight fraction	
Y_i	Yield of i	
Z	axial coordinate	
Abbreviatio	ons	
CCS	Carbon capture storage	
CCU	Carbon capture utilization	
CP	Concentration polarization	
DME	Dimethyl ether	
EXHT	External heat transfer	
EXMT	External mass transfer	
GHSV	Gas hourly space velocity	
INHT	Internal heat transfer	
INMT	Internal mass transfer	
MeOH	Methanol	
MTO	Methanol to olefins	
PBMR	Packed bed membrane reactor	
PBR	Packed bed reactor	
rWGS	reverse water gas shift	
SMR	Steam methane reforming	
SW	Sweep gas	
WGS	Water gas shift	
Greek symb	pols	

Friction factor

\mathbf{J}_{disp}	Jacobean containing the disper- sion contribution	$\Delta E_{act,i}$	Activation energy for reaction i
J_i	Flux of i	ΔH_{298K}	Heat of reaction at 298 K
\mathbf{J}_{nonlin}	Jacobean containing the non- linear contributions	Δp_{mem}	Trans-membrane pressure gradi- ent
J_{nerm}	Permeation flux	ε	Porosity
k	reaction rate constant	$\frac{1}{n}$	Catalyst efficiency
Kads i	Adsorption constant of i	$\stackrel{'}{\lambda}$	Thermal conductivity
k_{CP}	Mass transfer coefficient for con- centration polarization	μ	Viscosity
k_{CP}	Concentration polarization mass transfer coefficient	ν	stoichiometry
$K_{eq,i}$	Equilibrium constant for reac- tion i	arphi	Thiele modulus
k_{ext}	external mass transfer coefficient	ρ	density
k_{wall}	Thermal conductivity of reactor wall	$ au_{cat}$	Catalyst tortuosity
L_R	Reactor Length	subscripts	
M_i	Molar mass of i	avr	Average
n	order of the reaction	ax	Axial
Ν	Total number of grid points	bed	Reactor bed
N_C	Number of carbon atoms	bulk	bulk conditions
N_P	Prater number	cat	Catalyst
Nu	Nusselt number	dyn	Dynamic
Р	Pressure	eff	Effective
P_0	Pressure at atmospheric condi- tions	f	fluid
p_i	Partial pressure of i	forw	Forward
Pe_{ax}	Axial Peclet number	in	inlet
Pe_{Ent}	Entrance Peclet number	lim	Limiting
Pe_f	Fluid-mechanical Peclet number	Μ	Membrane
Pe_{rad}	Radial Peclet number	part	Particle
Perm	Permeance	perm	Permeation side
Pr	Prandtl number	R	Reactor
$Prod_i$	Production rate of i	rad	Radial
R	gas constant	rev	Reverse
r	Radial coordinate	\mathbf{S}	surface
r_i	Reaction rate of reaction i	\mathbf{SF}	superficial
R_i	Reaction rate of i	stat	Static
R_M	Membrane diameter	surf	Surface
r_{obs}	Observed reaction rate	W	Cooling water
R_{part}	Particle radius	superscrip	s
r_{surf}	Reaction rate at surface condi- tions	app	Apparent
Re_{S_i}	Reynold number Selectivity of i	k	Iteration number

Chapter 1

Introduction

The recent Climate Change Conference in Glasgow (COP 26 UN) has shown the dire need for new, innovative technologies to mitigate climate change. Already in 2015, at the previous Climate Change Conference (COP 21 in Paris), governments around the world have agreed to prevent global warming to exceed 1.5 °C compared to the pre-industrial temperature level. To achieve this, they established an agreement to reduce the usage of fossil fuels. Over 40 nations - including the US, India, Australia, Turkey, EU and China - have committed themselves to promoting affordable and clean technology by 2030, again stressing the importance of new, green technologies [3]. These green technologies are often aimed at preventing CO₂ emissions since CO₂ is the main component of greenhouse gasses, that cause global warming. CO₂ emissions can be prevented by replacing CO₂ emitting technologies by CO₂-neutral technologies (i.e. by replacing a coal power plant with wind or solar energy). However, in the short term the dependency of CO₂-emitting technologies is hard to reduce drastically to meet the agreements of the Climate Change Conference. Alternatively, CO₂ capture and storage (CCS) from the atmosphere or point-sources is a promising solution, that can be readily implemented [2]. According to the CCS technology, the captured CO₂ can be permanently stored in a depleted oil or gas reservoir. CO₂ capture and utilisation (CCU) would be more efficient since CO₂ could function as a cheap feedstock for valuable chemicals.

 CO_2 can be converted into CO, which is a feed-stock for many industrial applications, such as the Fischer-Tropsch process to produce hydrocarbons and the production of methane, formic acid, formaldehyde, methanol or dimethyl ether [27]. Amongst the products of CO_2 , methanol is one of the more promising. Several studies have pointed out the possibility of a methanol economy to reduce CO_2 emissions. Methanol serves as an important platform molecule for the production of olefins (methanol to olefins process) or dimethyl ether (methanol dehydration). These products can be used as fuels, which upon combustion close the CO_2 cycle if the CO_2 is captured (carbon circular economy) [30].

Within the CO_2 capture and utilisation process, the production of dimethyl ether (DME) via direct CO_2 hydrogenation has been recently recognized as one of the most promising routes. The reason for this is that DME has particularly promising properties as a transportation fuel and can therefore be utilised as a "sustainable" fuel. As a matter of fact, due to the lack of C-C bonds, no particulate matter, and little CO and unburned hydrocarbons are produced with the combustion of DME. Furthermore, DME has a low boiling point, leading to fast evaporation during injection and efficient combustion. And lastly, DME has similar properties (i.e. octane number) as transportation fuels commonly used in trucks and boats. Therefore, DME can be used for these engines with little to none adaptations. [2]. Apart from transportation fuel, DME can also be used as a refrigerant because it has no ozone-depleting potential and it can be used as an intermediate product for the production of light olefins [2].

1.1 DME Production

In industry, DME is produced from syngas, which is obtained from methane, coal or biomass. First, syngas is reacted into methanol. This is usually done in a catalytic packed bed reactor with a $Cu/ZnO/Al_2O_3$

catalyst [9]. In this step reaction 1 to 3 in Table 1.1 occur [2]. Then the methanol is purified from the unconverted gas and dehydrated to DME (reaction 4, Table 1.1) in a packed bed reactor over an acid catalyst. Commonly used acid catalysts include alumina, silicoaluminophaosphates (SAPO) and zeolites (HZSM-5). The methanol and DME synthesis can either occur simultaneously (direct route) or in two separate reaction steps with purification in between (indirect route) [2].

Table 1.1: Reactions involved in the CO_2 hydrogenation to DME

Reaction	Stoichiometry	ΔH_{298K}
1	$CO_2 + 3H_2 \Longrightarrow CH_3OH + H_2O$	$-49.5 kJ/mol_{\rm CO_2}$
2	$\rm CO_2 + H_2 \rightleftharpoons \rm CO + H_2O$	$+41.2kJ/mol_{\rm CO_2}$
3	$\rm CO + H_2 \rightleftharpoons \rm CH_3OH$	$-90.6kJ/mol_{\rm CO}$
4	$2 \operatorname{CH}_3 \operatorname{OH} \Longrightarrow \operatorname{CH}_3 \operatorname{OCH}_3 + \operatorname{H}_2 \operatorname{O}$	$-23.4kJ/mol_{DME}$

The traditional production of syngas (i.e., via steam reforming) is an energy-intensive process, emitting a significant amount of CO_2 . Therefore, the production of DME from syngas produced from fossil fuels is not durable or green. The synthesis of DME from the captured CO_2 and green H_2 (i.e., H_2 produced from renewable energy) results in a promising alternative, in view of the CO_2 valorization. Therefore, research has been focused on replacing CO with CO_2 in the production of DME [35].

1.1.1 Thermodynamics

The production of DME from CO_2 and H_2 suffers from strong thermodynamic limitations mainly due to the formation of a large volume of water, the thermodynamic stability of CO_2 and exothermicity of the reaction system [8].

In the reaction scheme (see Table 1.1) it is clear that water is a side product of both the synthesis of methanol and its subsequent dehydration to DME. Since all reactions are reversible, thus limited by a thermodynamic equilibrium, the production of water reduces the production of DME and the conversion of CO_2 . In the benchmark process, where CO is the main carbon source of DME synthesis, reaction 2 would occur in the opposite direction (WGS), removing the water produced by all other reactions. This synergy explains the higher CO_x conversions and DME yields achieved with syngas feedstock [1]. To be able to reach similar conversions with CO_2 as feedstock, water should be removed in-situ with, for example, a membrane reactor or reactive distillation [2].

The overall production of DME is an exothermic process, meaning that the equilibrium DME selectivity benefits from low reaction temperatures. However, due to kinetic limitations, the temperature should not be below 200°C [2]. At high temperatures, the endothermic reverse water-gas shift reaction is favoured. The equilibrium selectivity towards CO is close to 100% at high temperatures. Therefore the temperature should not rise above 260°C [8].

Reaction 1 and reaction 3 benefit from a high pressure because the amount of moles in the gas phase is reduced. Reaction 2 and reaction 4 are equimolar, thus not affected by pressure. Therefore, a higher pressure increases both CO2 conversion and methanol and DME selectivity. The yield of CO is reduced. Catizzonne et al. [8] concluded from extensive thermodynamic modelling that a minimum pressure of 30 bar should be used to achieve reasonable DME yields. In industry, usually, pressures between 50-100 bar are used [8].

Another important parameter for this reaction is the H_2/COx ratio in the feed. At low H_2/COx ratios the reverse water-gas shift reaction is favoured resulting in a high selectivity towards CO. At high H_2/COx ratios the CH₃OH production is favoured resulting in a high selectivity towards CH₃OH and DME [8]. Moreover, a high H_2/COx ratio prevents the formation of large carbons structures, blocking catalyst pores, thereby deactivating the catalyst. However, the DME yield increase for H_2/COx ratios above 3 is relatively small. Considering the high price of H_2 (which is usually mentioned as the economic bottleneck of DME production from CO₂), a high H_2/COx ratio is undesirable [35]. Therefore, a H_2/COx ratio of 3 is usually applied in industry.

1.1.2 Catalysts

Out of all the metals suitable for the formation of methanol out of CO_2 and H_2 , copper is the most active and therefore most used [8]. More specifically, a Cu-ZnO-Al₂O₃ catalyst is used, optionally with extra dopants to increase copper dispersion and overall stability. This catalyst, however, can be strongly deactivated by the formation of water [2,8]. Several supports for the copper catalyst can be used including ZnO/Al₂O₃ and CeZr/Al₂O₃. An important role of the support is to stabilize and activate the copper nano-particles, ultimately increasing the catalyst activity. The ZnO/Al₂O₃ support is most commonly used in industry [2].

To prevent excessive coke formation, the acid catalyst used for the formation of DME out of methanol should not have high acidity. Most commonly γ -alumina is used for this purpose. However, due to the weak Lewis acids-sites in γ -alumina, a temperature of at least 250 °C needs to be used or the alumina needs to be modified to increase activity [8]. Moreover, γ -alumina is strongly deactivated by water, which is produced in large volumes with the production of DME from CO₂. More recently, zeolites have been found to be an effective catalyst for this purpose. From all zeolites, HZSM-5 is one of the most investigated [8]. The zeolites have higher activity, allowing for lower operating temperatures in the one-step synthesis of DME. However, due to the higher activity, the formation of light hydrocarbons and coke is a well-known problem if zeolites are used as acid catalysts. The formation of coke and hydrocarbons can be tuned by adjusting the zeolite acidity and morphology. FER-zeolites have shown to have a high resistance to coke formation, while still having sufficient activity and DME selectivity [2, 8].

1.1.3 Reactor Design

For the production of DME, usually, a fixed bed reactor is used. The main advantages of this reactor are that it is simple and cheap. However, heat removal is known to be a problem. To mediate this a tubular reactor can be used with multiple small tubes containing catalytic particles. The tubes are placed in a shell where a cooling medium circulates to remove the heat and keep isothermal conditions [2,39]. Slurry bed reactors have proven to have better temperature control. However, these reactors exhibit severe mass transfer limitations and a significant loss of catalyst particles, causing the relatively low popularity of these types of reactors for the production of DME [2]. More recently, fluidized bed reactors are investigated for the production of DME. These types of reactors have good heat removal and mass transfer characteristics. However, this reactor type is still at the initial stage of laboratory testing and a significant loss of catalyst particles is a problem [2].

The production of methanol from CO_2 is a severely thermodynamically limited process. To be able to obtain similar conversions with CO_2 as a carbon source a novel reactor design is required. Most reactor designs aim at removing water in-situ to move the reaction equilibrium towards the products (Le Chatelier's principle) [2]. This is required because twice as much water is produced with CO_2 compared to syngas as a carbon source, which limits both the formation of methanol and DME [8].

Reactive distillation (RD) can be used to separate products during the reaction to move the reaction equilibrium to the product side, enhancing the conversion [2,39]. However, these units operate at a temperature range of 40-180 °C, whilst catalysts for the production of DME are only active from 200 °C. Therefore, reactive distillation is not yet an interesting process intensification [2].

Alternatively, membrane reactors are promising to overcome the severe thermodynamic limitations of the production of DME from CO_2 and H_2 . In a membrane reactor, a reactant is fed or a product is removed through a perm-selective barrier [39]. For the production of DME, H_2O is usually removed to move the equilibrium towards the products and because H_2O deactivates the catalyst [9]. Also, by removing water, the selectivity towards methanol and DME is enhanced [8]. In literature, a membrane reactor is proposed that could increase the CO_2 conversion by 36% and the DME yield by 46% [35].

1.1.4 Membrane Selection

Several types of membranes can be used for the selective removal of H_2O from the reaction zone in this process, such as inorganic membranes, polymeric membranes and ceramic membranes [9]. Polymeric membranes suffer from severe thermal and mechanical stability issues and are, therefore, difficult to apply in the DME production process [2]. Several studies mention ceramic membranes, and more specifically zeolite membranes, for the selective removal of H_2O . For example, a A-type zeolite membrane is reported to in-

crease the conversion of CO_2 of c.a. 6% in a packed bed reactor for the production of DME [16]. However, zeolite membranes often offer poor reproducibility and long term stability due to their instability in a hot and humid environment. Moreover, it is difficult to produce large zeolite membranes without cracks [2,24].

Recently inorganic carbon membranes have been recognized as interesting materials for this application. Carbon membranes are porous membranes obtained by the pyrolysis of a polymeric precursor. Depending on the carbonation conditions, the polarity and pore size of the membrane can be tuned. Polar groups can be introduced to the surface of the membrane, making the selectivity towards polar molecules, such as H_2O and methanol higher [34,35]. The pores in a carbon membrane are usually between 0.2 and 2 nm [34]. With this pore size and the high polarity of the membrane, capillary condensation can occur meaning that H_2O can condense in the membrane pores, even at higher temperatures. This condensation will block the pores preventing diffusion of reactants through the membrane and greatly increasing the selectivity of H_2O [34,35].

The benefits of using a carbon membrane over a zeolite membrane are that carbon membranes offer better thermal stability and water permeability and selectivity [34]. However, carbon membranes have been only proposed recently and require further attention to be an industrially interesting option.

1.2 Mass and Heat Transfer Phenomena

In all reactors, mass or heat transfer limitations can occur, limiting the conversion that is predicted by the kinetic system, because reactants cannot move to the reactive centres fast enough. In a packed bed membrane reactor these transfer limitations can occur at several stages: inside the catalyst particle (internal mass or heat transfer limitations), between the catalyst particle and the bulk fluid (external mass or heat transfer limitations) or between the bulk and the membrane (concentration polarization), [39]. This is a topic of interest since most studies assume a kinetic regime (i.e., no mass or heat transfer limitations) also for industrial-scale reactors, where most of the assumptions to neglect these phenomena do not hold anymore and a rigorous model is often required to assess the interplay of mass and heat transfer at different scales.

1.2.1 Internal Mass Transfer Limitations

If reaction rates inside a catalyst particle are fast and if diffusion rates are slow, the overall reaction rate inside a catalyst particle could be lower than the reaction rate at the surface of the catalyst particle. This is because reactants cannot diffuse inside the catalyst particle fast enough. Therefore, the concentration of reactants in the catalyst particle could be lower than the concentration of reactants at the surface of the catalyst particle, resulting in lower reaction rates (see Figure 1.1). These phenomena especially become significant for large catalyst particles and at high temperatures because these conditions give rise to high reaction rates and slow diffusion rates [15, 39].

To determine a priori what the effect of the internal mass transfer is going to be, the Thiele modulus (φ) is commonly used. The Thiele modulus is defined as the ratio of the reaction rate at the catalyst particle surface and the diffusion rate. For a nth order reaction of A \longrightarrow B in a spherical particle, the Thiele modulus is defined as shown in Equation 1.1 [15,39].

$$\varphi^2 = \frac{k \cdot C_A^n |_S \cdot R_{part}^2}{D_{eff} \cdot C_A} \tag{1.1}$$

From the Thiele modulus, the catalyst efficiency can be calculated. The catalyst efficiency is defined as the observed reaction rate, including internal diffusion limitations, divided by the bulk reaction rate, excluding internal diffusion limitations [15, 39]. For spherical particles, this efficiency is given by Equation 1.2.

$$\eta = \frac{r_{obs}}{r_{surf}} = \frac{3}{\varphi} \left(\frac{1}{\tanh \varphi} - \frac{1}{\varphi} \right)$$
(1.2)

For large values of the Thiele modulus, the catalyst efficiency for spherical particles can be described by $\eta = 3/\varphi$.



Figure 1.1: Concentration profiles for a particle with internal and external mass transfer limitations

The Thiele modulus, as defined in Equation 1.1 is only valid for irreversible reactions depending only on one concentration. Moreover, there should be no parallel or consecutive reactions, the reaction kinetics should be n^{th} order and the system should be isothermal.

However, in specific cases, the Thiele modulus can still be used to calculate the catalyst efficiency.

For Langmuir-Hinshelwood kinetics the Thiele modulus is given by Equation 1.3. The catalyst efficiency is calculated the same as for n^{th} order reactions (Equation 1.2) [15].

$$\varphi = \frac{R_{part}}{2} \sqrt{\frac{-\nu \cdot k}{D_{eff}}} \sqrt{\frac{K_{ads} \cdot C_A}{1 + K_{ads} \cdot C_A}} \left(2 \frac{1 + K_{ads} \cdot C_A}{K_{ads} \cdot C_A} \ln 1 + K_{ads} \cdot C_A - 1 \right)^{0.5}$$
(1.3)

For reversible reactions of $A \rightleftharpoons B$, a Thiele modulus is defined for the backward reaction and the forward reaction. These Thiele moduli are used to calculate the overall efficiency [15].

$$\varphi = \sqrt{\varphi_{forw}^2 + \frac{D_{eff,A}}{D_{eff,B}}\varphi_{rev}^2} \qquad \eta = \frac{\tanh\varphi}{\varphi}$$
(1.4)

For reactions of the form $A + B \longrightarrow 2C$, the concentration of reactant B is usually written in terms of reactant A (Equation 1.5) [15].

$$C_B = C_{B,surf} - \frac{D_{eff,A}}{D_{eff,B}} (C_{A,surf} - C_A)$$

$$(1.5)$$

For consecutive reactions of A \longrightarrow B \longrightarrow C, the efficiency of the conversion of reactant A is calculated using only the Thiele modulus of the first reaction. The concentration of B and C are then calculated using a selectivity, depending on the Thiele modulus of the reaction of A to B (φ_1) and B to C (φ_2). The selectivity of product B is then given by Equation 1.6 [15].

$$S_B = \frac{\varphi_1^2}{\varphi_1^2 - \varphi_2^2} \left(1 - \frac{\varphi_2 \tanh \varphi_2}{\varphi_1 \tanh \varphi_1} \right) + \frac{\nu_{1,1} C_{B,surf} D_{eff,B} \varphi_2 \tanh \varphi_2}{\nu_{2,1} C_{A,surf} D_{eff,A} \varphi_1 \tanh \varphi_1}$$
(1.6)

For parallel reactions of A \longrightarrow B and A \longrightarrow C, the efficiency for the conversion of A can be calculated by using the sum of the Thiele modulus of the first and the second reaction. The concentration of product B can then be determined by calculating the selectivity. This selectivity is dependent on the Thiele modulus of the first and second reaction, see Equation 1.7 [15].

$$S_B = \frac{1}{1 + \frac{\nu_{A,2}k_2}{\nu_{A-1}k_1}} \tag{1.7}$$

In the equation above, νA , 1 is the stoichiometry of A in the first reaction and νA , 2 is the stoichiometry of A in the second reaction.

