Dimethyl ether as building block for the production of green fuels

Citation for published version (APA):

Document status and date:
Published: 18/09/2018

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.
Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Dimethyl ether as building block for the production of green fuels

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op dinsdag 18 september 2018 om 13:30 uur

door

Carlos Eduardo Ortega Rojas

geboren te Maracaibo, Venezuela
Dit proefschrift is goedgekeurd door de promotoren en de samenstelling van de promotiecommissie is als volgt:

Voorzitter: prof.dr. N.A.J.M. Sommerdijk
1e promotor: prof.dr.-Ing. G.A. Kolb
2e promotor: prof.dr. V. Hessel
leden: dr.ir. J. van der Schaaf
        prof.dr. F. Gallucci
        Prof.dr. A.C. van Veen (University of Warwick)
        Prof.dr. M. Muhler (Ruhr University Bochum)

Het onderzoek of ontwerp dat in dit proefschrift wordt beschreven is uitgevoerd in overeenstemming met de TU/e Gedragscode Wetenschapsbeoefening.

“Dans les champs de l’observation le hasard ne favorise que les esprits préparés”

- Louis Pasteur

Inaugural Address as newly appointed Professor and Dean (Sep 1854) at the opening of the new Faculté des Sciences at Lille (7 Dec 1854)

To my wife and family

iii
Carlos Ortega

Dimethyl ether as building block for the production of green fuels

Table of Contents

Summary .............................................................................................................................................. xiii

Chapter 1. Introduction ....................................................................................................................... 16

1.1 In pursuit of a carbon neutral economy .................................................................................... 18
1.1.1 The BIOGO-for-Production project .................................................................................. 19
1.1.2 Other research approaches for the production of green gasoline ................................. 20
1.2 Zeolites as enabler materials: ZSM-5 case ........................................................................... 22
1.3 Chemistry of reactions ............................................................................................................. 24
1.3.1 Methanol to dimethyl ether ......................................................................................... 24
1.3.2 Oxygenates to hydrocarbons ...................................................................................... 25
1.4 Industrial perspective on the oxygenates conversion to hydrocarbons ......................... 29
1.4.1 MTG process by ExxonMobil ...................................................................................... 29
1.4.2 Topsoe Integrated Gasoline Synthesis (TIGAS) process ........................................... 35
1.5 Compact gas to liquid technologies .................................................................................... 39
1.6 Research scope ....................................................................................................................... 41

Chapter 2. Materials, Methods and Initial Tests ............................................................................... 44

2.1 Introduction ............................................................................................................................... 46
2.2 Materials .................................................................................................................................. 46
2.2.1 Catalysts .......................................................................................................................... 46
2.2.2 Silicon Carbide .................................................................................................................. 47
2.2.3 Gases and reagents .......................................................................................................... 47
2.3 The MTG Set-up ...................................................................................................................... 48
2.4 Experimental procedures ......................................................................................................... 53
2.4.1 Catalyst Characterization ............................................................................................... 53
2.4.2 Catalyst Oxidizing Treatment – Regeneration ............................................................... 57
2.4.3 Methanol to DME – Kinetic tests .................................................................................. 58
2.4.4 DME to Hydrocarbons – Evaluation of process parameters ....................................... 59
2.4.5 DME to Hydrocarbon – Kinetic tests ............................................................................ 61
2.5 Initial tests ............................................................................................................................... 62
2.5.1 Recycle reactor – evaluation of fluid dynamic behavior ................................................. 62
2.5.2 Fixed bed recycle reactor vs Microstructure reactor ...................................................... 63

A catalogue record is available from the Eindhoven University of Technology Library