The Thiele modulus approach is a simplified method to account for internal mass transfer limitations without using a complex and computationally expensive particle-column model. The methods described above are only valid in a specific situation due to various underlying assumptions. For a reversible system, with non-linear kinetics in a reaction network with parallel and consecutive reactions, none of the methods described above can be used and a more complicated particle-column model has to be solved [15].

1.2.2 Internal Heat Transfer Limitations

Similarly to intra-particle mass transfer, intra-particle heat transfer occurs when a lot of heat is generated or consumed due to fast reactions and when the effective thermal conductivity of the catalyst particle is slow. Internal heat transfer limitations occur for reaction systems at high temperatures (fast reactions) with large catalyst particle diameters (slower diffusion) [15,39].

If the reaction is exothermic, in a case where internal heat transfer is relevant (i.e., slower than the heat generation), the temperature inside the catalyst particle is higher than the temperature in the bulk. This results in faster reactions in the catalyst particle and catalyst efficiencies above unity. To evaluate the effect of internal heat transfer limitations, the Prater number is used (Equation 1.8). If the Prater number is above one, the catalyst efficiency could be above unity, if the Prater number is below one, the efficiency will always be below unity, [39].

$$N_P = \frac{-C_i|_S \Delta H D_i}{\lambda T|_s} \tag{1.8}$$

Internal heat transfer limitations are usually negligible, especially if compared to internal mass transfer limitations. This is because the solid catalyst particle can conduct heat well. This results in fast heat transport in the catalyst particle, and the absence of temperature profiles [15,39].

1.2.3 External Mass and Heat Transfer Limitations

External mass or heat transfer limitations occur when reactants or heat cannot freely move from the bulk of the fluid to the surface of the catalyst particles. This changes the effective temperature or concentration at the surface of the particle, thereby also changing the kinetic rate inside the particle [15], (see also Figure 1.1). In laminar systems, with little mixing or low superficial velocities and fast catalytic reactions, the effect of external mass or heat transfer can be significant, whereas, in turbulent systems with significant mixing or high superficial velocities, the external mass or heat transfer might not result in an overall effect on the reactor performance. For external mass transfer, the Mears Criterion could be used to determine if this phenomenon should be taken into account [15]. The Mears Criterion consists of calculating a dimensionless number (commonly known as Carberry or Mears number), with known parameters (Equation 1.9).

For values of the Carberry number smaller than 0.15, the difference between the concentration at the surface of the catalyst particle and in the bulk of the liquid is less than 5% [28]. For values of the Carberry number smaller than 0.15, external mass transfer is considered to be negligible and as a result, does not need to be modelled.

$$Ca = \frac{r_{obs} \cdot R_{part} \cdot |n|}{k_{ext} \cdot C_{bulk}} < 0.15 \tag{1.9}$$

In Equation 1.9, r_{obs} is the observed reaction rate R_{part} is the catalyst particle radius, n is the order of the reaction, k_{ext} is the external mass transfer coefficient and C_{bulk} is the concentration in the bulk of the fluid.

The external mass (or heat) transfer coefficient is a parameter that describes how fast the transfer of mass or heat is from the bulk of the fluid to the catalyst particle. This is a parameter that is usually calculated empirically depending on the physical properties of the fluid and the component. The most important properties are particle size, fluid velocity and diffusivity or thermal conductivity for external mass or heat transfer respectively [15].

External mass transfer especially becomes relevant if there are low internal velocities in the reactor and if the catalyst particle sizes are large. To see an effect of external mass transfer, the temperature needs to be high, to ensure that the kinetics are not the limiting factor [39].

1.2.4 Axial Dispersion

Packed beds are usually described as plug flow reactors (PFRs). In these reactors, there is no mixing in the axial direction. However, in a real reactor there might be some mixing due to diffusion, turbulent flow, flow around solid particles or radial velocity profiles [10]. To take this into account, axial dispersion could be used. The dispersion includes, apart from molecular diffusion, also the axial transport due, for example, (turbulent) flow around particles [10,39].

Axial dispersion becomes relevant in some cases. In general, the axial dispersion coefficient is larger for larger particle sizes and higher internal velocities [10]. If the catalyst particles are large compared to the reactor diameter, the bed-porosity near the catalyst wall could be higher than the average porosity of the catalytic reactor. This results in a faster velocity near the reactor wall increasing the axial dispersion (wall tunnelling effect) [10]. The ratio of the reactor length to the reactor diameter can also have an effect on the axial dispersion coefficient. If this ratio is low, the axial dispersion coefficient could be changed by entrance effects [10].

1.2.5 Concentration Polarisation

Concentration polarization is a phenomenon that can occur close to the surface of a membrane. If the mass transport towards the membrane is slow and the flux through the membrane is high (i.e., high permeability), concentration polarisation can become relevant. In these situations, the concentration near the membrane is different from the concentration in the bulk of the fluid, see Figure 1.2. This reduces the overall flux through the membrane and thereby the efficiency of the separation. The effect of concentration polarization is reduced by increasing the superficial velocity or increasing the particle size because this increases radial mixing or by using a larger membrane diameter [6, 10].

Most commonly, concentration polarization is described with a Sherwood-type of correlation, to account for the mass transfer limitations. For example, in the work of Boon [6], the following type of equation is used. This correlation was developed for dense palladium membranes. Concentration polarization for porous membranes is not commonly investigated.

$$Sh = \frac{k_{CP}d_h}{D_m} = 1.07 \left(ReSc\frac{d_h}{z}\right)^{0.42} = 1.07Gz^{0.42} \qquad Gz > 62$$
(1.10)

$$Sh = Sh_{inf} = 6.18 \qquad Gz < 62$$
 (1.11)

Here d_h is the hydraulic diameter, which is the annular space between the reactor wall and the membrane. The term d_h/z is added to account for entrance effects. Near the entrance, there are flat (concentration) profiles. In this region, the mass transfer behaves differently than in regions with developed (concentration) profiles [6].

Commonly, the Sherwood number is a function of the Schmidt number to the power 0.33. This originates from doing a Fourier analysis of mass transport in tube flow. This relation is also represented in the famous Chilton-Colburn relations [5].



Figure 1.2: Concentration profiles in the radial direction in the case of significant concentration polarization

1.3 Goal of the Study

The goal of this study is to model and define the relevant mass and heat transfer phenomena at the different scales, as described above, in a packed bed membrane reactor for the production of DME from CO_2 and H_2 . To generalise the purpose of this study tools will be developed or verified to quickly access the presence or impact of these mass and heat transfer limitations using a complex kinetic system consisting of arbitrary kinetics with consecutive, reversible and parallel reactions. These tools will also be developed using different kinetic systems, to show if the applicability also expands outside the kinetics used in this work. With these tools, one does not need to solve complex models to understand the relevant phenomena, and can quickly account for mass or heat transfer limitations using a simple (one dimensional) model. The phenomena of interest are internal mass and heat transfer limitations, external mass and heat transfer limitations, axial dispersion, radial dispersion and membrane concentration polarisation. Once the important phenomena are identified, an industrial-scale reactor will be evaluated to see how these phenomena influence the overall reactor performance. If a significant influence of mass or heat transfer limitations is found, an alternative reactor design will be proposed to mitigate these effects or increase productivity.

Chapter 2

Methods

In this section, the general numerical methods to model the system will be explained. Furthermore, the empirical correlations used to determine physical parameters are reported.

2.1 Numerical Methods

The governing equations that are used to solve the concentration, temperature, pressure and velocity profiles in the reactor can have a complex form. Due to the reaction kinetics, these equations have a non-linear character. This should be taken into account when solving the system. Also, due to convection and dispersion, first and second-order derivatives, need to be solved simultaneously, which further complicates the system. Therefore, specific numerical methods are required.

2.1.1 Discretization grid

To solve the concentration, pressure and velocity profiles, the (continuous) governing equations need to be discretized and evaluated at set points in space. This discretization can be done in multiple ways:

- 1. Concentrations, pressures and temperatures are defined on the faces of the grid and the gradients are defined at the centre of the grid.
- 2. Concentrations, pressures and temperatures are defined at the centre of the grid and the gradients are defined on the faces of the grid.

In this work, the concentrations, pressures and temperatures will be defined at the centres of the grid and the gradients will be defined at the faces of the grid.

2.1.2 Convective spatial discretization

In the chosen numerical system, the gradients are defined at the faces of the grid cells. As a consequence, the velocities are also defined on the faces of the grid cells. The convective terms are described by the product of a velocity and a concentration. To this end a first-order upwind discretization is used, meaning that the concentration at the face of the grid is equal to the concentration at the downstream grid centre. The more accurate second-order central-differencing scheme is not used because this scheme can cause severe numerical instability [26]. To calculate the gradient, the central differencing scheme is used, which is a finite difference method. For a uniform grid spacing in a slab geometry, this results in the expression in Equation 2.1 [26].

$$\frac{\partial vc}{\partial x}\Big|_{i} \approx \frac{(vc)|_{i-1} - (vc)|_{i}}{\Delta x}$$
(2.1)

$$\frac{\partial vc}{\partial x}\Big|_{1} \approx \frac{(vc)|_{0} - (vc)|_{1}}{\Delta x}$$
(2.2)

For the first grid-point the concentration at the left boundary is undefined, see Equation 2.2. For this concentration, a boundary condition is required. The value of this concentration is usually equal to the inlet concentration. However, more complex boundary conditions could exist. For these situations, the concentration at the first edge in the domain is described as reported in subsection 2.1.4.

2.1.3 Dispersion

For the discretization of the dispersion term, central differencing is used as well. For a uniform grid spacing in a slab geometry, this results in the expression in Equation 2.3 [26].

$$\frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \Big|_{i} \approx \frac{D|_{i=0.5}c_{i-1} - (D|_{i=0.5} + D|_{i+0.5})c|_{i} + D|_{i+0.5}c|_{i+1}}{\Delta x^2}$$
(2.3)

$$\frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \Big|_{1} \approx \frac{\left(D \frac{\partial C}{\partial x} \right) \Big|_{0} + D \Big|_{1.5} \frac{c|_{2} - c|_{1}}{\Delta x}}{\Delta x}$$
(2.4)

$$\frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \Big|_{N} \approx \frac{D|_{N-0.5} \frac{c|_{N-1} - c|_{N}}{\Delta x} + \left(D \frac{\partial C}{\partial x} \right) \Big|_{end}}{\Delta x}$$
(2.5)

For the gradients at the first edge and the last edge of the discretization domain, boundary conditions are used, as reported in subsection 2.1.4.

2.1.4 Discretization boundary conditions

In the model, the conditions and gradients at the first and last grid points (corresponding to, for example, the entrance and exit of the reactor) are defined by mixed or Robin boundary conditions, see Equation 2.6 and Equation 2.7 for the first and the last grid point in the domain, respectively [26].

$$-a_0 \frac{\partial c}{\partial x}\Big|_0 + b_0 \cdot c\Big|_0 = d_0 \tag{2.6}$$

$$a_L \frac{\partial c}{\partial x}\Big|_{end} + b_L \cdot c\Big|_{end} = d_L \tag{2.7}$$

Where a, b and c are constants depending on characteristics of the system and are equal to or greater than zero. The left-hand side of Equation 2.6 has a negative sign because the boundary conditions are specified in the normal direction.

Since general Robin boundary conditions are assumed, $c|_{x=0}$ is not necessarily equal to c_{in} . This is only the case for Dirichlet boundary conditions (i.e. a = 0). However, values of $c|_0$ and $\frac{\partial c}{\partial x}\Big|_{x=0}$ are required in the discretization scheme. These values should depend only on constants and discretized parameters in the grid. To this end, a second order (Lagrange) interpolation is done near the left boundary (at x = 0). The result for a uniform grid size is reported in Equation 2.8 [26].

$$c(x) \approx \frac{(x - \frac{1}{2}\Delta x)(x - \frac{3}{2}\Delta x)}{\frac{3}{4}\Delta x^2} c_{in} + \frac{x(x - \frac{3}{2}\Delta x)}{-\frac{1}{2}\Delta x^2} c|_1 + \frac{x(x - \frac{1}{2}\Delta x)}{\frac{3}{2}\Delta x^2}$$
(2.8)

Combining the equation above with the Robin boundary conditions and with the the derivative of c(x) at x = 0, the following two expressions for $C|_0$ and $\frac{\partial c}{\partial x}\Big|_{x=0}$ are obtained.

$$c|_{0} \approx \frac{3\Delta xd + 9ac|_{1} - ac|_{2}}{3\Delta xb + 8a}$$
 (2.9)

$$\left. \frac{\partial c}{\partial x} \right|_0 \approx \frac{-8d + 9bc|_1 - ac|_2}{3\Delta xb + 8a} \tag{2.10}$$

A similar approach for the boundary condition at the last grid point gives for $c|_{end}$ and $\frac{\partial c}{\partial x}\Big|_{end}$ [26]:

$$c|_{end} \approx \frac{3\Delta xd + 9ac|_N - ac|_{N-1}}{3\Delta xb + 8a} \tag{2.11}$$

$$\left. \frac{\partial c}{\partial x} \right|_{end} \approx \frac{8d - 9bc|_N + ac|_{N-1}}{3\Delta xb + 8a} \tag{2.12}$$

2.1.5 System of algebraic equations

To solve the governing equations, the discretized governing equations need to be solved for each grid cell. This results in a large system of algebraic equations that can be non-linear due to the reaction rates.

Equation 2.2 and Equation 2.1 are combined in one banded sparse matrix (\mathbf{J}_{conv}) . This matrix has non-zero entries on the diagonal and the band corresponding to the downstream grid point. This matrix can be multiplied with a vector of, for example, concentrations at the centres of the cells of the discretized grid. The constant terms that are a result of the boundary conditions are collected in vector \mathbf{b}_{conv} . This system is summarised in Equation 2.13.

$$\mathbf{f}_{conv} = J_{conv} * \mathbf{c} + \mathbf{b}_{conv} \tag{2.13}$$

The dispersion is collected in a set of algebraic equations in a similar fashion, as shown in Equation 2.14. A banded sparse matrix (\mathbf{J}_{disp}) is created with non-zero entries in the diagonal, the upstream grid point and the downstream grid point. The entries result from Equation 2.3. The constant values that resulted from boundary conditions are collected in a vector (\mathbf{b}_{disp}) .

$$\mathbf{f}_{disp} = J_{disp} * \mathbf{c} + \mathbf{b}_{disp} \tag{2.14}$$

The reaction rate can be calculated in each grid cell with the concentrations, temperature and pressure in the centre of the same grid cell and they do not need to be discretized. For a convection, dispersion, reaction system all terms need to be collected into one equation, this is shown in Equation 2.15.

$$\mathbf{f}_{conv} - \mathbf{f}_{disp} = \mathbf{f}_{react} \tag{2.15}$$

This equation needs to be solved, to obtain the steady-state concentration and temperature profiles in the domain of interest. However, due to the reaction kinetics, this system of equations is non-linear, and therefore more complicated to solve. To this end, a Newton Raphson scheme is used.

2.1.6 Newton Raphson Scheme

The Newton Raphson is an iterative numerical method to solve a system of (non-linear) equations. This method is based on the geometric properties of the tangent to the curve of f(x) = 0. Here, f(x) can be a random (non-linear) equation. The Newton Raphson scheme requires an initial approximation of the roots of the function. If this initial approximation is poor, the solution might not converge [25].

If the solution to the problem f(x) = 0 is equal to α and the initial guess for the solution is x_0 , a Δx can be defined such that $\Delta x = \alpha - x_0$. To find the value of Δx a Taylor approximation of $f(\alpha)$ can be done. This is shown in Equation 2.16 and 2.17.

$$f(\alpha) = f(x_0 + \Delta x) = f(x_0) + f'(x_0)\Delta x = 0$$
(2.16)

$$\Delta x = \frac{f(x_0)}{f'(x_0)}$$
(2.17)

The improved guess for the roots of f can than be defined as follows:

$$x_1 = x_0 + \Delta x = x_0 + \frac{f(x_0)}{f'(x_0)}$$
(2.18)

This can be done multiple times until the system converges (or the solution is found).

The Newton Raphson Scheme can easily be generalized to a system depending on multiple variables. This gives for the Taylor approximation

$$\mathbf{f}(\alpha) = \mathbf{f}(\mathbf{x}_0 + \Delta \mathbf{x}) = \mathbf{f}(\mathbf{x}_0) + \nabla \mathbf{f}(x_0) \Delta \mathbf{x} = \mathbf{f}(\mathbf{x}_0) + \mathbf{J}(x_0) \Delta \mathbf{x} = 0$$
(2.19)

Here, **f** is a vector whose solutions should be zeros and \mathbf{x}_0 is a vector of initial guesses for the solution. $\mathbf{J}(x_0)$ is the Jacobean matrix. This matrix contains all the derivatives of **f** to their respective variables (Equation 2.20).

$$J_{i,j} = \frac{\partial f_i}{\partial x_j} \tag{2.20}$$

To get to the solution of x, a system of linear equations should be solved. This gives

$$\mathbf{x}_1 = \mathbf{x}_0 - J^{-1}(\mathbf{x}_0)\mathbf{f}(\mathbf{x}_0) \tag{2.21}$$

For a reaction, the diffusion convection system **J** consists of a contribution of each of these phenomena. The discretized contributions for diffusion and convection are linear. Therefore, this can readily be implemented in the Jacobean matrix. The reaction terms can be non-linear, therefore, this term needs to be linearized. This is done as in Equation 2.20. The reaction terms are only dependent on the variables (i.e. concentrations pressures, and temperature) that are in the same grid cell. As a consequence, the Jacobean of a function with respect to variables in another grid cell is always zero. For the efficiency of the calculations, these contributions to the Jacobean are not evaluated, since the solutions are known à priori. This results in a block diagonal matrix (\mathbf{J}_{nonlin}) for the reaction terms. The resulting Jacobean is given in Equation 2.22.

$$\mathbf{J}_{tot} = \mathbf{J}_{disp} + \mathbf{J}_{conv} + \mathbf{J}_{nonlin} \tag{2.22}$$

The Newton Raphson Scheme is iterated until convergence is reached. Convergence is reached if the error is below a certain threshold. In this work, the threshold is set at 10^{-5} , with the error defined in Equation 2.23.

$$error = max\left(\left|\frac{f_{k+1} - f_k}{f_{k+1}}\right|\right)$$
(2.23)

2.1.7 Pressure Drop and Velocity Profiles

In a packed bed reactor the pressure decreases over the length of the reactor due to interactions of the gas mixture with the packing of the bed. The velocity of the gas mixtures varies along the length of the reactor due to reactions, pressure drops and/or permeation of species through a membrane. To calculate the velocity in the column the Darcy equation (Equation 2.24) is used [9].

$$v = -\frac{1}{\beta} \frac{\partial p}{\partial z} \tag{2.24}$$

Where β is the friction factor, which can be calculated from the Ergun equation (Equation 2.25) [14].

$$\beta = 150 \frac{(1 - \varepsilon_{bed})^2 \mu_f}{\varepsilon_{bed}^3 d_{part}^2} + 1.75 \frac{\rho_f (1 - \varepsilon_{bed} |v|)}{\varepsilon_{bed}^2 d_{part}}$$
(2.25)

Where μ_f is the viscosity of the fluid, as defined in subsection 2.2.6 and ρ_f is the density of the fluid calculated using the Peng-Robinson equation of state.

The pressure in the column is calculated using a continuity equation, as sown in Equation 2.26.

$$-\frac{\partial}{\partial z}\left(\rho_f \frac{1}{\beta} \frac{\partial p}{\partial z}\right) = \sum_i M_i R_i + \sum_i M_i \frac{\partial}{\partial z} \left(D_{ax,i} \frac{\partial C_i}{\partial z}\right)$$
(2.26)

To calculate the pressure profile in the column, a differential equation that is analogue to a diffusion-reaction system is used. That means that two boundary conditions are required to solve the pressure profile. To this end, an inlet velocity (v_{in}) and a pressure at the outlet (p_L) are set. This results in the boundary conditions in Equation 2.27 and 2.28.

$$\left. \frac{\partial p}{\partial z} \right|_0 = \beta_0 v_{in} \tag{2.27}$$

$$p_{end} = p_L \tag{2.28}$$

For the calculation of the velocity profile, a segregated approach is used. Within one iteration in the Newton Raphson scheme, the concentration and temperature profiles are calculated first using the velocity profile in the column from the previous iteration. These newly calculated concentrations and temperatures are used as a prediction to estimate physical parameters such as density, viscosity and the friction factor from Equation 2.25. With the predicted parameters the pressure profile in the column is calculated using Equation 2.26.

The left hand side of Equation 2.26 is discretized analog to the dispersion term (Equation 2.14). The reaction and dispersion terms are calculated using the predicted concentrations. This results in a system of linear differential equations that can be solved to determine the pressure profile.

With the Darcy equation, the new velocity profile in the column is calculated. Lastly, the concentrations in the column are corrected to match the total molar density determined from the Peng-Robinson equation of state. This scheme is commonly referred to as the prediction-correction algorithm.

2.2 Parameter selection

In this section, the correlations used to calculate various physical properties are shown and some of the underlying assumptions are discussed.

2.2.1 Diffusion coefficient

The molecular diffusion coefficient for binary mixture is given by Equation 2.29.

$$D_{m,i,j} = \frac{1.01 \cdot 10^{-7} \cdot T^{1.75} \sqrt{1/M_i + 1/M_j}}{p(v_{c,i}^{1/3} + v_{c,j}^{1/3})^2}$$
(2.29)

Here, $v_{c,i}^{3/2}$ is the diffusion volume of species i. The diffusion coefficient for a species in a mixture is given in Equation 2.30 [9].

$$D_{m,i} = \frac{1 - y_i}{\sum_{j,j \neq i} \frac{y_j}{D_{i,j}}}$$
(2.30)

For the Knudsen diffusion in the catalyst pores the well-known equation resulting from the kinetic theory of gasses is used, see Equation 2.31 [4].

$$D_{k,i} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M_i}} \tag{2.31}$$

It is assumed that the effective diffusion coefficient in the catalyst particles consists of Knudsen diffusion and molecular diffusion. The effective diffusivity should also be corrected for the particle tortuosity and porosity. This is shown in Equation 2.32 [4].

$$D_{eff,i} = \frac{\epsilon_{cat}}{\tau_{cat}} \left(\frac{1}{D_{k,i}} + \frac{1}{D_{m,i}} \right)^{-1}$$
(2.32)

2.2.2 Tortuosity

Since the tortuosity is difficult to determine experimentally, a correlation is used. To this end, a correlation for tortuosity in porous media is used [12]. This is shown below.

$$\tau_{cat} = \frac{\epsilon_{cat}}{1 - (1 - \epsilon_{cat})^{2/3}} \tag{2.33}$$

2.2.3 Thermal conductivity

The thermal conductivity of a pure gas is given by Equation 2.34 [19].

$$\lambda = \frac{C_1 \cdot T^{C_2}}{1 + C_3/T + C_4/T^2} \tag{2.34}$$

The thermal conductivity of a gaseous mixture is given by the Wassiljewa equation [37].

$$\lambda_{mix} = \sum_{i=1}^{N} \frac{\lambda_i \cot y_i}{\sum_{j=1}^{N} A_{ij} \cdot y_j}$$
(2.35)

Here A_{ij} is a coefficient that can be calculated by the Lindsay-Bromley relation [37].

$$A_{ij} = 0.25 \left(1 + \left(\frac{\mu_i}{\mu_j} \left(\frac{M_i}{M_j}\right)^{3/4} \frac{T+S_i}{T+S_j}\right)^{1/2} \right)^2 \frac{T+S_{ij}}{T+S_i}$$
(2.36)

Here, S_i , S_j and S_{ij} are Sutherland constants of pure gasses in normal conditions.

$$S_i = 1.5 \cdot T_{b,i} \tag{2.37}$$

$$S_{i,j} = F_s \sqrt{S_i \cdot S_j} \tag{2.38}$$

 F_s is a correction factor for polar species. If at least one of the species i or j is polar, F_s is 0.735, otherwise, F_s is equal to unity.

The thermal conductivity inside a catalyst particle is given by the equation of Coté and Konrad [17].

$$\lambda_{eff} = \lambda_{solid}^{1-\varepsilon_{part}} \cdot \lambda_{fluid}^{\varepsilon_{part}}$$
(2.39)

2.2.4 Specific heat

The specific heat is calculated with an empirical correlation taken from Perries' Handbook for Chemical Engineers [19].

$$C_{p,i} = C_{1,i} + C_{2,i} \left(\frac{C_{3,i}/T}{\sinh(C_{3,i}/T)} \right) + C_{4,i} \left(\frac{C_{5,i}/T}{\cosh(C_{5,i}/T)} \right)$$
(2.40)

Here, $C_{1,i}$ to $C_{5,i}$ are component specific empirical constants.

2.2.5 Heat of reaction

The heat of the reaction is dependent on the temperature and is calculated by integrating ΔC_p over the temperature from a reference temperature until the reaction temperature.

$$\Delta H_r(T) = \Delta H_{r,T_{ref}} + \int_{T_{ref}}^T \sum_i \nu_i \cdot C_{p,i} \cdot dT$$
(2.41)

2.2.6 Viscosity

The viscosity of an individual component is given by an empirical correlation from Perries' Handbook for Chemical Engineers [19].

$$\mu_i = \frac{C_{1,i} \cdot T^{C_{2,i}}}{1 + C_{3,i}/T + C_{4,i}/T^2}$$
(2.42)

Here, $C_{1,i}$ to $C_{4,i}$ are component specific empirical constants.

The viscosity of the mixture is calculated with the Wilke Method [36]. This method is based on the kinetic theory of gasses and provides good estimations in a wide range of operating conditions [37].

$$\mu_{mix} = \sum_{1=1}^{N} \frac{\mu_i \cdot y_i}{\sum_{j=1}^{N} y_i \phi_{i,j}}$$
(2.43)

$$\phi_{i,j} = \frac{(1 + (\mu_i/\mu_j)^{0.5} \cdot (M_i/M_j)^{0.25})^2}{(8(1 + M_i/M_j))^{0.5}}$$
(2.44)

Here, $\phi_{i,j}$ is a binary interaction parameter between components i and j.

2.2.7 External mass transfer coefficient

To determine the external mass transfer coefficient k_{ext} the correlations of Dwlvedi for packed beds are used [13]. This correlation is valid for Reynolds numbers between 0.1 and 14,000.

$$\frac{\varepsilon_{bed} \cdot k_{ext} \cdot Sc^{0.66}}{v_{SF}} = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}$$
(2.45)

$$Sh = \frac{k_{ext} \cdot d_{part}}{D_m} \tag{2.46}$$

$$Re = \frac{\rho_{fluid} \cdot v \cdot d_{part}}{\mu_{fluid}} \tag{2.47}$$

$$Sc = \frac{\mu_{fluid}}{\rho_{fluid} \cdot D_m} \tag{2.48}$$

2.2.8 External heat transfer coefficient

For the correlation for the external heat transfer, a similar correlation as for the external mass transfer is used. This correlation can be seen in Equation 2.49 [21]. This correlation is valid for Reynolds numbers between 0.1 and 10,000.

$$\frac{\varepsilon_{bed} \cdot h_{ext} \cdot Pr^{0.66}}{C_{p,mass} \cdot v_{SF} \cdot \rho} = \frac{2.876}{Re} + \frac{0.3023}{Re^{0.35}}$$
(2.49)

$$Pr = \frac{\mu C_{p,mass}}{\lambda} \tag{2.50}$$

2.2.9 Axial Dispersion

For the axial dispersion in packed beds a correlation based on the well-know work of of Gunn is used [10,20]. In this correlation two fluid regions are assumed: one nearly stagnant zone and one fast-flowing zone. This correlation is described in Equation 2.51, 2.52, 2.53, 2.54.

$$\frac{1}{Pe_{ax}} = \frac{Pe_m}{5}(1-p)^2 + \frac{Pe_m^2}{25}p(1-p)^3 \left(exp\left(-\frac{5}{p(1-p)Pe_m}\right) - 1\right) + \frac{1}{\tau_{col}Pe_m}$$
(2.51)

$$p = \frac{0.48}{Sc^{0.15}} + \left(\frac{1}{2} - \frac{0.48}{Sc^{0.15}}\right) exp\left(-\frac{75Sc}{Pe_m}\right)$$
(2.52)

$$Pe_{ax} = \frac{v_{SF} \cdot d_{part}}{D_{ax} \cdot \varepsilon_{col}} \tag{2.53}$$

$$Pe_m = \frac{v_{SF} \cdot d_{part}}{D_m \cdot \varepsilon_{col}} \tag{2.54}$$

The correlation used in this work, similar to most correlations found in literature [10], assumes no dependence of the axial dispersion coefficient on the reactor length or reactor diameter. However, literature shows that in certain conditions there can be a significant dependence, especially when the ratio between the reactor length and reactor diameter (L_R/D_R) is low or when the ratio between the reactor diameter and the particle diameter (D_R/d_{part}) is low. For the reactor height to be negligible when calculating the axial dispersion coefficient L_R/D_R should be higher than 5 [10]. To neglect the effects of wall tunnelling due to a large particle diameter compared to column diameters, the D_R/d_{part} should be at least 15 [23].

2.2.10 1D Global Heat Transfer Coefficient

If heat is removed from the reactor with external cooling, three phenomena in series occur in the radial direction: 1) the heat is first transferred from the centre of the reactor to the walls (h_{int}) ; 2) the heat is conducted through the reactor wall (k_{wall}) and 3) the heat is transferred to the cooling medium which circulates in the mantle (h_{ext}) . Therefore, a global heat transfer coefficient (U) can be calculated as a function of the three distinct heat transfer coefficients describing the aforementioned phenomena. This is represented in Equation 2.55.

$$\frac{1}{U} = \frac{1}{h_{int}} + \frac{D_R ln D_M / D_R}{2 \cdot k_{wall}} + \frac{D_R}{D_M \cdot h_{ext}}$$
(2.55)

Here U is the overall heat transfer coefficient, h_{int} is the internal heat transfer coefficient, D_R is the inner diameter of the reactor, D_M is the outer diameter of the reactor, k_{wall} is the thermal conductivity of the reactor wall (the thermal conductivity of stainless steel) and h_{ext} is the thermal conductivity in the cooling medium.

For the internal heat transfer, a correlation that describes the heat transport to the reactor wall in a packed bed reactor is used (Equation 2.56) [19].

$$Nu = \frac{h_{int} \cdot d_{part}}{\lambda} = 0.17 \left(\frac{Pr}{0.7}\right)^{0.33} \cdot Re^{0.79}$$

$$\tag{2.56}$$

Where Nu, is the Nusselt number

If boiling water is used (i.e. constant medium temperature) in the cooling mantle Equation 2.57 can be used to describe the external heat transfer coefficient [38].

$$h_{ext} = 7.96 \cdot (T - T_{wall})^3 \cdot \left(\frac{P_{wall}}{P_0}\right)$$

$$(2.57)$$

Here, T_{wall} is the temperature of boiling water, P_{wall} is the pressure in the cooling mantle and P_0 is atmospheric pressure. The pressure in the cooling mantel is set by the vapour pressure of water boiling at T_{wall} , which can be calculated from thermodynamic properties.

2.2.11 Radial Dispersion

Similarly as for the axial dispersion, a correlation of Gunn is used for the radial dispersion [20]. Once again a diffusive and convective transport is assumed. The correlation can be seen in Equation 2.58.

$$\frac{1}{Pe_{Rad}} = \frac{1}{Pe_f} + \frac{\varepsilon}{\tau ReSc}$$
(2.58)

$$Pe_{Rad} = \frac{v_{SF} \cdot d_{part}}{D_{Rad} \cdot \varepsilon_{col}} \tag{2.59}$$

Here Pe_f is the fluid-mechanical Peclet number. For spheres, this equation is given by Equation 2.60.

$$Pe_f = 40 - 29e^{-7/Re} \tag{2.60}$$

2.2.12 Radial Heat Transfer

According to Zehner and Schlünder, the radial conductivity can be described by a stagnant conductivity due to the solid particles and a dynamic radial conductivity due to the fluid, this can be seen in Equation 2.61 [42, 43].

$$\lambda_{Rad} = \lambda_{stat} + \lambda_{dyn} \tag{2.61}$$

The static thermal conductivity is dependent on the solid particles in the packed bed reactor [43]. There are three particles in the reactor, the zeolite catalyst, the $Cu-ZnO-AlO_3$ catalyst and the inert SiC particles. For the zeolite catalyst and the copper catalyst, the same thermal conductivity of AlO_3 particles is assumed. The overall static thermal conductivity is assumed to be the average thermal conductivity of SiC particles and the catalyst particles, see Equation 2.62.

$$\lambda_{stat} = D_{cat}\lambda_{AlO_3} + (1 - D_{cat})\lambda SiC \tag{2.62}$$

The dynamic viscosity is given by Equation 2.63 [11, 43].

$$\frac{\lambda_{dyn}}{\lambda_f} = \frac{1}{10} RePr \tag{2.63}$$

2.3 Kinetics

In this work, the kinetics of Graaf for the methanol catalyst, more recently re-parametrized by Portha et all [18, 33] are used. The model of Graaf assumes two adsorption sites on the catalyst and three reactions: the CO hydrogenation reaction (Equation 2.64), the CO_2 hydrogenation reaction (Equation 2.66) and the water-gas shift reaction (Equation 2.65). The reaction rates are as follows:

$$r_{1} = k_{1} \frac{K_{ads,CO} \cdot (p_{CO} \cdot p_{H2}^{1.5} - \frac{p_{MeOH}}{p_{H2}^{0.5} \cdot K_{eq,1}})}{(1 + K_{ads,CO} \cdot p_{CO} + K_{ads,CO2} \cdot p_{CO2}) \cdot (p_{H2}^{0.5} + \frac{K_{ads,H2O}}{K_{ads,H2}^{0.5}} p_{H2O})}$$
(2.64)

$$r_{2} = k_{2} \frac{K_{ads,CO2} \cdot (p_{CO2} \cdot p_{H2}^{0.5} - \frac{p_{CO} \cdot p_{H2O}}{p_{H2}^{0.5} \cdot K_{eq,2}})}{(1 + K_{ads,CO} \cdot p_{CO} + K_{ads,CO2} \cdot p_{CO2}) \cdot (p_{H2}^{0.5} + \frac{K_{ads,H2O}}{K_{ads,H2}^{0.5}} p_{H2O})}$$
(2.65)

$$r_{3} = k_{3} \frac{K_{ads,CO2} \cdot (p_{CO2} \cdot p_{H2}^{1.5} - \frac{p_{MeOH} \cdot p_{H2O}}{p_{H2}^{1.5} \cdot K_{eq,3}})}{(1 + K_{ads,CO} \cdot p_{CO} + K_{ads,CO2} \cdot p_{CO2}) \cdot (p_{H2}^{0.5} + \frac{K_{ads,H2O}}{K_{ads,H2}^{0.5}} p_{H2O})}$$
(2.66)

The equilibrium, kinetic and adsorption constants are described by Equation 2.67 to 2.69 Respectively. The corresponding parameters are reported in Table 2.1.

$$\log_{10}(K_{eq,i}) = \frac{A_i}{T} + B_i \tag{2.67}$$

$$k_i = k_{i,0} exp\left(\frac{-\Delta E_{act,i}}{T \cdot R}\right)$$
(2.68)

$$K_{ads,i} = K_{ads,i,0} exp\left(\frac{-\Delta H_{act,i}}{T \cdot R}\right)$$
(2.69)

For the dehydration catalyst (DME catalyst) the kinetic model developed by Ortega for a commercial ZSM-5 zeolite is used [31]. The reaction rate is shown in Equation 2.70.

$$r_{4} = k_{4} \cdot K_{ads,MeOH} \frac{P_{MeOH}^{2} \left(1 - \frac{P_{H2O} \cdot P_{DME}}{P_{MeOH}^{2} \cdot K_{eq,4}}\right)}{(1 + K_{ads,MeOH} \cdot P_{MeOH} + K_{ads,H2O} \cdot P_{H2O})^{2}}$$
(2.70)

The adsorption constants of water and methanol are given by Equation 2.69. The kinetic constant is defined by Equation 2.68. The parameters for these equations can be found in Table 2.1. For the equilibrium constant Equation 2.71 is used.

$$K_{eq,4} = exp\left(\frac{4019}{T} + 3.707 \cdot ln(T) - 2.783 \cdot 10^{-3} \cdot T + 3.8 \cdot 10^{-7} \cdot T^2 - \frac{6.56 \cdot 10^4}{T^3} - 26.64\right)$$
(2.71)

Equilibrium Constants					
Constant	A [K]	В	Unit		
$K_{eq,1}$	5139	-12.6291	bar^{-2}		
$K_{eq,2}$	-2073	2.029	-		
$K_{eq,3}$	3066	-10.592	bar^{-2}		
Kinetic Cons	stants				
Constant	k_0	$\Delta E_{act} \left[\frac{kJ}{mol}\right]$	Unit		
k_1	$4.89 \cdot 10^{7}$	113.0	$\frac{mol}{ka_{cat}sbar^{-1}}$		
k_2	$1.53\cdot 10^{10}$	129.0	$\frac{mol}{kq_{cat}sbar^{-0.5}}$		
k_3	$1.71 \cdot 10^{1}$	51.605	$\frac{mol}{kg_{cat}sbar^{-1.0}}$		
k_4	$1.69 \cdot 10^{-2}$	103.4	$\frac{mol}{kg_{cat}sbar^{-1}}$		
Adsorption (Constants				
Constant	$K_{ads,0}$	$\Delta H_{ads} \left[\frac{kJ}{mol}\right]$	Unit		
$K_{ads,CO}$	$2.16 \cdot 10^{-5}$	-46.8	bar^{-1}		
$K_{ads,CO2}$	$7.05 \cdot 10^{-7}$	-61.7	bar^{-1}		
$\frac{K_{ads,H2O}}{K_{ads,H2}^{0.5}}$	$6.37\cdot 10^{-9}$	-84.0	$bar^{-0.5}$		
$K_{ads,MeOH}$	$1.54 \cdot 10^{-4}$	-44.5	bar^{-1}		
$K_{ads,H2O}$	$3.12 \cdot 10^{-10}$	-89.6	bar^{-1}		

Table 2.1: The kinetic constants used in this work

2.3.1 Permeance

In this reactor model, alumina supported carbon molecular sieve membrane (Al-CMSM) is considered to be integrated as the membrane module. This membrane allows for high permeability and selectivity of water. The permeance of all components is a function of temperature [35]. Within this group, a series of permeability experiments have been conducted at various temperatures. The permeance has been fitted on this data in the form of an Arrhenius equation, shown in Equation 2.72. The parameters to calculate the permeance are reported in Table 2.2. DME is assumed to barely permeate through the Al-CMSM, and therefore the permeance constant of DME has been assumed to be zero [35].

$$J_{perm,i} = J_{perm,0,i} \cdot exp\left(\frac{A_{perm,i}}{T}\right)$$
(2.72)

Component	$J_{perm,0} \left[\frac{mol}{bar \cdot m^2} \right]$	A_{perm}
CO_2	0.1088	-3770.59
CO	0.2119	-2254.52
H_2	3.479	-2549.2
MeOH	1.58E-06	3770.59
h ₂ o	0.003562	1232.45

Table 2.2: The permeance constants of the permeating components

2.4 Performance Indicators

In this work, the conversion, selectivity, yield and production rate are used to evaluate the overall performance of the reactor.

The CO_2 conversion is calculated according to Equation 2.73. If a membrane is used, the definition of the conversion changes to account either for the CO2 that did not react because of permeation through the membrane or for the CO2 that enters the catalytic bed due to back-permeation.

$$X_{CO2} = \frac{F_{CO2,in} - F_{CO2}}{F_{CO2,in}}$$
(2.73)

$$X_{CO2} = \frac{F_{CO2,R,in} - F_{CO2,R} - (F_{CO2,M} - F_{CO2,M,in})}{F_{CO2,in} + F_{CO2,perm}}$$
(2.74)

Where X_{CO2} is the conversion of CO₂, F_{CO2} is the flow of CO₂ in the reactor, $F_{CO2,M}$ is the flow of CO₂ in the membrane and $F_{CO2,in}$ is the inlet flow of CO₂ in the reactor. $F_{CO2,perm}$ is the amount of CO₂ that enters the reactor via the membrane (co-feeding), if CO₂ leaves the reactor via the membrane (back permeation), this term is set to zero.

The selectivity is defined in Equation 2.75 for the PBR and in Equation 2.76 for the PBMR.

$$S_i = \frac{\nu_i}{\nu_{CO2}} \frac{F_i}{F_{CO2,in} - F_{CO2}}$$
(2.75)

$$S_i = N_C \frac{F_{i,R} + F_{i,M}}{F_{CO2,R,in} - F_{CO2,R} - (F_{CO2,M} - F_{CO2,M,in})}$$
(2.76)

Here, N_C is the number of carbon atoms in a molecule (i.e. two for DME and one for CO and methanol). Lastly, the yield and the productivity are defined in Equation 2.77 and 2.78.

$$Y_i = S_i \cdot X_{CO2} \tag{2.77}$$

$$Prod_i = \frac{\nu_{CO2}}{\nu_i} Y_i \cdot F_{CO2,in} \tag{2.78}$$

Here, Y_i is the yield of species i and $Prod_i$ is the productivity of species i.
Chapter 3

Particle scale

First, the heat and mass transfer phenomena are investigated at the particle scale. This is done to evaluate internal mass and heat transfer limitations by modelling the concentrations and temperature inside the catalyst particles. If internal mass or heat transfer limitations are not limiting in the range of conditions defined relevant to this system, their effect can be neglected when setting up the reactor model.