Copyright © 2018 by Carlos Ortega

Printed by: GVO drukkers en vormgevers B.V, The Netherlands

Cover design: Jenny Campos
Figure 4-9. Quasiadiabatic test reaction in a single-pass test of 24 h. ZSM5-SAR58, WHSV = 10 h⁻¹, Tini = 350 °C, Pt = 1 bar, pure DME in feed. .................................................................................................................................115
Figure 4-10. Catalytic bed temperature profile. Catalyst ZSM5-SAR88. ..................................................116
Figure 4-11. Quasiadiabatic test reaction in a single-pass test of 24 h. ZSM5-SAR100, WHSV = 10 h⁻¹, Tini = 350 °C, Pt = 1 bar, pure DME in feed. .................................................................117
Figure 4-12. Catalytic bed temperature profile. Catalyst ZSM5-SAR100..................................................118
Figure 4-13. Thermogravimetric analysis of fresh and spent samples (TOS = 24 h). Samples tested at WHSV = 10 h⁻¹, Tini = 350 °C, Pt = 1 bar, pure DME in feed. .................................................................118
Figure 4-14. Catalytic performance as a function of pressure. Row 1: 2.5 bar; row 2: 5.5 bar; columns A to C are catalysts ZSM5-SAR23, ZSM5-SAR58 and ZSM5-SAR100.........120
Figure 4-15. Thermogravimetric analysis (TGA) of catalyst samples tested at 2.5 bar and 5.5 bar, TOS = 3 h. ........................................................................................................................................ 121
Figure 4-16. Partial pressure variation of MeOH and DME vs. conversion. (A) pDME,feed = 0.1 bar; (B) pDME,feed = 0.5 bar; and (C) pDME,feed = 1.0 bar .........................................................122
Figure 4-17. Effect of temperature on the product distribution of the hydrocarbon fraction present in the product stream. Experiments carried out at molar fraction of DME in the feed of 0.1 (A), 0.5 (B) and 1.0 (C), WHSV = 25 h⁻¹, and total pressure of 1 bar. ..............................124
Figure 4-18. Effect of WHSV on the product distribution of the hydrocarbon fraction present in the product stream. The experiments were carried out at a molar fraction of DME in the feed of 0.1 (A), 0.5 (B) and 1.0 (C), T = 350 °C, and total pressure of 1 bar. 127
Figure 4-19. Effect of the partial pressure of DME in the product distribution of the hydrocarbon fraction present in the product stream. Experiment carried out at 325 °C (A), 350 °C (B) and 375 °C (C). In all cases WHSV = 25 h⁻¹ and total pressure of 1 bar. ................................................................................................................................................128
Figure 5-1. Conversion of oxygenates versus time. Molar fraction of DME in the feed is 1 and the WHSV corresponds to (A) 25 h⁻¹; (B) 75 h⁻¹ and (C) 125 h⁻¹.................................134
Figure 5-2. Schematic diagram of the reaction........................................................................................................135
Figure 5-3. Evolution of mass fraction of C₂⁻C₅ olefins with time. Data collected at yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹ and (C) 125 h⁻¹.................................136
Figure 5-4. Mass fraction of C₂⁻C₅ versus conversion of oxygenates. Experiments were performed at WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min. ........................................................................................................137
Figure 5-5. Evolution of mass fraction of the LPG lump with time. Experimental conditions: yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹; and (C) 125 h⁻¹. ........................................137
Figure 5-6. Mass fraction of the LPG lump versus conversion of oxygenates. Experimental conditions: WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min. ........................................................................................................................................138
Figure 5-7. Evolution of mass fraction of the C₆⁺ lump with time. Experimental conditions: yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹; and (C) 125 h⁻¹.................................138
Figure 5-8. Mass fraction of C₆⁺ fraction versus conversion of oxygenates. Experimental conditions: WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min. ........................................................................................................................................139
Figure 5-9. (A) Data extrapolation; (B) Residuals from data analysis. Experimental conditions: WHSV = 125 h⁻¹, yDME in feed = 0.1, and T = 325 °C .................................................................141
Figure 5-10. (A) Data extrapolation; (B) Residuals from data analysis. Experimental conditions: WHSV = 25 h⁻¹, yDME in feed = 1.0, and T = 375 °C .................................................................142
Figure 5-11. Oxygenates’ conversion rate. Experimental (circles), quadratic polynomial fit (continuous line), and fit with equation (5-2) (dashed line). Rows represent conditions of WHSV of 25 h⁻¹, 75 h⁻¹ and 125 h⁻¹, while columns represent temperatures of 325 °C, 337 °C, 350 °C, 362 °C, and 375 °C, respectively. ........................................................................................................................................143
Figure 5-12. Lump mass fraction extrapolated to t = 0. (A1) Oxygenates; (A2) Ethylene; (B1) Propylene; (B2) Butenes; (C1) Propane and butanes; (C2) C₆⁺ fraction. ........................................................................145
Figure 5-13. Arrhenius plots for the rate of oxygenates conversion extrapolated to time t=0. Data measured at different WHSV in the range of 25 h⁻¹ to 125 h⁻¹. Graphs (A), (B), and (C) represent experiments at molar fraction of DME in the feed of 0.1, 0.5 and 1...146
Figure 6-1. MTH dual cycle mechanism. ........................................................................................................160
Figure 6-2. Arrhenius plots. Logarithmic rate versus inverse temperature, for six lumps: Oxygenates, Ethylene, Propylene, Butenes, Saturated C₂-C₅ and C₆⁺ liquid fraction. ....163
Figure 6-3. Parity plots of mass fraction of the different lumps in water-free basis. Kinetic model: Developed in-house: mass fraction of (A) oxygenates; (B) ethylene; (C) propylene; (D) butenes; (E) saturated C₂-C₅; (G) C₆⁺ liquid fraction. .................................................................................................164
Figure 6-4. Mass fraction of C₆⁺ olefins and C₆⁺ lump in water-free basis. Data for WHSV = 25 h⁻¹ and temperature in the range of 325 °C to 375 °C .................................................................166
Figure 6-5. Mass fraction of the different lumps in water-free basis versus space time. Symbols represent experimental values and lines represent model prediction. The graphs correspond to different temperatures (A) 325 °C; (B) 337 °C; (C) 350 °C; and (D) 362 °C. ........................................................................................................................................167
List of Tables

Table 1-1, Kinetic parameters of alkenes methylations over HZSM-5. .......................... 28
Table 1-2, Process conditions and product specifications. .............................................. 34
Table 2-1, Tubular reactor characteristics ...................................................................... 49
Table 2-2, Summary of equipment used during research project. ...................................... 55
Table 2-3, Process variables modified in the kinetic experimental program. ...................... 59
Table 2-4, Process variables used in DTH conversion ....................................................... 60
Table 2-5, Factors and levels used in the experimental program .......................................... 61
Table 2-6, Experimental conditions during RTD measurements ........................................ 62
Table 2-7, FBRR and MSR characteristics ..................................................................... 63
Table 2-8, MSR vs RR. Experimental details ................................................................... 64
Table 2-9, Methanol conversion as function of regeneration cycle .................................... 68
Table 3-1, Testing criteria to neglect heat and mass transfer limitations .............................. 77
Table 3-2, Physicochemical constraints ........................................................................... 79
Table 3-3, Results from testing criteria to neglect heat and mass transfer limitations ......... 85
Table 3-4, Summary of kinetic models tested ................................................................. 90
Table 3-5, Kinetic models and OF values ......................................................................... 91
Table 3-6, Summary of kinetic parameters ...................................................................... 96
Table 3-7, Entropies of adsorption and maximum entropy according to guideline ............ 97
Table 3-8, Akaike’s information criterion ........................................................................ 98
Table 4-1, Textural properties of catalyst ....................................................................... 108
Table 4-2, Theoretical and calculated acidity .................................................................... 112
Table 6-1, Results from testing criteria ........................................................................... 154
Table 6-2, Performance comparison of some kinetic models available in literature .......... 156
Table 6-3, Kinetic parameters from kinetic models available in literature .......................... 158
Table 6-4, Estimated kinetic parameters for the in-house developed model ..................... 168

Summary

The development and growth of population has also lead to an increasing energy demand. It is expected that the global energy demand will rise by ~ 16 % between 2015 and 2040, while the gasoline demand will suffer an increase of ~ 13 %. This, coupled with decreasing oil reserves, an increasing concern on climate change and the impact of CO₂ emissions on the environment has led to the development and growing use of alternative energies and biofuels.