3.1 Method

The most common approach for modelling internal mass transfer phenomena is via the Thiele modulus. However, due to the complex kinetic system, this approach is not appropriate. Therefore, a rigorous model of the catalyst domain has to be implemented, where the concentrations and temperatures are explicitly modelled.

3.1.1 Governing equations and boundary conditions

In the catalyst particle, chemical reactions take place. For this chemical reaction to take place, reactants need to diffuse inside the pores of the catalyst particle and products need to diffuse out of the pores to reach the bulk phase. Convection in the catalyst particle is considered to be negligible. The catalyst particle is assumed to be spherical and at a steady-state, which results in the mass balance shown in Equation 3.1.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{eff,i}\cdot r^2\frac{\partial C_i}{\partial r}\right) - R_i = 0 \tag{3.1}$$

Here, r is the radius of the catalyst particle, $D_{eff,i}$ is the effective diffusivity of component i, as defined in subsection 2.2.1, C_i is the molar concentration of component i and R_i is the reaction rate of component i per volume of catalyst.

Due to a chemical reaction, heat is generated inside the catalyst particle. This heat is transported in the catalyst particle only by thermal conductivity. The governing equation for the temperature inside the catalyst particle is reported in Equation 3.2.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda_{eff}\cdot r^2\frac{\partial T}{\partial r}\right) + \sum \Delta H \cdot r = 0 \tag{3.2}$$

Here, λ_{eff} is the effective thermal conductivity inside the catalyst particle, as defined in 2.2.3.

In the centre of the catalyst particle, a Neumann boundary condition is defined, due to the symmetry of the system. This boundary condition is the same for both temperature and concentration (Equation 3.3).

$$\left. \frac{\partial C_i}{\partial r} \right|_{r=0} = 0 \qquad \left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \tag{3.3}$$

At the surface $(r = R_{part})$ of the catalyst particle, the concentration or temperature is the same as in bulk fluid, assuming that there are no external mass transfer limitations. In this case, a concentration or temperature is imposed at the edge of the catalyst particle, resulting in the Dirichlet boundary condition (Equation 3.4).

$$C_i|_{r=R_p} = C_{i,bulk} \qquad T|_{r=R_p} = T_{bulk} \tag{3.4}$$

3.1.2 Model implementation

To numerically solve the governing equations with the given boundary conditions, the diffusive terms are discretized using a central differencing scheme. The (non-linear) reaction rates are included in the non-linear Jacobean of the Newton-Raphson scheme.

Since steeper gradients are expected near the catalyst surface, the grid size is smaller near the catalyst surface compared to the grid size near the centre of the catalyst particle. This is done to allow for fewer grid points in the catalyst particles, leading to faster simulations.

In this system, there are two different types of catalyst particles. As a result, the concentration of the reactants and products are different in the two catalyst particles. Therefore, the equations should be solved for the two catalyst particles separately. This is done by assuming per component and temperature two different values: one for the methanol catalyst and one for the DME catalyst. The bulk concentrations that appear in the boundary conditions on the edge of the catalyst particles are the same for both particles. The diameter of both catalyst particles should be the same, and both catalyst particles have the same radial discretization.

The effective diffusivity and thermal conductivity are calculated in the centre and at the surface of the catalyst particle. In limited cases, with large (concentration or temperature) profiles the values at the centre and surface of the catalyst particles differ by only a few per cent. Therefore, it can be concluded that the thermal conductivity and effective diffusivity are weak functions of the radial position. As a result the effective diffusivity and thermal conductivity are taken out of the derivative of Equation 3.1 and 3.2 respectively.

3.1.3 Grid size analysis

To determine the sufficient number of grid points in the catalyst particles, a grid size analysis is performed. An error is defined with respect to a large reference grid, as in Equation 3.5. If the error with respect to the large reference grid is lower than 10^{-5} the grid size is considered accurate.

$$Error = max\left(\left|\frac{C - C_{ref}}{C_{ref}}\right|\right)$$
(3.5)

Depending on the gradients in the system, a different amount of grid points is required. For a system with steep gradients, more grid points are required. To obtain a number of grid points that yield reliable results for all simulations, the parameters are set such that the steepest gradients are obtained that are within the operating conditions of the reactor. This is done for a large catalyst particle of 10 mm.

In Figure A.1 in the appendix, the maximum error calculated in the radial direction of the particle for different grid sizes is reported as a function of the number of grid points. With a grid size of 100, corresponding to a Δr of 0.1 mm, the error is below the set tolerance. Therefore, a Δr of at most 0.1 mm in the radial direction is chosen for all simulations in this work.

3.1.4 Verification

To verify the reaction-diffusion model, the numerical model is compared to an analytical solution for a first order-irreversible and elemental reaction of $A \longrightarrow B$ in the first catalyst and a reaction of $B \longrightarrow C$ in the second catalyst. Inside the catalyst particles, a constant effective diffusivity is assumed. To quantify the numerical model, an error is defined with respect to the analytical solution. The definition of the error can be seen in Equation 3.6.

$$Error = max \left(\left| \frac{C_{model} - C_{analytical}}{C_{analytical}} \right| \right)$$
(3.6)

The results of this comparison can be seen in Figure A.2 in the appendix. The numerical model and the analytical model predict the same concentration profiles in the catalyst particle, with a maximum error of $1.82E^{-5}$. This is an indication that the numerical model is implemented correctly.

3.2 Results

3.2.1 Internal Mass Transfer Limitations

To assess the relevance of internal mass transfer limitations, the concentration profiles inside the catalyst particle are simulated. The concentration profiles are first determined in a limiting condition that may give rise to internal mass transfer limitations (i.e. in a situation with fast reaction rates and slow diffusion rates). If in these limiting conditions, there is no effect of internal mass transfer, it is acceptable to neglect internal mass transfer limitations. To obtain fast reaction rates and slow diffusion rates, a catalyst particle with a large diameter of 10 mm and a temperature of 270 °C are chosen. The results in terms of concentration of the reactants and products as a function of the particle radius are depicted in Figure 3.1 and Figure 3.2.



Figure 3.1: The concentration of the reactants in the catalyst particles ($T_{surf} =$ 270 °C, P = 40 bar, $d_{part} =$ 10 mm)

From this result, we can conclude that in the limiting conditions, concentration gradients for all products and reactants are significant. The concentration gradients are especially steep for the DME catalyst. The reason for this is that the DME catalyst is a zeolite with small pores (around 3 nm). Due to these small pores, the diffusion of reactants and products is slower compared to a catalyst with larger pores. Moreover, the methanol dehydration reaction is faster than the methanol formation reaction [18]. Therefore, the internal mass transfer limitations are more relevant for the zeolite catalyst, leading to a steeper concentration gradient. The presence of concentration profiles means that internal mass transfer limitations are a relevant mass transfer phenomena, that needs to be taken into account when modelling the reaction of CO_2 and H_2 to DME.

3.2.2 Internal Heat Transfer Limitations

Similarly to the internal mass transfer limitations, internal heat transfer limitations are significant if there are steep temperature profiles in the catalyst particles. These steep profiles occur when the heat production is high due to fast reaction rates and the heat transport is slow due to large particle diameters. Therefore, as for the mass transfer limitations, temperature profiles are first determined in these limiting conditions, to assess the relevance of the phenomena. The results are shown in Figure 3.3.



In the limiting situation for heat transfer, the absolute temperature difference between the centre and the edge of the catalyst particle is around 0.1 °C for both catalyst particles. That is a relative difference of less than 0.01 %. The fast internal heat transfer is due to the fast heat transport in the solid catalyst particle. The absence of internal heat transfer limitations is also often observed in literature [39]. Because the internal heat transfer is not limiting, the internal heat transfer is not modelled and the interior of the catalyst particles is considered to be isothermal.

3.3 Modified Thiele Modulus

The internal mass transfer limitations are modelled by explicitly modelling the interior of the catalyst particle. This is required due to the high complexity of the kinetics, consisting of parallel, non-linear, consecutive and reversible reactions. Modelling the catalyst particles explicitly is computationally expensive, and therefore an alternative method to estimate the internal diffusion limitations is attractive. However, non of the á priori methods described in subsection 1.2.1 are suitable to estimate the catalyst efficiency for the current system. Therefore, another correlation is required to estimate the catalyst efficiency from the Thiele modulus. To

see if there is a correlation, a generalised, component-specific Thiele modulus is defined as can be seen in Equation 3.7. The corresponding, component-specific, efficiency is defined according to Equation 3.8.

$$\varphi_i = \frac{V_{part}}{A_{part}} \sqrt{\frac{r_{i,surf}}{D_{eff,i}C_{i,surf}}}$$
(3.7)

$$\eta_i = \frac{r_{i,obs}}{r_{i,surf}} \tag{3.8}$$

The catalyst

temperatures,

and

Several simulations with the rigorous diffusion-reaction model are carried out, varying the particle radius (0.1-20 mm), temperature (200 - 270 °C), pressure (30-40 bar), catalyst geometries (slab, cylindrical, spherical) and surface compositions. From the simulation results, the efficiency per component is calculated and reported as a function of the corresponding Thiele modulus in Figure 3.4.



From Figure 3.4 it can be concluded that there is no clear correlation between the Thiele modulus and the efficiency. This means that the Thiele modulus, as defined in Equation 3.7, cannot be used to estimate the catalyst efficiency.

The Thiele modulus is defined as the reaction rate divided by the diffusion rate. The diffusion rate in this ratio is proportional to the term $D_{eff}C_{i,surf}$. A specific component will always diffuse from a high to a low concentration. Therefore, its diffusion rate is proportional to a concentration difference between two points (i.e., the surface and centre of the particle). In this case (i.e., with the definition of the Thiele modulus as in Equation 3.7), the diffusion rate only depends only on the concentration at the catalyst surface, which implies that the concentration at the centre of the catalyst particle is zero. If a reaction is irreversible, the concentration at the centre of the catalyst particle could become zero. However, due to the reversible equilibrium reactions, the concentration of any species will never become zero, but it would go towards an equilibrium value. This thermodynamic limit could explain why the Thiele modulus does not correlate well with the catalyst efficiency (Figure 3.4). For example, when surface concentrations are close to thermodynamic equilibrium, the reaction rates are low, but the diffusion rate could still be high because the diffusion rate is not affected by thermodynamics. If this diffusion rate would be corrected for the thermodynamic equilibrium, the diffusion rate would be low as well. This thermodynamic equilibrium concentration can be calculated with the surface pressure, temperature, composition and equilibrium constants of the reactions occurring in the catalyst particle. As a result, the Thiele modulus can be corrected to account for the thermodynamic equilibrium, as in Equation 3.9 which we call modified Thiele modulus (φ_{mod}).

$$\varphi_{i,mod} = \frac{V_{cat}}{A_{cat}} \sqrt{\frac{r_{i,surf}}{D_{eff,i}(C_{i,eq} - C_{i,surf})}}$$
(3.9)

For the modified Thiele modulus the same analysis is done as for the general Thiele modulus. The results are reported in a similar fashion in Figure 3.5.



Figure 3.5: efficiency as function of the modified Thiele modulus for systems with varying pressures, particle diameters, particle geometries compositions $(T_R = 200$ -270 °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20 \text{ mm}$

Adjusting the Diffusion rate for the equilibrium concentration has a clear effect on the correlation between the modified Thiele modulus and the efficiency. The modified Thiele modulus and the efficiency are correlated for systems with different particle sizes, pressures, temperatures, geometries and surface compositions. However, for CO this correlation does not hold (see Figure A.3 in the appendix). Several reasons could be given for this. The kinetic model predicts initial concentrations of CO that are above the thermodynamic equilibrium concentration. For example: at 230 °C and 40 bar the equilibrium concentration of CO is around 11 mol/m^3 whereas the kinetic model predicts concentrations above 20 mol/m^3 . The poor correlation of CO could also be due to complex kinetic interactions. Since CO is an intermediate product, the profile of CO in the catalyst particle is not monotonous decreasing or increasing over the radius of a catalyst particle, but it has a maximum or minimum value, depending on operating conditions. This means that CO could diffuse in multiple directions in the catalyst particle. This is something that is not taken into account in the (modified) Thiele modulus.

To check if the correlation of the modified Thiele modulus and the catalyst efficiency found for this kinetic system is general, the same analysis is carried out for different kinetic systems. For the methanol catalyst, four different kinetic schemes have been selected and evaluated. For the Kinetics of Bussche & Forment [40], Graaf [18], Heckel [22] and Park [32] the correlation between the modified Thiele modulus and the catalyst Efficiency is shown in Figure A.4 to A.7 in the Appendix. It can be seen that for different kinetic systems, the correlation still holds.

Since, apart from CO in the methanol catalyst, the modified Thiele modulus correlates quite well with the catalyst efficiency, a function could be fitted that links the Thiele modulus to the catalyst efficiency. This function should go to unity for small values of the Thiele modulus (i.e., kinetic limiting regime) and should go to zero for large values of the Thiele modulus (i.e., diffusion limiting regime). A function of the form of Equation 3.10 is chosen because it shows the correct behaviour for large and small values of the Thiele modulus.

$$\eta_i = \frac{1}{(1+a\cdot\varphi_i^2)^b} \tag{3.10}$$

The values for a and b are fitted per catalyst (i.e., methanol and DME catalyst) and component. The obtained values of a and b are shown in table 3.1.

Spherical									
Component	Catalyst	a	b	$10^6 * D_{eff}$	$10^{-6} \frac{a}{D_{eff}}$	$\frac{D_{eff,lim} \cdot a}{D_{eff}}$			
$\rm CO_2$	MeOH	1.09	0.47	1.07	1.02	0.99			
H_2	MeOH	3.07	0.50	2.76	1.11	1.08			
MeOH	MeOH	0.89	0.54	0.97	0.92	0.89			
H_2O	MeOH	1.56	0.46	1.36	1.15	1.11			
DME	DME	1.03	0.48	0.42	2.44	1.03			
MeOH	DME	1.28	0.48	0.53	2.44	1.03			
H_2O	DME	1.80	0.48	0.74	2.44	1.03			
Cylindrical									
CO_2	MeOH	0.86	0.50	1.07	0.80	0.91			
H_2	MeOH	2.63	0.52	2.76	0.95	1.08			
MeOH	MeOH	0.86	0.55	1.13	0.76	0.86			
H_2O	MeOH	1.22	0.50	1.36	0.90	1.01			
DME	DME	1.00	0.51	0.42	2.37	1.00			
MeOH	DME	1.08	0.51	0.45	2.37	1.00			
H_2O	DME	1.51	0.51	0.64	2.37	1.00			
Slab									
CO_2	MeOH	1.00	0.53	1.07	0.94	0.91			
H_2	MeOH	2.74	0.54	2.76	0.99	0.97			
MeOH	MeOH	0.96	0.55	0.97	0.99	0.96			
H_2O	MeOH	1.40	0.53	1.36	1.03	1.00			
DME	DME	0.96	0.53	0.42	2.27	0.96			
MeOH	DME	1.03	0.53	0.45	2.27	0.96			
H_2O	DME	1.45	0.53	0.64	2.28	0.96			

Table 3.1: The dependency of a on effective diffusivities

It should be noted that the value of b is close to 0.5 for all components, catalysts and catalyst geometries. This means that for large values of the modified Thiele modulus the efficiency approaches a system that scales linearly with $1/\varphi$. This behaviour is also observed for the theoretical systems described in subsection 1.2.1 [39]. The reappearance of theoretical values is an indication that the correlation shows physical behaviour.

The parameter changes significantly per component and catalyst. Therefore a dependence that is component and catalyst specific, such as the effective diffusivity, is expected. Generally, a is lower for slow diffusing species and lower for the second catalyst, which is more diffusion-limited. This also suggests that the value of a might be dependent on the effective diffusivity. Therefore the value of a is divided by the effective diffusivity of the component.

It can be seen that if the value of a is divided by the effective diffusivity, the values of a/D_{eff} approach the same value for each catalyst. However, if this is again normalised with the effective diffusivity of the slowest diffusing species in each catalyst particle, the numerical value for both catalysts and all geometries is close to unity. This gives rise to the approximate formula of a in Equation 3.11. The dependence of the efficiency on the slowest diffusing species is also physically reasonable since the reactive system is more affected by the slowest diffusing species.

$$a_i = \frac{D_{i,eff}}{D_{lim,eff}} \tag{3.11}$$

The correlations found for the parameters a and b with Equation 3.12, give rise to the following formula for the efficiency:

$$\eta_i = \frac{1}{(1 + \frac{D_{i,eff}}{D_{lim,eff}}\varphi_i^2)^{0.5}}$$
(3.12)

To check if the correlation can predict the efficiency well, the efficiency is calculated with the rigorous particle model and with the correlation in various conditions. The efficiencies from the rigorous model are plotted versus the results from the correlation (Figure 3.6). The closer the results are to the line y=x (i.e., the red line), the better the efficiencies are predicted by the correlation.



Figure 3.6: The catalyst efficiency from the rigorous model and the correlation for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions ($T_R = 200$ -270 °C, $P_{R,in} = 30$ -40 bar, $d_{part} = 0.1$ -20 mm)

Especially for the DME catalyst, the efficiencies are well predicted with the correlation. For this catalyst, the predicted and modelled efficiencies are almost the same. For the methanol catalyst, the correlation works less well. This is likely due to the more complex reaction system in the methanol catalyst. However, the correlation does predict the efficiency for the methanol catalyst always within 5% of the modelled result, meaning that the correlation also works for the methanol catalyst.

3.4 Conclusions

In this section, we learnt that in some situations, significant concentration gradients in the catalyst particle exist. In a system with catalyst particles of 10 mm at 270°C, the concentration of methanol increases by almost 100% from the edge to the centre of the catalyst particle, significantly influencing the kinetics. Therefore, internal mass transfer limitations should be taken into account when modelling the reactor. In all relevant conditions, the temperature difference between the centre of the catalyst particle and the edge of the catalyst particle is less than 0.01%. Therefore, the effect of internal heat transfer limitations is neglected when setting up the reactor model, and the catalyst particles are considered to be isothermal.

Since no simplified approach already exists in literature, a correlation is found here, by comparing simulation data obtained from the rigorous particle model with the standard and general definition of Thiele modulus and efficiency. The Thiele modulus is modified, to include thermodynamic equilibrium data. This modified Thiele modulus is plotted against the catalyst efficiency for systems with different catalyst geometries, surface compositions, kinetic systems, pressures, temperatures and catalyst diameters. In all cases, the modified Thiele modulus shows a strong correlation with the catalyst efficiency. A correlation is fitted to estimate the catalyst efficiency based on the modified Thiele modulus. The fitted values are linked to known parameters such as diffusion coefficients. The fitted efficiency closely matches the numerically calculated efficiencies. This is a promising result because this allows for the calculation of the catalyst efficiency without having to model the interior of the catalyst particles, which is computationally expensive.

Chapter 4

Particle-Fluid interphase

In this section, the mass and heat transfer phenomena in the particle-(bulk)fluid interphase will be discussed. More specifically, the external mass and heat transfer limitations will be evaluated.

4.1 Method

To model external mass and heat transfer, a mass or heat transfer flux needs to be considered to describe either the mass or heat transport from the bulk fluid phase to the surface of the catalyst particle.

4.1.1 Governing equations and Boundary Conditions

Equation 4.1 and Equation 4.2 are used to describe the mass and heat transfer flux from the bulk of the fluid to the catalyst surface, respectively.

$$J_i = k_{ext} \cdot (C_i|_{bulk} - C_i|_{r=R_p}) \tag{4.1}$$

$$J_i = h_{ext} \cdot (T|_{bulk} - T|_{r=R_p}) \tag{4.2}$$

Here, k_{ext} and h_{ext} are the external mass and heat transfer coefficients, as described in subsection 2.2.7 and subsection 2.2.8 respectively.

If a particle model is used, the external heat or mass transfer coefficients can be implemented in the particle model by adjusting the boundary conditions at the surface of the catalyst particle as defined in subsection 3.1.1. Instead of a Dirichlet boundary condition, where a concentration is imposed, a flux is imposed at the boundary of the catalyst particle (Equation 4.3). This flux is then described by Equation 4.1 or Equation 4.2.

$$D_{eff,i}\frac{\partial C_i}{\partial r}\Big|_{r=R_p} = k_{ext} \cdot (C_{i,bulk} - C_i|_{r=R_p}) \qquad \lambda_{eff}\frac{\partial T}{\partial r}\Big|_{r=R_p} = h_{ext} \cdot (T_{bulk} - T|_{r=R_p}) \tag{4.3}$$

In section 3.3 it was shown that the internal mass transfer limitations can also be estimated without modelling the concentration inside the catalyst particle, but using the modified Thiele modulus approach. Because of that, the external mass transfer cannot be modelled by including it in the boundary conditions of the particle model. Therefore, a mass balance over the solid catalyst phase is set up. In this mass balance, there is a reaction term, including the catalyst efficiency to account for internal mass transfer limitations, and an external mass or heat transfer term. This mass balance has to be set up for both catalyst particles separately because the concentrations at the methanol catalyst surface can be different from the concentrations at the DME catalyst surface. The equations for the mass conservation at the two catalyst surfaces are the following:

$$\eta_{cat1,i} \cdot \rho_{cat1}^{app} \cdot r_{cat1,i} - k_{ext,i} \cdot (C_i|_{bulk} - C_i|_{solid,cat1}) = 0$$

$$(4.4)$$

$$\eta_{cat2,i} \cdot \rho_{cat2}^{app} \cdot r_{cat2,i} - k_{ext,i} \cdot (C_i|_{bulk} - C_i|_{solid,cat2}) = 0$$

$$(4.5)$$

Here, $\eta_{i,cat}$ is the component-specific efficiency in a catalyst of component i. In the first catalyst, there are two independent reactions. Therefore two independent components are defined, in this case, CO₂ and H₂. For these components, the component-specific catalyst efficiency is calculated using the correlation in Equation 3.12. For CO, methanol and water the efficiencies are calculated using reaction stoichiometry and mass balances. For the second catalyst, there is only one independent reaction, here methanol is chosen as the independent component for which the efficiency is determined. The efficiency for DME and water in the second catalyst is determined via mass conservation balances.

In subsection 3.2.2 it was shown that internal heat transfer limitations are negligible. Therefore, the effect of the external heat transfer cannot be included in the boundary condition of the particle model, since the temperature profile is not modelled inside the catalyst particle. A heat balance over the solid catalyst particle is set up to account for the external heat transfer. In this balance, there is a generation term due to the heat generated by the reactions and a heat transfer term due to external transport.

Due to the use of the component-specific catalyst efficiency, only the reaction rate per component is known, and not necessarily the reaction rate per reaction. Because the CO hydrogenation, the CO_2 hydrogenation and the water-gas shift reaction in the methanol catalyst are linearly dependent on each other, it is not possible to determine the exact rate of these three reactions, if only the reaction rates per component are known. This could be a problem because the heat of reaction is defined per reaction, therefore the reaction rate per reaction should be known. If CO_2 reacts to CO and CO reacts to methanol the same amount of heat is generated if CO_2 directly reacts to methanol. This can be used to circumvent the issue that the reaction rates are linearly dependent on each other. For the generation of reaction heat, it is assumed that all CO_2 reacts to CO and that all methanol is formed by the hydrogenation of CO. In this way, only two reactions have to be used, from which the exact rate and reaction enthalpy is known. The reaction rate of reaction 4 in the DME catalyst is simply equal to the reaction rate of DME because there is only one reaction in the DME catalyst. The heat conservation at the two catalyst particles is described by Equation 4.6 and 4.7.

$$\Delta H_{r,2}r_{CO2,cat1} - \Delta H_{r,3}r_{CH3OH,cat1} - h_{ext} \cdot (T|_{bulk} - T|_{solid,cat1}) = 0$$

$$\tag{4.6}$$

$$-\Delta H_{r,4}r_{DME,cat2} - h_{ext} \cdot (T|_{bulk} - T|_{solid,cat2}) = 0$$

$$(4.7)$$

In the equation, $r_{i,cat1}$ is the formation or reaction rate of component i in the first catalyst. If the catalyst efficiency is used r_i is given by Equation 4.8. If a particle model is used, r_i is given by the flux towards the catalyst particle. This is shown in Equation 4.9.

$$r_{i,cat1} = \eta_{i,cat1} \rho_{cat1}^{app} r_{i,cat1} \tag{4.8}$$

$$N_{i,cat1} = \frac{3 \cdot D_{eff,i,cat1}}{R_p} \frac{\partial C_i}{\partial r} \bigg|_{r=R_p}$$
(4.9)

4.1.2 Model Implementation

If a particle model is used, the effect of the external mass or heat transfer is incorporated into the boundary condition of the mass balance in the catalyst particle. The external mass or heat transfer coefficient is calculated using the pressure, concentrations, temperature and velocity of the previous iteration in the Newton Raphson scheme. With the new external transfer coefficient, the boundary condition of the mass and heat balances in the catalyst particle, are updated every iteration until convergence. If the particle model is not used because the catalyst efficiency is used or because the internal transfer limitations are not modelled, three values per concentration of all components and per temperature are defined. Meaning that, for example, in one grid cell there are three different CO_2 concentrations defined: one belonging to the concentration at the surface of the methanol catalyst, one belonging to the concentration at the DME catalyst surface and one belonging to the concentration in the bulk of the fluid. For the solid concentration the mass balance in Equation 4.4 is solved and for the temperature in the solid phase the energy balance in Equation 4.6 is solved. Both the reaction term and the external transfer term of these equations are non-linear and end up in the non-linear part of the Jacobean in the Newton Raphson scheme.

4.2 Results

External mass or heat transfer will have a limiting effect if the kinetics are fast, the catalyst particles are large and the superficial velocity in the column is low [15]. As a result, simulations in these limiting conditions of high temperature (i.e., 270 °C), large catalyst particle (i.e., 10 mm) and low velocity (0.001-10 m/s) if external mass or heat transfer has a significant effect. If external mass or heat transfer has no effect in these conditions, it can be neglected in the reactor model. To have a more clear picture of the effect of external mass and heat transfer, the simulation results are reported in terms of the ratio between the concentration or temperature at the catalyst surface and the concentration or temperature in the bulk phase $(C_{surf}/C_{bulk}$ and T_{surf}/T_{bulk} , respectively) as a function of the superficial velocity.

4.2.1 External Mass Transfer Limitations

The effect of external mass transfer limitations is depicted in Figure 4.1, in which two dashed horizontal lines are reported to represent a 1% deviation from unity.



In a limiting case, at low superficial velocities, the external mass transfer can have a significant effect, with surface concentrations deviating up to 9% from the bulk concentration. Since in some cases the external mass transfer can have a significant effect, it should be taken into account when modelling the packed bed membrane reactor. However, in this analysis, the effect of internal mass transfer is not taken into account. Internal mass transfer also has a significant effect in the same process conditions as external mass transfer, (i.e. large particle size and high temperature). Internal mass transfer could reduce the reaction rate, mitigating the effect of external mass transfer. Therefore, the same analysis is done, but now with a model including internal mass transfer. Results are reported in Figure 4.2.

It can be seen that if internal mass transfer is taken into account, the effect of external mass transfer is reduced. Now, the concentration at the edge of the catalyst particle deviates up to 6% from the bulk concentration at low superficial velocities.



Figure 4.2: The normalised surface concentration for different super facial velocities for a model including internal mass transfer $(T_{bulk} = 270 \text{ °C}, P_R = 40 \text{ bar}, d_{part} = 10 \text{ mm})$

In literature, the Mears criterion is often used to check if external mass transfer has a limiting effect and should be modelled [15]. However, the problem is that the Mears Criterion is derived for power-law kinetics and not for the kinetic system that is used to model the reactions in the methanol or DME catalyst. Also, since the reactions are reversible, occurring in parallel and in series, the order of the reaction is undefined. To check the validity of the Mears Criterion, the relative difference between the surface concentration and the bulk concentration derived via the rigorous model is reported versus the Mears parameter (or Carberry number). This is done for different particle sizes, pressures, temperatures, surface compositions and superficial velocities. Since the order of the reaction cannot be calculated, the value of n (Equation 1.9), is set to unity. The results can be seen in Figure 4.3, the horizontal line corresponds to a deviation of 5% and the vertical line corresponds to a value of the Mears parameter of 0.15.



Figure 4.3: The relative difference between surface and bulk concentration for different superficial velocities, temperatures and particle sizes ($T_{bulk} = 200-250$ °C, $P_R = 30-40$ bar, d_{part} = 1-20 mm $v_{SF} = 0.001-1$ m/s)

For values of the Mears parameter smaller than 0.15, the difference between the surface concentration and the bulk concentration is less than 5%. This is in line with the results found for power-law kinetics. A concentration difference of less than 5% is considered to be negligible. Therefore, the Mears criterion can also be used for this complex kinetic system.

4.2.2 External Heat Transfer Limitations

The effect of external heat transfer limitations is depicted in Figure 4.4.



For the temperature there does not seem to be a limiting velocity even in a situation where heat transfer should be quite limiting, due to the very low velocity. Usually, external heat transfer is limiting because of the low thermal conductivity of gasses [15]. However, hydrogen has a relatively high thermal conductivity in the order of 0.2 W/(mK) in comparison with most gasses with thermal conductivities in the order of 0.03 W/(mK). This could, partially, explain the absence of external heat transfer limitations. To confirm this theory, the same simulations are carried out by artificially setting the thermal conductivity of hydrogen to the same value as the thermal conductivity of CO_2 . The results are reported in Figure 4.5.



Figure 4.5: The normalised surface temperature for different superficial velocities for a system with a lowered thermal conductivity of hydrogen ($T_{bulk} = 270$ °C, $P_R = 40$ bar, $d_{part} = 10$ mm)

It can be seen that if the thermal conductivity of hydrogen is artificially lowered, a larger effect of the external heat transfer can be observed. This means that external heat transfer limitations are less relevant if the hydrogen content in the gas phase is high. At the beginning of the reaction, there is a high hydrogen content, and therefore a relatively high thermal conductivity of the gas. At high conversions, the hydrogen

content is lower, resulting in lower thermal conductivity. However, at high conversions, the kinetic reaction rate is also much slower. Therefore, even at low hydrogen concentrations, the external heat transfer can be neglected.

4.3 Conclusions

In this chapter, we learned that external mass transfer limitations can have a significant impact on the concentration at the catalyst surface in limiting situations. Therefore, the external mass transfer limitations should be taken into account in the packed bed membrane reactor model. However, if internal mass transfer is taken into account, the effect of external mass transfer limitations is lower. The Mears-Criterion, that is originally developed for systems with power-law kinetics, can be used as an indication to decide whether to neglect or not external mass transfer. If the Mears-Criterion is lower than 0.15, the surface concentration at the catalyst particles deviates less than 5% from the bulk concentration.

The effect of the external heat transfer is negligible in a limiting situation, where the external heat transfer should be quite slow. Therefore, external heat transfer does not need to be taken into account when modelling this reactor. The reason why external heat transfer has a small effect on the temperature at the catalyst surface is due to the high thermal conductivity of hydrogen.

Chapter 5

Packed Bed Reactor

In this section, the co-effect of both internal (i.e., intra-particle) and external (i.e., fluid-particle) mass transfer will be evaluated in combination with the reactor model, to assess their influence on the overall reactor performance. Thereafter, the axial dispersion will be discussed and the relevance thereof will be assessed.

5.1 Method

5.1.1 Governing Equations and Boundary Conditions

In the packed bed reactor there is a convective flow, reaction and, in some cases, axial dispersion. The reactor is assumed to be in steady-state, there are no radial concentration, temperature, pressure or velocity profiles (i.e., a one-dimensional model). The governing equation for the model without axial dispersion and the model with axial dispersion can be seen in Equation 5.1 and Equation 5.2 respectively.

$$\frac{\partial vC_i}{\partial z} = R_i \tag{5.1}$$

$$\frac{\partial}{\partial z} \left(vC_i - D_{ax} \frac{\partial C_i}{\partial z} \right) = R_i \tag{5.2}$$

Here, D_{ax} is the axial dispersion term as defined in subsection 2.2.9.

The reaction term is different depending on which mass transfer effects are taken into account. If no internal and external mass transfer effects are taken into account, the reaction term is given by Equation 5.3. If only internal mass transfer is assumed to be relevant, the reaction term is given by Equation 5.4 or Equation 5.5. Equation 5.4 is implemented if a rigorous particle model is used to model the internal mass transfer limitations. Equation 5.5 is implemented if the modified Thiele modulus approach is used to calculate the internal mass transfer limitations. If external mass transfer is taken into account, the reaction term is given by Equation term is given by Equation 5.4 or Equation 5.6. Equation 5.4 is used when the external mass transfer is taken into account in the boundary condition of the particle model, in other words, when the particle model is solved simultaneously. Equation 5.6 is implemented if the external mass transfer is incorporated directly in the reaction term with a mass transfer coefficient (k_{ext}) when the particle model is not solved.

$$R_i = D_{cat} \cdot (1 - \varepsilon_{bed}) \cdot (x_{vol,cat1} \cdot \rho_{cat1} \cdot r_{cat1,i} + x_{vol,cat2} \cdot \rho_{cat2} \cdot r_{cat2,i})$$
(5.3)

$$R_{i} = D_{cat} \cdot (1 - \varepsilon_{bed}) \frac{6}{d_{part}} \left(x_{vol,cat1} \cdot D_{eff,cat1,i} \frac{\partial C_{cat1,i}}{\partial r} \bigg|_{r=R_{part}} + x_{vol,cat2} \cdot D_{eff,cat2,i} \frac{\partial C_{cat2,i}}{\partial r} \bigg|_{r=R_{part}} \right)$$
(5.4)

$$R_i = D_{cat} \cdot (1 - \varepsilon_{bed}) \cdot (\eta_{cat1,i} \cdot x_{vol,cat1} \cdot \rho_{cat1} \cdot r_{cat1,i} + \eta_{cat2,i} \cdot x_{vol,cat2} \cdot \rho_{cat2} \cdot r_{cat2,i})$$
(5.5)

$$R_{i} = D_{cat} \cdot (1 - \varepsilon_{bed}) \frac{6}{d_{part}} (x_{vol,cat1} \cdot k_{ext,i} \cdot (C_{bulk,i} - C_{surf,cat1,i}) + x_{vol,cat2} \cdot k_{ext,i} \cdot (C_{bulk,i} - C_{surf,cat2,i}))$$
(5.6)

In these equations, D_{cat} is the catalyst dilution factor (based on volume) and x_{vol} is the volumetric fraction of a catalyst.

The governing equation for the heat is analogous to the governing equation for mass and is given in Equation 5.7. The axial heat dispersion is not taken into account since this term is seldom significant and also often neglected in literature [7].

$$\frac{\partial}{\partial z} \left(v \cdot \sum_{i} (C_i \cdot C_{p,i}) \cdot T \right) = \sum \Delta H_i \cdot R_i$$
(5.7)

Here, C_p is the molar heat capacity as defined in subsection 2.2.4. Similar to the governing equation for mass, the reaction term is dependent on what transfer effects are taken into account.

At the beginning of the reactor, the concentration of all components and the temperature are specified. This results in a Dirichlet boundary condition for the mass and energy balance, as shown Equation 5.8.

$$C_i|_{z=0} = C_{i,in} \qquad T|_{z=0} = T_{in} \tag{5.8}$$

At the exit of the reactor, the concentration and temperature gradient should be zero. This results in a Neumann boundary condition for the mass and energy balance, as shown Equation 5.9.

$$\left. \frac{\partial C_i}{\partial z} \right|_{z=L} = 0 \qquad \left. \frac{\partial T}{\partial z} \right|_{z=L} = 0 \tag{5.9}$$

5.1.2 Model Implementation

The convective term in Equation 5.1 and the dispersion term in Equation 5.2 are modelled as described in subsection 2.1.5. The reaction term is included in the non-linear part of the Jacobean.

If internal mass transfer phenomena are included, a particle model needs to be coupled to the reactor model. Therefore, in every reactor grid cell, a particle model is resolved for both catalyst particles. Both catalyst particles are solved over the same radial coordinates. This allows for a simplification of the model. The two particles with six components and a temperature each are modelled as one particle with twelve components and two temperatures. This results in a two-dimensional model: one dimension is the length of the reactor (z) and one dimension is the particle radius (r). The particle model is coupled to the reactor model by implementing Equation 5.4 in the reaction term in the governing equation of the reactor. The reactor model is coupled to the particle model with the boundary conditions of the particle model. The concentration at the edge of the particle is set equal to the concentration in the fluid phase in the reactor model. The reactor model and the particle model are solved simultaneously using the Newton-Raphson scheme until convergence.

If external mass transfer is taken into account, but the particle model is not modelled, two values for each concentration and temperature are used. One value represents the concentration or temperature in the bulk of the fluid (C_{fluid}, T_{fluid}) and one value represents the concentration or temperature at the catalyst surface (C_{surf}, T_{surf}) . The two concentration are linked through a mass transfer term (k_{ext}) , which represent the external mass transfer. The reaction takes place at the catalyst surface, while in the fluid convection and, in some cases, dispersion, take place.

5.1.3 Grid Size Analysis

In Figure B.1 (in the appendix) the maximum relative error with respect to a large grid size (i.e., 500 grid points) calculated in the axial direction is reported as a function of the number of grid points used. These errors are calculated for a system with steep gradients to simulate a system with the largest numerical errors. With a grid size of 250, corresponding to a ΔL of 4 cm, the error is below the set tolerance of 10^{-5} , . Therefore, a grid size of 4 cm in the axial direction of the reactor is used for all simulations in this work.

5.1.4 Verification

The model is first verified by checking if the total mass in the reactor is conserved. The result is reported in Figure C.1 (in the appendix), where, the normalized mass (i.e., actual mass divided by the mass fed to the reactor), is plotted as a function of the reactor axial coordinate. The mass decreases slightly over the length of the packed bed reactor. However, this decrease is smaller than the accuracy set in the model. Therefore, it can be concluded the model correctly predicts mass conservation.

To further verify the packed bed reactor model, the numerical models are compared to an analytical model for a first-order irreversible reaction of A \longrightarrow B. This is done for a convection-reaction model, a convection reaction model including internal mass transfer and a convection-diffusion-reaction model. For this comparison the numerical errors are calculated using Equation 3.6. The results can be seen in Figure B.2 to B.4 in the appendix. The maximum numerical errors are 7.910^{-5} , 5.510^{-4} and 4.310^{-4} for the convection-reaction model, the convection model including internal mass transfer and the convection-diffusion-reaction model respectively.

5.2 Results

In previous sections, it has been shown that both internal and external mass transfer can have a significant effect. In this section, the effect of these phenomena will be evaluated in a packed bed reactor model. Moreover, the applicability of the modified Thiele modulus for estimating the conversion and selectivity will be evaluated. Internal and external heat transfer phenomena will not be modelled, since the results of the previous chapter showed that their effect is not significant. Additionally, the relevance of axial dispersion is assessed.

5.2.1 Internal Mass transfer Limitations

In subsection 3.2.1 it was shown that large catalyst particles at high temperatures can have significant internal mass transfer limitations. The objective here is to understand if these internal mass transfer limitations also affect the conversions of CO_2 and selectivities towards CO, MeOH and DME. This analysis is proposed in two situations favouring internal mass transfer limitations: 1) at a large catalyst diameter (10 mm) with varying temperatures (200 - 270 °C) and at a high temperature (270 °C) with varying particle diameters (0.25 -20 mm). The results are depicted in Figure 5.2 and Figure 5.1 where CO_2 conversion and product selectivity obtained for a model which considers- (stars) and a model which neglects (solid line) internal mass transfer phenomena (INMT) are compared.

It can be seen that at high temperatures (Figure 5.1) and large particle diameters (Figure 5.2) the conversion and selectivity start deviating significantly. In particular, CO_2 conversion is lower (with 5%) when calculated with a model that accounts for intra-particle diffusion limitations and, at the same time, the product distribution is affected. Especially the selectivity towards DME for a model including internal mass transfer is lower at high temperatures and large particle diameters (up to 40% lower). This is due to the lower pore diameter and the faster reaction kinetics of the zeolite catalyst, in comparison to the methanol catalyst. Internal mass transfer can have a significant influence on the conversion and selectivity of the reaction of hydrogen and CO_2 to DME. Therefore, it should be taken into account when modelling the packed bed membrane reactor.

5.2.2 Modified Thiele Modulus

In section section 3.3 an alternative method to account for intra-particle diffusion limitations, based on a simplified Thiele modulus-efficiency approach, was proposed as an alternative to the rigorous particle model. In this section, the accuracy of this method in predicting the effect of INMT on the reactor performance is assessed, comparing the results with the one obtained solving the particle model. This can be seen in



Figure 5.3 and 5.4, where the results reported in Figure 5.2 and Figure 5.1 are reproduced and compared with the Thiele modulus approach (circles).

The simplified method predicts the trends in conversion and selectivity with high accuracy in the range of 0-3 mm for the catalyst particle diameter and 200-250 °C for the reaction temperature, displaying a maximum deviation of 5% for both conversion and selectivity. However, in severely internally mass transfer limited situations (i.e. particle diameter larger than 5 mm and reaction temperatures above 250 °C), the modified Thiele modulus approach tends to overestimate the internal mass transfer, resulting in a lower conversion, compared to the model that solves the mole balances in the particles. The selectivity, however, seems better predicted over the entire range of operating conditions. To assess when the deviation of the simplified Thiele modulus model becomes significant, the value of the relative error in conversion or selectivity is set out against the modified Thiele modulus. Results are reported in Figure 5.5.