Biofuels can be produced via different routes, such as the Fischer-Tropsch route or the methanol route. The latter refers to the production of syngas (mixture of H₂ and CO) from bio-based materials and its subsequent transformation into methanol, followed by dehydration to dimethyl ether (DME), and the conversion of DME to hydrocarbons. The last step has drawn more attention in recent years, which is linked to the advantages that DME provides in the valorization of feed streams of low H₂/CO ratio, which are formed from feedstocks such as biomass or coal.

DME has proven applicability both as intermediate and final product. In fact, the direct use of DME as transportation fuel has been proven and put into practice. Given the flexibility of this starting material, the first part of this research focuses on the production of DME via dehydration of methanol using a commercial ZSM-5 catalyst. This is done in contrast to the conventional methanol to DME technology that uses γ-alumina as dehydration catalyst. It could be shown that the conversion with ZSM-5 can be carried at lower temperatures, keeping the same selectivity as the conventional process, and improving the maximum attainable conversion which is limited by equilibrium.

Experimental studies and mathematical modeling were used to develop and identify a suitable kinetic model. The kinetic measurements were performed at a total pressure of 1 bar, partial pressure of methanol (pm) from 0.3 bar to 1 bar, temperatures from 140 °C to 190 °C, weight hourly space velocities (WHSV) from 15 h⁻¹ to 100 h⁻¹, and two different amounts of water in the feed (0 and 30 wt.%). Kinetic parameters of the different models were calculated and evaluated against physicochemical constraints and guidelines on entropy values. In fact, the evaluation of entropies was the key factor to differentiate between rival models. The selected kinetic model supports a mechanism in which methanol suffers dissociative adsorption and a surface reaction is the rate determining step (RDS).
The second part of this research focuses on the use of DME as an intermediate for hydrocarbon synthesis. An evaluation of the effect of process parameters on conversion and selectivity and a kinetic study to describe the conversion of DME into hydrocarbons was carried out. The development of the kinetic model considered main steps of the established reaction mechanism, namely the dual cycle mechanism. These steps included:

(i) formation of aromatic intermediates (polymethylbenzenes);
(ii) dealkylation of the intermediates to produce ethylene and propylene;
(iii) methylation of small olefins to increase the chain size of the hydrocarbons;
(iv) hydrogenation of ethylene, propylene and butenes to produce the corresponding saturated compounds; and
(v) dimerization reactions between propylene and butenes to produce higher hydrocarbons. The kinetic parameters of this new model were estimated from regression analysis using kinetic data measured under gradientless conditions and the Athena Visual Studio Software. The experimental data were measured in a gradientless fixed bed external-recycle reactor over a wide range of conditions, with temperatures from 325 °C to 375 °C, weight hourly space velocities (WHSV) from 25 h⁻¹ to 125 h⁻¹, a total pressure of 1 bar and undiluted DME as feed. The newly developed model allowed a good description of the experimental results, showed better performance than models available in literature for the methanol-to-gasoline reaction, and rendered kinetic parameters that met physicochemical and statistical constraints, showing good agreement with results from density functional theory (DFT) calculations reported by other authors.
CHAPTER 1

Introduction

"Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less"

Marie Curie (1867-1934)
1.1 In pursuit of a carbon neutral economy

The development and growth of population have also lead to an increasing energy demand, which is expected to increase by approximately 16 % between 2015 and 2040 [1]. Similar trends are observed for fuels, such as liquefied petroleum gas (LPG), gasoline or diesel, as shown in Figure 1-1 for the period 2016 – 2040 [2]. In particular reference to the gasoline fraction, the Organization of the Petroleum Exporting Countries (OPEC) has predicted a rise in its demand from 25.1 million barrels per day (MM bpd) to 28.4 MM bpd [2], which represents an increase of approximately 13 %.

Figure 1-1. Outlook of global demand of oil products from 2015 to 2040.