Figure 5.5 shows that if the highest modified Thiele modulus in the system, is larger than 2, the relative error of the conversion or selectivity exceeds 5%. This corresponds to a catalyst efficiency of approximately 90%.



Figure 5.3: Conversion of CO_2 and the selectivity of CO, MeOH and DME for varying particle diam-The solid line eters. is a model without internal mass transfer, the astrixes is a model with internal mass transfer and the circles is the alternative Thiele modulus model. $(T_R = 270 \ ^{\circ}\text{C}, P_{R,in} = 40)$ bar, GHSV = $500 \ 1/hr$, $C_{H2}/C_{CO2} = 3, d_{part} =$ 0.1-20 mm, $L_R = 10$ cm, $D_R = 2.6 \text{ cm}, D_{cat} = 0.33,$ $w_{vol,cat1} = 0.5)$

Figure 5.4: Conversion of CO_2 and the selectivity of CO, MeOH and DME for varying operating temperatures. The solid line is a model without internal mass transfer, the astrixes is a model with internal mass transfer and the circles is the alternative Thiele modulus model. $(T_R = 200-270 \ ^{\circ}\text{C}, P_{R,in} =$ 40 bar, $GHSV = 500 \ 1/hr$, $C_{H2}/C_{CO2} = 3, d_{part} = 10$ mm, $L_R = 10 \text{ cm}, D_R = 2.6$ cm, $D_{cat} = 0.33, w_{vol,cat1}$ = 0.5)

5.2.3 External Heat Transfer Limitations

In section 4.2 it was shown that external mass transfer can have a significant influence on the concentration at the catalyst particle surface in some limiting situations. The next step is to check if external transfer can also have a significant influence on the conversion and selectivity in the packed bed reactor in the same limiting conditions. To ensure that the kinetics are not limiting, the analysis is done at a high temperature of 270 °C. Furthermore, to maximise external transfer limitations, the analysis is carried out at varying velocities and a large particle diameter of 10 mm. Since it has been shown that internal mass transfer can be relevant, internal mass transfer is considered in these models. Lastly, the analysis is done at a small reactor length of 10 cm to avoid a thermodynamically limited conversion and selectivity, which would occur at large reactor lengths. The result of this analysis is depicted in Figure 5.6.

In the limiting situation, and at all velocities, the conversion and the selectivity of DME, CO and methanol are not affected by external mass transfer because the values for a model with (stars) and without (solid lines) external mass transfer are similar. At a low inlet velocity of 0.001 m/s, the selectivity towards DME is approximately 3.5% lower, and the selectivity towards methanol is approximately 3.5% higher when

Figure 5.5: The relevant error in conversion and selectivity for various operating conditions ($T_R = 200$ -270 °C, $P_{R,in} = 30$ -40 bar, GHSV = 100-500 1/hr, $C_{H2}/C_{CO2} = 1$ -3, $d_{part} =$ 0.1-20 mm, $L_R = 10$ cm, $D_R = 2.6$ cm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$)

Figure 5.6: Conversion of CO₂ and the selectivity of CO, MeOH and DME for varing surperfical inlet velocities. The solid line is a model without external mass transfer and the astrixes is a model with external mass transfer ($T_R = 270$ °C, $P_{R,in} = 40$ bar, $C_{H2}/C_{CO2} = 3, d_{part} = 10$ mm, $L_R = 10$ cm, $D_R = 2.6$ cm, $D_{cat} = 0.33, w_{vol,cat1} = 0.5$)



considering external mass transfer. The absence of a large effect of external mass transfer can be explained by the reduced kinetic reaction rate due to intra-particle diffusion limitations which are maximized in the same conditions.

Considering that an inlet superficial velocity of 0.001 m/s, an operating temperature of 270 °C and a particle diameter of 10 mm are not operating conditions that are commonly used and relevant in industry and the small difference in selectivity at the low inlet velocities, the effect of external mass transfer limitations on the reactor performance in all practical situations is negligible.

5.2.4 Axial Mass Dispersion

To understand if axial dispersion could be relevant, the conversion and selectivity are predicted and compared for a model that takes into account axial dispersion and a model that does not take into account axial dispersion. In both models, internal mass transfer limitations are taken into account. The axial dispersion coefficient mainly depends on the molecular diffusion coefficient, particle diameter and fluid velocity [10]. Therefore, to obtain a situation that favours axial dispersion, a high temperature, in combination with a large particle diameter should be used to obtain a high molecular diffusion coefficient. At high velocity, the axial dispersion coefficient is higher, as well as the convective transport. Therefore, the effect of an increased velocity on the axial dispersion is less evident. In Figure 5.7, the conversion and selectivity are shown at a high reaction temperature (270 °C) and large catalyst diameter (10 mm) for various superficial velocities.



Figure 5.7: Conversion of CO₂ and the selectivity of CO, MeOH and DME for varying superficial inlet velocities. The solid line is a model without axial dispersion and the astrixes is a model with axial dispersion $(T_R = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, C_{H2}/C_{CO2} = 3, d_{part} = 10 \text{ mm}, L_R = 10 \text{ cm}, D_R = 2.6 \text{ cm}, D_{cat} = 0.33, w_{vol,cat1} = 0.5)$

In a situation favouring axial dispersion, there is no significant effect on both conversion of CO_2 and the selectivity towards CO, MeOH and DME for all velocities. Axial dispersion has no relevant effect on the model of the packed bed reactor and does not need to be taken into account.

5.3 Conclusions

Internal mass transfer can have a significant impact on the conversion of CO_2 and the selectivity towards CO, MeOH and DME in the packed bed reactor. Therefore, the internal mass transfer should be modelled. Internal mass transfer can be modelled with the use of the alternative Thiele modulus as defined in section 3.3. Up to a catalyst efficiency of 90%, the results with this alternative method are the same as a model that models the interior of all catalyst particles explicitly, up to an accuracy of 5%. For lower catalyst efficiency the deviation of the conversion and selectivity in the reactor becomes larger. However, the modified Thiele modulus approach predicts the same trends in conversion and selectivity as the more elaborate model. This new method can therefore always be used to assess, in a relatively simple manner, if internal mass transfer is relevant and if it is relevant, how significant this effect is.

In a situation favouring external mass transfer limitations, the conversion and selectivity were evaluated at different superficial inlet velocities. It was found that the conversion of CO_2 and selectivity towards DME are barely affected at all inlet velocities. At low inlet velocities, the selectivity of DME is slightly lower and the selectivity towards methanol is slightly higher. However, considering that this change in selectivity is negligible (i.e., in the order of 3.5%) and that the operating conditions favouring external mass transfer are not industrially viable, the effect of external mass transfer can be neglected, at least in all practical situations.

Finally, the conversion and selectivity predicted by a model which accounts for axial dispersion do not deviate significantly from the ones calculated without any axial dispersion phenomena, even when using operating conditions where the effect of axial dispersion should be relevant the most. Therefore, axial dispersion is not relevant and does not need to be accounted for when modelling the packed bed membrane reactor.

Chapter 6

Packed Bed Membrane Reactor

In this section, the membrane is incorporated into the reactor model, with all the relevant mass or heat transfer phenomena found in the previous chapter. Thereafter, the hypothesis of an adiabatic reactor model is removed, and an external cooling source at the reactor wall is added for heat management purposes. The model here developed is used to assess if the intra-particle diffusion phenomena affect the performance of an industrial-scale packed bed membrane reactor, which was designed and optimized via a simplified approach in a previous project. Furthermore, the effect of the zeolite weight fraction is assessed and further optimized, given the findings reported in the previous chapters.

6.1 Method

6.1.1 Governing Equations and Boundary Conditions

An extra mass transfer term, to account for the permeation flux of the components through the membrane, is added to Equation 5.1 of the packed bed reactor. Since in subsection 2.2.9, it was found that axial dispersion does not significantly influence the concentration profiles in the reactor, this term is not included in the governing equation for the packed bed membrane reactor, which gives rise to the following mass balance:

$$\frac{\partial}{\partial z}(v \cdot C_i) = R_i - a_{mem} \cdot J_{perm,i}(P_{R,i} - P_{M,i})$$
(6.1)

The reaction term R_i is described in 5.5 if internal mass transfer is taken into account via the Thiele modulus and in 5.4 if internal mass transfer is taken into account via the particle model. a_{mem} represents the membrane area per reactor volume, $J_{perm,i}$ is the permeance of the membrane of component i, as defined in subsection 2.3.1, and $P_{R,i}$ and $P_{M,i}$ are the partial pressure of component i in the reactor and the membrane, respectively.

To remove the heat produced by the reactions and keep isothermal conditions, an external cooling mantle with flowing boiling water is chosen as a heat management strategy. This solution was found efficient in a previous study and is often proposed in literature and industry. Heat is removed from the reactor via the evaporation of water, which is then kept at a constant temperature (i.e., latent heat), and does not require a dedicated energy balance. To account for the heat removal, an extra term is added to the governing equation of the PBR. The temperature in the cooling mantle is assumed to be constant. From experimental results it was shown that the temperature in the membrane and the reactor was the same, suggesting a fast heat transfer between the membrane and the reactor [34]. The feed temperature of the membrane and the reactor are the same. Because the heat transfer between the reactor and the membrane is fast and since the feed temperature is the same an overall heat balance over the membrane and the reactor can be set up, as shown below.

$$\frac{\partial}{\partial z} \left(\sum_{i} (v_R C_{i,R} + v_M C_{i,M}) \cdot C_{p,i}) \cdot T \right) = -\sum \Delta H_i \cdot R_i - a_{heat} \cdot U \cdot (T_R - T_{water})$$
(6.2)

Here, a_{heat} is the area available for heat transfer per reactor volume, U is the heat transfer coefficient as defined in subsection 2.2.10 and T_{water} is the temperature of the boiling water.

The boundary conditions and the calculation of the velocity and pressure drop in the reactor are the same as the PBR and have been reported in section 5.1.

In the membrane, constant pressure, steady-state conditions and no radial profiles are assumed. No reaction takes place in the membrane, due to the absence of catalytic particles. In the membrane, species are exchanged with the reactor by flux through the membrane. This results in the governing equation in Equation 6.3 for mass balance.

$$\frac{\partial}{\partial z}(v \cdot C_{m,i}) = a_M \cdot J_{perm,i}(P_{R,i} - P_{M,i})$$
(6.3)

Here, $C_{m,i}$ is the concentration of species i in the membrane.

For the membrane, there are two boundary conditions: 1) at the beginning of the membrane an inlet concentration is defined and at the end of the membrane, 2) the flux is set to zero.

$$C_i|_{z=0} = C_{i,in} \qquad \frac{\partial C_i}{\partial z}\Big|_{z=L} = 0 \tag{6.4}$$

The total flow rate into the membrane is related to the total flow rate into the reactor via the sweep gas ratio, which is the ratio of the inlet volume of the membrane and the inlet volume flow of the reactor $(\varphi_{v,R}/ / varphi_{v,M})$. The membrane is placed along the length of the entire reactor (i.e., $L_M = L_R$).

6.1.2 Model Implementation

In each grid cell, a new set of concentrations is added, which correspond to the concentrations in the membrane. The mass transfer term between the reactor and the membrane (i.e., the permeance of all components, J_i) is added to the non-linear terms of the Jacobean in the Newton-Raphson scheme. The velocity profiles, convection terms and reaction terms are implemented in the same manner as the packed bed reactor in subsection 5.1.2.

6.1.3 Model Verification

Similar to the model of the packed bed reactor, the mass conservation derived via a total mass balance is used to verify the model. In this total mass balance, the flow in the reactor side and the membrane side are taken into account. The results can be seen in Figure C.2 in the appendix. It can be seen that the (normalised) mass flow drops slightly. However, this drop in mass is less than the tolerance set in the PBMR model. Therefore, it can be concluded that mass is conserved in the PBMR model.

6.2 Results

Here, a one-dimensional PBMR model, which accounts for all relevant mass/heat transfer phenomena (i.e., intra-particle diffusion limitations) is developed, to predict the performance of a membrane reactor for the CO2 hydrogenation to DME. This model, together with the previously described PBR, is used as a tool to evaluate more rigorously, the performance of an industrial scale PBR and PBMR, designed and optimized in a previous study carried out in our group. In particular, the objective is to understand if mass transfer phenomena affect the reactor performance and if the reactor configuration should be adjusted to achieve the same performance. The large-scale PBR and PBMR initial configuration is summarised in Table 6.1. The corresponding reactor performances for a model that does not account for INMT (i.e., the simplified model used for the design) and for a model that considers INMT, are reported in Table 6.2.

Reactor Property	Unit	Value PBR	Value PBMR
Inlet Temperature	°C	200	200
Inlet Pressure	bar	40	40
GHSV	1/hr	32.11	32.11
Feed H_2/CO_2 ratio	mol/mol	3	3
Length Reactor	m	18.23	17.72
Internal Reactor Diameter	m	3.65	3.54
Reactor wall thickness	cm	8	8
Cooling Water Temperature	°C	190	178
Membrane Diameter	mm	-	10
Number of Membranes	-	-	366
Pressure gradient across the Membrane	bar	-	5
Sweepgas flow ratio	m_{SW}^{3}/m_{B}^{3}	-	1
Methanol Fraction Sweepgas	mol%	-	6.37
Sweepgas H_2/CO_2 ratio	$\mathrm{mol}/\mathrm{mol}$	-	3
Bed Porosity	m_{void}^3/m_B^3	0.4	0.4
Catalyst Dilution Factor	m_{cat}^3/m_{sol}^3	0.66	0.66
Zeolite weight fraction	wt%	50	50
Catalyst particle diameter	mm	0.25	0.25

Table 6.1: The reactor properties for an industrial packed bed reactor and a packed bed membrane reactor

Table 6.2: The reactor Performance for an industrial packed bed reactor and a packed bed membrane reactor with and without INMT

Reactor Performance	Unit	PBR		PBMR	
		Without INMT	With INMT	Without INMT	With INMT
CO2 Conversion	%	37.96	37.95	52.28	52.27
DME Selectivity	%	83.71	83.8	97	97
MeOH Selectivity	%	13.42	13.36	0	0
CO Selectivity	%	2.87	2.84	3	3
DME Productivity	$\rm kg/hr$	457	457	666	665

In Table 6.2 it can be seen that internal mass transfer has no significant effect on the reactor performance at large (pilot/industrial) scale. However, in this reactor, conditions that do not result in a high effect of internal mass transfer (i.e. small particle size and an average temperature of below 220 °C) were chosen for different reasons. In particular, a temperature of 220 C was found as a result of a trade-off between catalyst weight and DME selectivity. On the other hand, a small particle size was selected, to minimize the effect of internal diffusion limitation, which was not considered initially.

A particle size of 0.25 mm is not common in industry [15]. Industrial catalyst particles have a characteristic size of a few millimetres. Therefore, the effect of using an industrially relevant particle size is assessed on both the conversion and selectivity. The results can be seen in Figure 6.1. The particle size also affects the heat transfer to the wall of the reactor, as can be seen in Equation 2.56. To be able to determine the effect of larger catalyst particles, the cooling water temperature is adjusted to keep the average temperature of the reactor at 220 °C for varying particle sizes.

Interestingly, even at high catalyst particle diameters (i.e. up to 10 mm), the effect of internal mass transfer is limited. For a diameter of 10 mm, the conversion is reduced by 0.88% and the DME selectivity is increased by 0.65%. On the contrary, in subsection 3.2.1 it is shown that at large particle sizes the efficiency of the catalyst particles is reduced significantly. For the zeolite catalyst, this happens even at 200 °C (i.e., at a



Figure 6.1: Conversion of CO_2 and the selectivity of DME for varying particle diameters. The solid line is a model without internal mass transfer and the astrixes is a model with internal mass transfer (Reactor conditions are reported in Table 6.1, $d_{part} = 0.25-10$ mm, $T_w = 153-178$ °C)

°C)

catalyst diameter of 10 mm the catalyst efficiency is 90%). Therefore, the catalyst efficiency for both catalyst particles in the large-scale reactor model is calculated over the reactor length, using a particle diameter of 3.1 mm, which corresponds to the commercially available catalysts for this reaction. T

Methanol Catalyst DME Catalyst 0.45 0.4 0.99 Catalyst Efficiency [-] Catalyst Efficiency [-] 0.98 0.92 0.92 Figure 6.2: Catalyst Efficiency for the methanol 0.15 and DME catalyst over the length of the membrane re- $Eta_{avr} = 0.98$ 0.94 $Eta_{avr} = 0.21$ 0.1 actor (Reactor conditions are reported in Table 6.1, 0.93 L 0 0.05 L 0 $d_{part} = 3.1 \text{ mm}, T_w = 176$ 5 10 15 20 5 10 15 20 Reactor Length [m] Reactor Length [m]

For both catalyst particles, an initial decrease in catalyst efficiency is observed. This is caused by the initial increase in temperature in the PBMR (see Figure C.3 in the appendix). For the methanol catalyst, an average catalyst efficiency of 98% is observed. Therefore, the internal mass transfer has little effect on the conversion of CO_2 to methanol. For the second catalyst, however, an average catalyst efficiency of 21% is observed. Here, internal mass transfer limitations have a large effect on the catalyst performance. However, this is not observed in the overall reactor performance (Table 6.2). To explain this an analysis of where the limitations for conversion lie in this system is proposed here. To determine these limitations, the thermodynamic equilibrium concentration of methanol for the copper catalyst and the DME concentration for the zeolite catalyst is compared with the concentration of methanol and DME in the PBMR. The results can be seen in Figure 6.3 for a PBMR model including internal mass transfer.



Figure 6.3: The real and equilibrium concentration of methanol and DME over the length of the industrial scale membrane reactor. (Reactor conditions are reported in Table 6.1, $d_{part} = 3.1$ mm, $T_w = 176$ °C)

For the copper catalyst, the concentration at the surface of the catalyst particle is lower than the equilibrium concentration of methanol. This means that the reaction is kinetically limited. In other words, increasing the reaction rate of this reaction would result in a higher conversion of CO_2 . For the DME catalyst, however, the thermodynamic equilibrium concentration is equal to the real DME concentration. This means that this reaction is limited by thermodynamics, rather than by kinetics. Increasing the kinetic rate of the DME catalyst does not result in a different conversion or DME selectivity, since the limitations of this process lie in the thermodynamic regime. This explains why the low catalyst efficiency of the DME catalyst does not affect the overall conversion or selectivity. The reaction rate is sufficiently fast to allow the methanol-to-DME reaction to achieve the thermodynamic equilibrium. For this reason, the reduced kinetic rate due to internal mass transfer does not change the overall performance.

Because the reaction of methanol to DME is limited by thermodynamics, a fraction of the zeolite catalyst can be removed from the reactor, without changing the overall conversion and selectivity of the reactor. To see when (i.e., at which zeolite mass fraction) the overall conversion and selectivity are affected by the DME formation rate, the conversion and selectivity are plotted for a reactor with a constant methanol catalyst mass and a varying DME catalyst mass. To reduce the DME catalyst mass, the DME catalyst is replaced with inert particles. This can be seen in Figure 6.4.

The conversion and selectivity are largely unaffected by reducing the amount of DME catalyst in the membrane reactor. Approximately 90% of the DME catalyst mass can be removed without affecting the conversion and selectivity. Using a DME catalyst weight fraction of 50% is therefore likely not economically optimal since a large part of the zeolite catalyst does not change the overall reactor performance. To verify if in a situation with little DME catalyst, the reactor is indeed kinetically limited by the formation rate of DME from methanol, the same thermodynamic analysis as in Figure 6.3 is done. This can be seen in Figure 6.5.

If 90% less DME catalyst is used, the thermodynamic equilibrium concentration of DME in real concentration in the reactor differs. This means that now the conversion is kinetically limited.

6.2.1 Optimal Zeolite weight fraction

In the reactor configuration reported in Table 6.1 the zeolite weight fraction is too high. The optimal zeolite weight fraction is likely significantly lower than the zeolite weight fraction used because the reaction of methanol to DME is thermodynamically limited.

To gain further understanding of what the optimal zeolite weight fraction might be, the zeolite weight fraction is varied to give the highest DME yield. This is done for an increasing catalyst particle size to investigate the effect of internal mass transfer on the optimal zeolite weight fraction. This is done for a small-scale,



isothermal reactor with and without a membrane (Figure 6.6).

Two things can be observed: when a membrane is used, the optimal zeolite weight fraction is slightly higher (up to 0.5%) and at larger particle diameters, the optimal zeolite weight fraction for a model that takes into account internal mass transfer is significantly higher (up to 7%). When a membrane is used to selectively remove water, the formation of methanol is enhanced first. The reaction leading to the methanol synthesis produces a large volume of water and, as a result, benefits more from its removal (i.e., higher methanol formation rate). The presence of more methanol and less water alters the equilibrium of the system (i.e., dynamic thermodynamic equilibrium). In particular, more DME can be potentially formed. This corresponds to a larger fraction of zeolite catalyst to achieve the dynamic equilibrium in the membrane reactor.

At larger catalyst particle sizes, the effect of internal mass transfer becomes higher. The zeolite catalyst has smaller pores than the methanol catalyst and the methanol dehydration reaction is faster than the CO_2 hydrogenation reaction. Therefore, the zeolite catalyst is more limited by internal mass transfer and has a lower catalyst efficiency than the methanol catalyst. If internal mass transfer results in severe limitations, for example, at large particle diameters, the methanol dehydration reaction to DME becomes slower. Therefore,



Figure 6.6: The optimal zeolite weight fraction for various particle diameters $(T_R = 220 \text{ °C}, P_{R,in} = 40 \text{ bar}, \text{ GHSV} = 1000 \text{ 1/hr}, C_{H2}/C_{CO2} = 3, d_{part} = 0.1\text{-}10 \text{ mm}, L_R = 1 \text{ m}, D_R = 2.8 \text{ cm}, D_{cat} = 0.33, \text{SW} = 1, D_{mem} = 10 \text{ mm}, \Delta p_{mem} = 5 \text{ bar})$

more zeolite catalyst is needed, resulting in a higher optimal zeolite catalyst weight fraction. The zeolite weight fraction, however, needs to be optimized in each satiation separately, since, apart from catalyst particle diameter, it is also dependent on the operating temperature and GHSV [41]. Due to the complex interactions of various operating conditions, it is difficult to determine a general optimal zeolite weight fraction.

To underline the importance of carefully choosing a zeolite weight fraction, an optimization of the zeolite weight fraction is proposed for the large-scale packed bed membrane by maximizing the DME production rate, while keeping the conversion of CO_2 and the selectivity towards DME as close to the values reported in Table 6.2. For this optimization, the average temperature of the reactor is kept constant at 220 °C and the GHSV is increased so that the ratio of the volume of methanol catalyst and the volumetric inlet flow at normal conditions of reactants is constant (i.e., constant contact time with respect to the first catalyst). This analysis is proposed for a model with (stars) and without (line) internal mass transfer limitations. In Figure 6.7 the conversion, selectivity and productivity are shown.

Over a large range of zeolite weigh fractions (i.e., 5%-50%), the conversion and selectivity are largely unaffected (i.e., reduced with less than 3%). However, the DME productivity is doubled decreasing the zeolite weight fraction from 50% to 5%, meaning that in one reactor twice as much DME can be produced. The reason for this is the higher GHSV, which guarantees the same reactor performance. However, from Figure 6.7, it is possible to notice how, decreasing the zeolite fraction below 5%, decreases the DME selectivity and CO_2 conversion more significantly, also causing a drop in the productivity. The reason for this is that if the GHSV is increased, the reactants are in the reactor for a shorter period. Therefore, less water is removed from the reaction mixture, resulting in a lower DME selectivity. To overcome this, more membranes could be placed in the industrial reactor or the GHSV could be reduced.

At low zeolite catalyst weight fractions, the model that takes into account internal mass transfer predicts lower conversions, selectivities and DME production rates. As discussed before, this is because the zeolite catalyst is more limited by internal mass transfer. As a result, when INMT is taken into account, the DME production rate is generally lower when the intra-particle diffusion limitations are relevant, requiring more zeolite to achieve the thermodynamic equilibrium.



Figure 6.7: The conversion of CO₂, the selectivity of DME and the productivity of DME in a PBMR for various DME catalyst weight fractions Table 6.1, $d_{part} =$ 3.1 mm, $T_w = 158$ -178 °C, $X_{wt,DMEcat} = 0.1$ -50%)

6.3 Conclusion

The effect of internal mass transfer on a large-scale reactor used in previous work is investigated. With this reactor configuration, no effect of internal mass transfer was found for both the PBR and the PBMR. The absence of this effect can be explained by the usage of small catalyst particles in the reactor and a high zeolite catalyst weight fraction. The reaction rate of the methanol dehydration reaction in the zeolite catalyst is fast and is limited by thermodynamics when high zeolite catalyst weight fractions are used, which makes the effect of intra-particle diffusion limitation irrelevant. At lower weight fractions, the effect of internal mass transfer becomes relevant, lowering the conversion and DME selectivity, by 3% and 5%, respectively if a DME catalyst weight fraction of 0.5% is used.

Due to the fast reaction rate of the methanol dehydration, this reaction achieves easily its thermodynamic equilibrium. As a result, it was found that a large fraction of the zeolite catalyst can be removed with limited to no effect on the conversion/selectivity. The zeolite fraction can be further optimized both for the PBR and PBMR, accounting also for the internal mass transfer limitations. If a membrane is used, the optimal zeolite weight fraction is slightly higher (up to 0.5%). This is because the methanol formation is more limited by the production of water. Therefore, when water is removed, more methanol is produced, which alters the thermodynamic equilibrium, allowing for higher DME production. As a result, more zeolite catalyst is required to approach the equilibrium. If internal mass transfer is taken into account, the optimal zeolite weight fraction is significantly higher, up to twice as high at large catalyst particle diameters. This is because the zeolite catalyst is much more limited by internal mass transfer than the methanol catalyst. It has been shown that carefully choosing the zeolite weight fraction needs to be selected case by case because the optimal weight fraction is influenced by several operating conditions such as temperature, GHSV and particle size.

Chapter 7

Two Dimensional Reactor

In this section, a two-dimensional (membrane) reactor model is developed. In this model, one dimension (z) describes the length - or axis - of the reactor and the second dimension (r) describes the radius of the reactor. This model will be used to investigate the phenomenon of concentration polarization along the membrane surface, that is, a locally higher or lower concentration of species close to the membrane surface compared to the bulk. This model relies on the following assumptions:

- 1. In the membrane, there is no radial concentration, velocity, pressure or temperature profile
- 2. The radial component of the velocity is negligible
- 3. There is no radial pressure profile
- 4. The velocity in the axial direction along the radius of the reactor is constant
- 5. There are no angular pressure, concentration, velocity or temperature gradients

The flow-rate in the membrane and in the reactor are usually the same (SW=1). However, due to the much smaller cross-section of the membrane, the velocity in the membranes is higher than in the reactor. Moreover, the membranes are relatively thin $(L_M/D_M >> 50)$. These conditions do not favour radial temperature and concentration profiles, justifying the assumption to neglect radial concentration and pressure profiles in the membrane tube. In reality, in the PBR, there is a velocity in the radial direction, mainly due to the membrane flux. Therefore, this assumption could lead to poor results [29]. However, the axial dispersion coefficient used in this model, also partially takes into account a flux in the radial direction. In literature, it is not uncommon to neglect radial pressure profiles [6, 29]. Therefore, radial pressure profiles are also neglected in this work. If the particle diameter is sufficiently small compared to the reactor radius, the velocity profiles along the radial direction are usually found to be flat [10]. This is, in part, because large ratios (at least 15) of D_R/d_{part} result in a uniform porosity over the radius of the reactor. The modelled reactor is symmetrical around the axis, which yields in the absence of annular gradients.

7.1 Methods

7.1.1 Governing Equations and Boundary Conditions

The governing equation for reaction and convection in a packed bed is extended to also account for radial dispersion. Since the reactor is cylindrical, the curvature needs to be taken into account, by employing a cylindrical coordinate system. In the governing equation, there is no mass transfer term due to the membrane. The membrane flux takes place at the boundary between the reactor and the membrane and is, therefore, incorporated into the boundary conditions. This results in the following mass balance for the reaction side (Equation 7.1).

$$\frac{\partial vC_i}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{rad}\frac{\partial C_i}{\partial r}\right) = r_i \tag{7.1}$$

Here, D_{rad} is the radial dispersion coefficient, as defined in subsection 2.2.11. The governing equation for the mass flow in the membrane is the same as Equation 6.3.

The governing equation for heat is similar to the governing equation for mass. An extra term for heat transport in the radial direction is added to account for the enthalpy flow due to the dispersion of species. The cooling at the reactor wall is not in the governing equation since this happens at the reactor wall. This cooling is now incorporated into the boundary conditions.

$$\frac{\partial}{\partial z} \sum_{i} (v_R C_{i,R} C_{p,i}) T_R + \frac{1}{r} \frac{\partial}{\partial r} \left(r \left(\sum_{i} (J_{disp,i} C_{p,i}) T_R - \lambda_{rad} \frac{\partial T_R}{\partial r} \right) \right) = -\sum \Delta H_i \cdot R_i$$
(7.2)

Here J_{disp} is the flux in the radial direction due to dispersion and λ_{rad} is the radial conductivity as defined in subsection 2.2.12. For the membrane, the governing equation for heat is given in Equation 7.3.

$$\frac{\partial}{\partial z} \sum_{i} (v_M C_{i,M} C_{p,i}) T_M = a_M (h_M + \sum_{i} (J_{perm,i} C_{p,i})) (T_R - T_M)$$
(7.3)

 T_M represents the temperature in the membrane and h_M is the heat transfer coefficient for heat transport through the membrane. h_M is calculated by considering heat transport through the thin carbon layer and through the support layer [34].

In the reactor, there are four boundary conditions for mass and four boundary conditions for heat. For the membrane, there are two boundary conditions for mass and heat. At the entrance of the reactor and at the exit of the reactor the boundary conditions are the same as for the 1D packed bed membrane reactor: at the entrance, the temperature and concentrations are defined (Dirichlet boundary conditions) and at the exit, the mass and heat fluxes are zero (Neumann boundary conditions). This can be seen below.

$$C_{i,R}|_{z=0} = C_{i,R,in} \qquad \frac{\partial C_{i,R}}{\partial z}\Big|_{z=L} = 0$$
(7.4)

$$C_{i,M}|_{z=0} = C_{i,M,in} \qquad \frac{\partial C_{i,M}}{\partial z}\Big|_{z=L} = 0$$
(7.5)

$$T_R|_{z=0} = T_{R,in} \qquad \left. \frac{\partial T_R}{\partial z} \right|_{z=L} = 0 \tag{7.6}$$

$$T_M|_{z=0} = T_{M,in} \qquad \left. \frac{\partial T_M}{\partial z} \right|_{z=L} = 0 \tag{7.7}$$

At the reactor wall, the mass flux is zero because no mass is leaving the reactor through the reactor wall (Equation 7.8, left side). For heat, there is a flux at the reactor wall due to the heat management configuration (i.e., cooling jacket with boiling water), which is described by the overall heat transfer coefficient U (Equation 7.6, left side). At the membrane surface, a mixed boundary condition for mass due to the flux through the membrane can be defined. The flux at the membrane surface is equal to the permeation flux through the membrane (Equation 7.8, right side). Similarly, for heat, a mixed boundary condition due to the heat-flux through the membrane is defined. For heat, there is an extra term to account for the enthalpy flux due to the permeation of molecules (Equation 7.6, right side).

$$\left. \frac{\partial C_{i,R}}{\partial r} \right|_{r=R_R} = 0 \qquad -D_{rad} \left. \frac{\partial C_{i,R}}{\partial r} \right|_{r=R_M} = -Perm(P_R - P_M) \tag{7.8}$$

$$-\lambda_{rad} \frac{\partial T_R}{\partial r}\Big|_{r=R_R} = -U(T_R - T_{water}) \qquad -\lambda_{rad} \frac{\partial T_i}{\partial r}\Big|_{r=R_M} = -(h_M + \sum_i (J_{perm,i}C_{p,i}))(T_R - T_M) \quad (7.9)$$

7.1.2 Numerical Implementation

To solve the system a three-dimensional matrix is created, the first dimension spans over the number of components and the temperature, the second dimension spans over the radial grid points and the third entry spans over the axial grid points. In this matrix, the concentrations in the membrane are included as well. To do this, one extra grid point in the radial direction is added, containing the concentrations in the membrane. The convection and dispersion terms are discretized as described in subsection 2.1.5.

The boundary conditions in the radial direction are dependent on the flux and on the concentration at the boundary. However, the membrane flux is defined in terms of partial pressure and not in terms of molar concentration. To resolve this, the permeation flux is linearized using a first-order Taylor approximation. The Taylor approximation is done around the concentration of the previous iteration. This can be seen in Equation 7.10.

$$-\frac{\partial C_{i,R}}{\partial r}\Big|_{r=R_M} = \frac{-Perm(P_R - P_M)}{D_{rad}} = F_i = F_i |k - 1_{r-R_M} + \frac{dF_i}{dC_{i,R}}\Big|_{r-R_M}^{k-1} (C_{i,R}|_{r=R_M}^k - C_{i,R}|_{r=R_M}^{k-1})$$
(7.10)

Here k is the current iteration and k-1 is the previous iteration. In this form, the boundary condition can be implemented as a general Robin boundary condition. In each iteration, the boundary condition is linearized until convergence. For the heat flux at both the catalyst wall and the membrane surface, a Robin boundary condition is used.

7.1.3 Grid size analysis

In Figure D.1 in the appendix, the error can be seen for various grid sizes in the radial direction in the column. The error is defined with respect to a grid size of 200 grid points in the radial direction. These errors are calculated for a reactor with steep radial gradients to create a system with the largest numerical errors. With a grid of 70 points, corresponding to a Δr of 0.15 cm, the error is below the set tolerance of 10^{-5} . Therefore, a grid size of at most 0.15 cm in the radial direction in the column is taken for all simulations in this work.

7.1.4 Verification

To verify the 2D model, the total mass conservation is first assessed. The result is reported in Figure D.2 in the appendix. In this figure, the mass is normalised with the mass that is fed to the column. The mass decreases slightly over the length of the packed bed membrane reactor. However, this decrease is smaller than the accuracy set in the model. Therefore, it can be concluded that mass is conserved in this model, verifying the packed bed reactor model.

If a constant velocity, constant radial dispersion coefficient, a first-order reaction of $A \longrightarrow B$, a constant concentration of A at the reactor wall and no permeation trough the membrane are assumed the radial concentration profile of A should become independent of the axial coordinate for high reactor lengths. Moreover, this concentration profile should become equal to the analytical solution of a first-order reaction-diffusion system in cylindrical coordinates. In Figure D.3 in the appendix, the radial concentration profile is shown for various axial coordinates. It can be seen that for high reactor lengths, the radial concentration profile approximates the analytical solution, which further verifies the model.

7.2 Results

7.2.1 Concentration polarization

Similarly to the previous sections, it is first assessed whether radial transport is slow enough to yield significant concentration profiles in a limiting situation, favouring the formation of such profiles. In the case of concentration polarization, a limiting situation corresponds to a high temperature (270 °C), to assure fast permanence through the membrane combined with small catalyst particle diameters (0.25 mm) and low internal velocities (0.001 m/s) to reduce radial mass transfer. The results are depicted in Figure 7.1.



Figure 7.1: Radial concentration profiles in the 2D packed bed membrane reactor in the middle of the column. $(T_R = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, \text{GHSV} = 50 \text{ 1/hr}, C_{H2}/C_{CO2} = 3, d_{part} = 0.25 \text{ mm}, L_R = 0.5 \text{ m}, D_R = 10 \text{ cm}, D_{cat} = 0.33, w_{vol,cat1} = 0.5, D_M = 10 \text{ mm}, P_M = 35 \text{ bar}, \text{SW} = 1.0)$

From Figure 7.1 it can be concluded that in the limiting situation for radial transport, significant radial concentration profiles develop close to the membrane surface. These concentration profiles hinder the effectiveness of the membrane by reducing the driving force which govern the permeation flux through the membrane. Especially for water, a steep concentration profile can be observed. This can be explained by the fact that water is the component that permeates fastest (i.e., is least limited by the permeation trough the membrane). As a consequence, less water is removed from the reaction environment, which would lower the overall reactor performance. To assess the effect of the concentration polarization on the reactor performance, a set of simulations is done in the limiting situation for concentration polarization ($d_{part} = 0.25$ mm, GHSV = 50 1/hr) at various reactor temperatures (200 - 270 °C). The results can be seen in Figure 7.2.

Figure 7.2: Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) for various temperatures. (T_R = 200-270 °C, $P_{R,in}$ = 40 bar, GHSV = 50 1/hr, C_{H2}/C_{CO2} = 3, d_{part} = 0.25 mm, L_R = 0.5 m, D_R = 10 cm, D_{cat} = 0.33, $w_{vol,cat1}$ = 0.5, D_M = 10 mm, P_M = 35 bar, SW = 1.0)



From this first assessment, it can be concluded that concentration polarization does significantly influence the CO_2 conversion and selectivity towards DME, CO or methanol. These effects should be considered when modelling these types of reactors. At higher temperatures, the effect of concentration polarization is higher. Nevertheless, even if the efficiency of the membrane is reduced because of concentration polarization, the PBMR still outperforms a PBR.

7.2.2 Correlation Concentration Polarization

A two-dimensional model is computationally expensive. Moreover, setting up such a model is more complicated than the one-dimensional counterpart. Therefore, a mass transfer correlation is desirable to be able to include the effects of concentration polarization in a 1D model. Boon et al. [6] have suggested a correlation to account for concentration polarization. However, this correlation significantly underestimates the effect of concentration polarization (see Figure D.4 in the appendix). This is likely due to the fact that this correlation is developed for palladium membranes in a empty column. In this work there are particles and reactions in the column, altering the transport of molecules to the membrane. In literature, there is no correlation for concentration polarization for carbon molecular sieve membranes in a packed bed. Therefore, a correlation is developed in this work. Sherwood-type of correlations are commonly used for predicting mass transfer coefficients (k_{CP}) for concentration polarization. Therefore, a correlation in the form of Equation 7.11 will be used to predict the mass transfer coefficient for concentration polarization.

$$Sh = aRe^b Sc^c Ent^d \tag{7.11}$$

$$Sh = \frac{k_{CP}d_h}{D_m} \tag{7.12}$$

$$Re = \frac{\rho_f v_{SF} d_h}{\mu_f \varepsilon} \tag{7.13}$$

$$Sc = \frac{\mu_f}{\rho_f D_m} \tag{7.14}$$

Here, a, b, c, and d are constants that should be fitted and *Ent* is a dimensionless number that accounts for entrance effects. The characteristic length in the Reynolds- and Schmidt-number is chosen to be the hydrodynamic length (d_h , the space between the reactor wall and the membrane). The Reynolds number (Re) is divided by the porosity of the reactor (ε) to obtain the interstitial velocity instead of the superficial velocity (v_{SF}).

From the 2D model a mass-transfer coefficient can be calculated, that can be used to determine a Sherwood number. A similar approach is used that was used to determine the correlation for the catalyst efficiency using the modified Thiele modulus. The mass transfer coefficient is calculated in a lot of different operating conditions. These mass transfer coefficients are used to generate a large data-set of Sherwood numbers, that will be used to fit the parameters in Equation 7.11. The different conditions include: GHSV (100-2000 1/hr), temperature (200 - 250 °C), pressure (30 - 40 bar), sweep gas ratio (0.5 - 2), inlet compositions (H₂/CO₂ = 1-4), reactor length (0.1-10 m), diameter (0.02-1 m), membrane diameter (5 - 20 mm), particle diameter (0.25-10 mm), catalyst dilution factor (0.25-0.5), catalyst weight fractions ($w_{vol,cat1} = 0.25-0.75$)). The data set is also used to determine a proper definition for *Ent* and to decide whether the radial dispersion coefficient or the molecular diffusion coefficient is better to use in the Schmidt and Sherwood numbers. A bulk-membrane mass transfer coefficient can be calculated from the model by Equation 7.15.

$$k_{CP} = \frac{J_{perm}}{\langle C_R \rangle - C_{R,S}} \tag{7.15}$$

Here J_{perm} is the permeation flux through the membrane, $\langle C_R \rangle$ is the average concentration in the radial direction and $C_{R,S}$ is the concentration in the reactor at the membrane surface.

In Equation 1.10 the factor d_h/z is used to account for the entrance effects. This factor has a high value for low values of z, hence is more significant close to the entrance of the reactor. Two effects are important to consider when considering the entrance effects. First, how fast the (concentration) profiles are formed, or in other words how fast the transport in the radial direction occurs. And second how long the fluid has been in the column. To account for both phenomena a type of entrance Peclet number is defined. In this number, the characteristic time for dispersion in the radial direction is divided by the characteristic time for convection in the axial direction. If this number is large, the radial profiles have likely not been formed yet, and for low values of this number, the fluid is has spent enough time in the column for radial profiles to have formed. The definition of the entrance Peclet number (Pe_{Ent}) is shown in Equation 7.16.

$$Pe_{Ent} = \frac{vd_h^2}{zD_{rad}} \tag{7.16}$$

To compare the entrance Peclet number and the already used ratio of the hydrodynamic length and axial coordinate the values of a, b, c and d are fitted for both cases. For all data points generated by the 2D-model, the parameters a, b, c and d are derived via parametric fitting of the Sherwood number obtained via Equation 7.15. A parity plot representing the quality of the fit (i.e., comparison of Sh obtained from the correlation and the Sh calculated via the 2D model) is shown in Figure 7.3.



It can be seen that if the entrance Peclet number is used (Figure 7.3b) instead of d_h/z (Figure 7.3a), the quality of the fit improves (the points are closer to the line y=x). This means that the correlation using the Peclet number better predicts the Sherwood number than when the ratio of the hydrodynamic length and the axial coordinate is used. Therefore, it is decided to use the entrance Peclet number to account for entrance effects.

If the molecular diffusivity is used, many aspects affecting radial transport, such as particle size or the tortuosity of the column are not accounted for in the correlation for concentration polarization. Therefore, the same correlation for the Sherwood number is derived using the radial dispersion coefficient instead of the molecular diffusivity in the Sherwood number and the Schmidt number. The same analysis has been done as above, this can be seen in Figure 7.4.

If the radial dispersion coefficient is used (Figure 7.4b), instead of the molecular diffusivity (Figure 7.4a), the points are closer to the line y=x. This means that the correlation improves if the radial dispersion coefficient is used. Therefore, the radial dispersion coefficient is used in the Sherwood number and the Schmidt number in this correlation.

The fitted values of a, b c and d are reported in Table 7.1.

First, it can be noticed that the values for the constant (a), and the exponents of the Reynolds number (b), Schmidt number (c) and the entrance Peclet number (d) have a reasonable value since they do not deviate much from results found in literature [15, 39]. Moreover, the exponent of the Schmidt number is close to 0.33, which is a value commonly found in these types of correlations [5, 15]. These are indications, that this


Figure 7.4: The Sherwood number determined from the 2D model and the Sherwood number calculated from a correlation using two the radial dispersion coefficient and the molecular diffusivity ($T_R = 200$ -250 °C, $P_{R,in} = 35-40$ bar, $GHSV = 200-2000 \ 1/hr,$ $C_{H2}/C_{CO2} = 2-3, d_{part} =$ $0.25-5 \text{ mm}, L_R = 0.1-10 \text{ m},$ $D_R = 5-200$ cm, $D_{cat} =$ $0.25-0.5, w_{vol,cat1} = 0.25-$ 0.75, $D_M = 5-20$ mm, P_M = 35-40 bar, SW = 0.5-2.0)

Table 7.1: The fitted values for Equation 7.11

Constant	Value	Refitted value
a	0.4628	0.4338
b	0.3509	0.3583
с	0.3179	0.3330
d	0.2640	0.2634

correlation has a physical basis. Since the exponent of the Schmidt number is close to 0.33, this exponent is fixed to this value and the other constants are refitted. This is done because $Sc^{0.33}$ is derived from analytical solutions of similar problems, therefore this assumption has a theoretical basis. The refitted values are also shown in Table 7.1. Refitting the value of a, b and d does not change the quality of the fit.

To asses if the proposed correlation can predict the correct behaviour of the PBMR, Figure 7.2 is reproduced but now including an estimation of the conversion and selectivities using the correlation developed in this work. This is shown in Figure 7.5.



Figure 7.5: Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) and a 1D model with the proposed correlation (circles) for various temperatures. $(T_R = 200-270 \ ^{\circ}\text{C}, P_{R,in} =$ 40 bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3, d_{part} =$ $0.25 \text{ mm}, L_R = 0.5 \text{ m},$ $D_R = 10 \text{ cm}, D_{cat} = 0.33,$ $w_{vol,cat1} = 0.5, D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)

It can be seen that the correlation predicts the same trends in conversion and selectivity as the 2D model. However, the reduction of conversion due to concentration polarization is overestimated for higher temperatures since the correlation (stars) predicts lower conversions than the 2D model (circles). Nevertheless, the estimation of the correlation is within an error of 5% with respect to the two-dimensional model. On the other hand, the selectivity of DME, CO and methanol is well predicted over the entire range of temperatures (Figure 7.5b).

Entrance effects are only relevant at the beginning of the reactor. Therefore, it is not correct to account for the entrance effects, via the entrance Peclet number, over the entire length of the reactor. The fact that the entrance effects are accounted for, even in situations where the concentration profiles are already developed, could be the reason for the overestimated reduction of CO_2 conversion due to concentration polarization. To mitigate this effect, two different regimes are defined, one regime with developing concentration profiles (i.e. near the reactor entrance) and one region with developed profiles (i.e., near the reactor exit). It is assumed that if the time for dispersion in the radial direction and the time for convection in the axial direction are the same (i.e., $Pe_{ent} = 1$) the concentration profiles have developed. For values of the entrance Peclet number lower than unity, the entrance effects are not accounted for. With this adaptation, the values of a, b, and d are refitted and the same analysis as in Figure 7.5 is carried out, to see if the conversions are better predicted, as can be seen in Figure 7.6.

Figure 7.6: Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) and a 1D model with the proposed correlation (circles) for various temperatures. $(T_R = 200-270 \ ^{\circ}\text{C}, P_{R,in} =$ 40 bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3, d_{part} =$ $0.25 \text{ mm}, L_R = 0.5 \text{ m},$ $D_R = 10 \text{ cm}, D_{cat} = 0.33,$ $w_{vol,cat1} = 0.5, D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)



From this figure, it is evident that accounting for the entrance effects only near the reactor entrance yields a correlation that predicts the effect of concentration polarization better. Therefore, the proposed adaptation of neglecting entrance effects for values of the Peclet number below unity is included in the final correlation in this work. The final result is shown in Equation 7.17 and 7.18.

$$Sh = \frac{k_{CP}d_h}{D_{rad}} = 0.43Re^{0.36}Sc^{0.33}Pe^{0.26}_{ent} = 0.43\left(\frac{\rho_f v_{SF}d_h}{\mu_f \varepsilon}\right)^{0.36}\left(\frac{\mu_f}{\rho_f D_{rad}}\right)^{0.33}\left(\frac{vd_h^2}{zD_{rad}}\right)^{0.26} \qquad Pe_{ent} > 1$$
(7.17)

$$Sh = \frac{k_{CP}d_h}{D_{rad}} = 0.43Re^{0.36}Sc^{0.33} = 0.43\left(\frac{\rho_f v_{SF}d_h}{\mu_f \varepsilon}\right)^{0.36} \left(\frac{\mu_f}{\rho_f D_{rad}}\right)^{0.33} \qquad Pe_{ent} \le 1$$
(7.18)

Alternative Reactor Design

Concentration polarization does influence the reactor performance significantly. In literature, the velocity in the column is identified as the most important parameter influencing radial transport of molecules in the packed bed reactor [20]. Therefore, it is checked if increasing the velocity in the column, while keeping the total volume of the column the same, mitigates the effect of concentration polarization. In Figure 7.7, the difference in CO_2 conversion and DME, CO and MeOH selectivity between a model with concentration polarization (X_{CP} and S_{CP}) and a model without concentration polarization (X_{NoCP} and S_{NoCP}) is shown.



Figure 7.7: The difference of CO₂ conversion and DME, CO and MeOH selectivity between a model accounting for CP and a model not accounting for CP ($T_R = 270$ °C, $P_{R,in}$ = 40 bar, GHSV = 50 1/hr, $C_{H2}/C_{CO2} = 3$, d_{part} = 0.25 mm, $D_{cat} = 0.33$, $w_{vol,cat1} = 0.5$, $D_M = 10$ mm, $P_M = 35$ bar, SW = 1.0)

A clear decrease of CO₂ conversion and selectivity difference can be observed if the superficial velocity is increased. This shows that increasing the L_R/D_R ratio is an efficient method to mitigate concentration polarization effects.

Radial Heat transfer

Due to the heat flux due to the flow of enthalpy caused by the dispersion of molecules, the heat balances gave severe errors or did not converge. This is due to a bug in the code or because the numerical solver used in this work is not fit to solve these types of systems. However, for radial heat transfer to the wall of the reactor or to the membrane, well-established correlations are available [35]. Therefore, the effect of radial heat profiles could still be accounted for, making the need for a non-isothermal two-dimensional model less high.

7.3 Conclusions

In this chapter, it has been shown that radial concentration profiles could occur in a limiting situation, which corresponds to a situation in which the mass transport from the bulk phase to the membrane is the slowest. In the same limiting situation, these profiles do have a significant effect on the conversion (lowered up to 7%) and selectivity (for DME lowered up to 5%).

A Sherwood-type of correlation is proposed to account for concentration polarization phenomena, without having to solve a more complex 2D model. The correlation derived in this study, via parametric fitting of the result obtained from the 2D model, showed to predict conversion and selectivities of the 2D model in a sufficiently accurate way (max. error of 2%) This correlation accounts for entrance effects via a type of Peclet number that represents the ratio of the characteristic time for dispersion and the characteristic time for convection. Based on the Peclet number, two regimes are defined: 1) a regime with developing profiles (Pe > 1) and 2) a regime with developed profiles (Pe < 1). The entrance Peclet number is only accounted for in the regime with developing profiles. The constant that was fitted to the power of the Schmidt number in the Sherwood-type of correlation, had a value that is often seen in the literature (i.e. $Sc^{0.33}$), adding to the reliability of the proposed correlation.

Increasing the L_R/D_R ratio is an efficient method to mitigate the effects of concentration polarization. If this ratio is increased the difference in reactor performance between a model with and a model without concentration polarization decreases.

The heat balances could not be implemented in the 2-D model because this resulted in severe numerical errors. However, because heat transport to the wall in a packed bed and to a tube in a packed bed is well described in literature, this problem is not as relevant as the problem described for mass transfer.

Chapter 8

Conclusions

This study demonstrated that internal mass transfer and concentration polarization both could influence the reactor performance of a packed bed membrane reactor used for the conversion of CO_2 and H_2 to DME. Internal heat transfer, external heat and -mass transfer and axial dispersion were not found to have a significant effect on the behaviour of the reactor. For internal mass transfer limitations and concentration polarization, a 2-D model is used. Since both phenomena are found to be relevant, a 3D model would be necessary, to account for both internal mass transfer and concentration polarization, simultaneously. However, in this study useful tools are developed to account for these effects without having to develop a (computationally expensive) 2-D model.

In literature, no correlation exists to account for internal mass transfer in a system that consists of parallel, reversible and consecutive reactions with complex Langmuir-Hinselwood type of kinetics. In this work, a modified Thiele modulus approach that can predict the catalyst efficiency in such situations is developed. In the modified Thiele modulus, the diffusion term is adjusted for the thermodynamic equilibrium concentration. Thereafter, a correlation for the catalyst efficiency is proposed. The correlation predicts an efficiency of $1/\varphi$ for large values of the Thiele modulus, which is a result often seen in literature, deriving from analytical solutions. The modified Thiele modulus approach predicts the same CO₂ conversions and DME, CO and methanol selectivities as a rigorous particle-reactor model within a maximum deviation of 5%. For high values of the Thiele modulus (i.e. above 2), the Thiele modulus approach overestimates the effect of intraparticle diffusion limitations, resulting in a lower conversion. In any case, this correlation can be used to determine if intra-particle diffusion limitations can be relevant and what the magnitude of this effect will be. The modified Thiele modulus approach proposed in this work can be considered general, since it was developed using different particle geometries and different kinetic systems.

External mass transfer can significantly change the concentration at the catalyst particle surface with respect to the bulk of the fluid (i.e. a deviation of above 5%). However, if both internal mass transfer and external mass transfer are accounted for, external mass transfer has little influence. This is because these phenomena become relevant in the same conditions (i.e., large particle diameter and high temperature). The lowered kinetic rate due to internal mass transfer results in the absence of a large effect of external mass transfer.

The Mears-criterion is commonly used to assess the relevance of external mass transfer phenomena. However, similarly to the conventional Thiele modulus approach, this criterion was developed for power-law kinetics. Therefore, it was verified if values of the Mears number below 0.15 also result in a small effect of external mass transfer using the complex kinetic system of this work. If the value of the Mears number is below 0.15, the concentration at the surface of the catalyst particle and the concentration in the bulk of the fluid differs less than 5%. Therefore, the Mears Criterion is also a reliable tool for this type of complex kinetics.

A Sherwood-type correlation is proposed to account for concentration polarization around a membrane in a packed bed membrane reactor. In this correlation, a Peclet number is used to describe the entrance effects. This Peclet number is the ratio of the characteristic time of diffusion in the radial direction and the characteristic time of convection in the axial direction. This correlation can predict with high accuracy (deviation of less than 5 % with respect to the 2-D model) the effect of concentration polarization on CO_2 conversion and DME, CO and methanol selectivity.

Even in situations with significant concentration polarization phenomena, a PBMR still outperforms a PBR. The effect of concentration polarization is most efficiently mitigated by increasing the velocity of the gasses in the column. This can be done by, for example, using a higher L_R/D_R ratio.

Furthermore, in this study a further optimization of the PBMR and PBR for the production of DME from CO_2 and H_2 is proposed, in view of the phenomena found to be relevant. The optimization is mostly based on the zeolite fraction considered in the catalytic bed. In literature, usually, a zeolite catalyst weight fraction of 50% is used. However, due to the fast methanol dehydration reaction, less zeolite catalyst weight fraction is optimized, the production of DME in a large-scale reactor can be doubled with small losses of CO_2 conversion (3%) and DME selectivity (5%). If internal mass transfer is accounted for, the optimal zeolite weight fraction is because the zeolite catalyst is more limited by intra-particle diffusion limitations than the copper catalyst.

8.1 Recommendations

The biggest flaw in this work is the absence of a verification case with experimental data. Due to issues with the experimental setup, the data could not be generated in time. In future work, this should be done. A possibly interesting verification case from literature could be done with the experimental data from the paper of Wild at all [41]. In this paper, the experimental optimal DME catalyst weight fraction is higher than the value predicted by their models. A possible reason for this could be intra-particle diffusion limitations since it was shown in this work that this could result in a higher optimal DME catalyst weight fraction. If the models accounting for intra-diffusion limitations predict the optimal zeolite weight fraction from Wild et all. better, this could serve as a verification case.

The 2-D models still contain assumptions that might result in poor or unreliable results. In future studies, the concentration, pressure and temperature profiles in the radial direction of the membrane could be accounted for. More importantly, accounting for a radial component of the velocity could result in different results, since the radial velocity might mitigate the effect of concentration polarization. The model could be made more generic by also including deviating radial porosity and velocity profiles.

More attention could be paid to the heat balances of the 2-D model. Due to a bug or due to an inadequate numerical solving method the solution did not converge. Different discretization schemes or solvers could be implemented to check if the solution converges.

To test if the correlation proposed in Equation 7.17 is general, different membrane permeabilities could be implemented into the model. If for different membrane permeabilities Equation 7.17 still is applicable, no adaptation has to be done. If for different permeabilities the fitted coefficients change, another term could be added accounting for the permeability of the membrane. A possible interesting addition could be a type of Damköhler number, where instead of the reaction rate, the permeability is used. It should be noted that, despite the unchanged permeance, the sweep gas ratio and the trans-membrane pressure do change, hence the total permeation flux is varied in this work. Since with different permeation fluxes, the correlation still predicts good values for the mass transfer resistance due to concentration polarization, it is not expected that different permeation constants have a big effect on the shape of the correlation.

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Appendices

Appendix A

Particle Schale



Figure A.1: The error as function of the number of grid points in the catalyst particle radial direction. $(T_{in} = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, d_{part} = 10 \text{ mm})$

Figure A.2: The numerical solution and analytical solution for a simple first order reaction in the catalyst particles $(k_1 = 1 \text{ mol/s/m3}, k_2 = 2 \text{ mol/s/m3}, P_R = 40 \text{ bar}, d_{part} = 10 \text{ mm}, D_{eff} = 10^{-5})$

Figure A.3: The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions including CO $(T_R = 200-270 \ ^{\circ}C, P_{R,in} =$ 30-40 bar, $d_{part}\ =\ 0.1\mathchar{-}20$ mm)





With correction

1

Without correction

Figure A.4: The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Bussche & Froment [40] $(T_R =$ 200-270 °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm)



Figure A.5: The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Graaf [18] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm)



Figure A.6: The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Heckel [22] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm)



Figure A.7: The catalyst efficiency as function of the modified Thiele modulus for systems with varying pressures, temperatures, particle diameters, particle geometries and surface compositions for the kinetics of Park [32] ($T_R = 200-270$ °C, $P_{R,in} = 30-40$ bar, $d_{part} = 0.1-20$ mm)

Appendix B

Packed bed Reactor



Figure B.1: The error as function of the number of grid points in the column. $(L_R = 10 \text{ m}, D_R = 2 \text{ m}, T_{in} = 270 \text{ °C}, P_{R,in} = 40 \text{ bar}, GHSV_{R,in} = 50 \text{ 1/hr}, d_{part} = 0.25 \text{ mm}, D_cat = 3 m_{sol}^3/m_{cat}^3, w_{cat,1} 0.5 m_{cat,1}^3/m_{cat}^3)$



Figure B.2: The numerical solution (solid line) and analytical solution (asterisks) for a first order reaction in the column without internal mass transfer and dispersion ($k_1 = 1 \text{ mol/s/m3}$, $P_R = 40 \text{ bar}$, $v_{in} = 0.1 \text{ m/s}$)



Figure B.3: The numerical solution and analytical solution for a first order reaction in the column without dispersion ($k_1 = 1$ mol/s/m3, $P_R = 40$ bar, $v_{in} = 0.1$ m/s, $d_{part} = 10$ mm, $D_{eff} = 10^{-5}$)



Figure B.4: The numerical solution and analytical solution for a first order reaction in the column without internal mass transfer $(k_1 = 1 \text{ mol/s/m3}, P_R = 40 \text{ bar}, v_{in} = 0.1 \text{ m/s}, D_{ax} = 10^{-3})$

Appendix C

Packed bed Membrane Reactor



Figure C.1: The normalised mass flow over the lenght of the column. (T_R = 270 °C, $P_{R,in}$ = 40 bar, C_{H2}/C_{CO2} = 3, d_{part} = 10 mm, L_R = 10 cm, D_R = 2.6 cm, D_{cat} = 0.33, $w_{vol,cat1}$ = 0.5)



Figure C.2: The normalized mass flow in the industrial scale membrane reactor (Reactor conditions are reported in Table 6.1)



Figure C.3: The temperature over the length of the industrial scale membrane reactor. (Reactor conditions are reported in Table 6.1, $d_p = 3.1$ mm, $T_w = 176$ °C)

Appendix D

Two Dimensional Reactor



Figure D.1: The error as function of the number of grid points in the radial direction in the column. $(L_R = 1 \text{ m}, D_R = 10 \text{ cm}, T_{in} = 220 \text{ °C}, P_{R,in} = 40 \text{ bar}, GHSV_{R,in} = 50 \text{ 1/hr}, d_{part} = 0.25 \text{ mm}, D_cat = 3 m_{sol}^3/m_{cat}^3, w_{cat,1} 0.5 m_{cat,1}^3/m_{cat}^3, D_{mem} = 10 \text{ mm}, \text{SW} = 1, P_{mem} = 35 \text{ bar})$



Figure D.2: The normalized mass flow in the 2D membrane packed bed reactor model ($L_R = 1$ m, $D_R = 10$ cm, $T_{in} = 220$ °C, $P_{R,in} = 40$ bar, $GHSV_{R,in} = 50$ 1/hr, $d_{part} = 0.25$ mm, $D_cat = 3 m_{sol}^3/m_{cat}^3$, $w_{cat,1}$ 0.5 $m_{cat,1}^3/m_{cat}^3$, $D_{mem} = 10$ mm, SW = 1, $P_{mem} = 35$ bar)



Figure D.3: The radial concentration profile for various reactor lengths ($k = 1 \text{ mol/s/m3}, C_{in} = C_{wall}$ = 100 mol/m3, $v_{in} = 0.1$ m/s, $D_{rad} = 10^{-5}, L_R = 1$ m, $D_R = 0.2$ m, $D_M = 10$ mm)



Figure D.4: Conversion and Selectivity in the packed membrane reactor for a 1D model (solid line) and a 2D model (asterisks) and a 1D model with the correlation of Boon [6] (circles) for various temperatures. ($T_R = 200\text{-}270$ °C, $P_{R,in} = 40$ bar, GHSV $= 50 \text{ 1/hr}, C_{H2}/C_{CO2} = 3$, $d_{part} = 0.25 \text{ mm}, L_R = 0.5$ m, $D_R = 10 \text{ cm}, D_{cat} =$ $0.33, w_{vol,cat1} = 0.5, D_M$ $= 10 \text{ mm}, P_M = 35 \text{ bar},$ SW = 1.0)