This thirst for energy and fuels, coupled with decreasing oil reserves, growing concern on climate change, and the impact of CO₂ emissions on the environment have led to the development and increasing use of alternative energies and biofuels. By the year 2040, the cumulative growth of non-fossil fuel is expected to increase by ca 50 % [1].

Biofuels can be produced via different technologies, such as Fischer-Tropsch or methanol to hydrocarbons (MTH). The latter refers to the production of syngas (a mixture of H₂ and CO) from bio-based materials, which is further transformed into methanol. Then, the methanol is dehydrated to dimethyl ether (DME), and, in the final step, DME is converted to hydrocarbons. The last step has drawn more attention in recent years, which is linked to the advantages that DME provides in the valorization of feed streams of low H₂/CO ratio, which are formed from feedstocks such as biomass or coal.

The OPEC predictions in reference to the growth of non-fossil fuels might be conservative. I used to believe that a worldwide change from fossil to renewable resource would take decades. However, in recent years I noticed two turning points. The first is the signing of The Paris Climate Agreement. Although widely criticized for its poor control, it is a worldwide recognition that something must be done in regards to climate change and CO₂ emissions. The second is the attitude that China has taken in reference to climate change. They have continuously closed coal powered plants and for the period 2017-2020 they have assigned a budget of 360 billion US$ for renewable energy [3].

1.1.1 The BIOGO-for-Production project

BIOGO-for-Production is the acronym used for the project “Catalytic Partial Oxidation of Bio Gas and Reforming of Pyrolysis Oil (BioOil) for an Autothermal Synthesis Gas Production and Conversion into Fuels”, which was developed within the Seventh Framework Programme (FP7) of the European Union’s Research and Innovation Programme. The project was carried out under grant agreement No. 604296. Its main goal was to create a fully integrated and comprehensive process for the production of biofuels using novel heterogeneous nanocatalysts, sustainable resources and innovative microreactor technology [4]. A simplify block diagram of the overall process is shown in Figure 1-2.

BIOGO-for-Production, or just BIOGO, was conceived as a response to the challenges faced by the European petrochemical market, which range from raw material supply to sustainability and ecological pressures. To meet sustainability demands, clean and innovative technologies must transform production processes. Therefore, the main technical objectives focused on the development of new methods of coating nanocatalysts on innovative microstructured reactors to carry out chemical transformations. These included [5]:

- Design and develop nanocatalysts tailored for reforming of biogas and bio-oils, methanol synthesis, methanol to gasoline (MTG) conversion, and hydrogenation of bio-oils to diesel-grade chemicals
- Prove the scaled-up manufacturing potential for the catalysts production process
- Integrate the entire processes chain at mini-plant scale for the production of gasoline from biomass
At Eindhoven University of Technology, the attention was centered in two main activities: (i) the kinetic analysis of the oxygenates conversion to hydrocarbons; and (ii) the development of an integrated process scheme that included process simulation and life cycle assessment (LCA) of the process. A list of partners and further information on the BIOGO project can be found at https://www.biogo.eu/.

1.1.2 Other research approaches for the production of green gasoline

There is an increasing interest in the use of green gasoline and research in this area has become more relevant in recent years. Below, two research projects related to green fuel synthesis are described. They are considered relevant since they have good resemblance to the BIOGO project.

The first project is *Gasoline from Wood via Integrated Gasification, Synthesis, and Methanol-to-Gasoline Technologies* project [6]. It was developed by the National Renewable Energy Laboratory’s (NREL’s) in the USA, and its goal was to perform a feasibility study for the production of gasoline from biomass [6]. The study considered the use of syngas from a biomass-fed facility with a throughput of 2000 dry metric ton/day. In the first stage of the process, the syngas is produced via the thermochemical gasification of biomass in fluidized bed operating at 883 °C. Then, the syngas is cleaned and sent to the methanol synthesis units. In this unit, syngas is transformed into methanol in a fixed bed reactor using copper/zinc oxide/alumina catalyst, operating with a H2/CO ratio of 2.1, at 300 °C and 5.1 MPa. Finally, methanol is converted into hydrocarbons in a fluidized-bed reactor that uses ZSM-5 as catalyst. The reactor is operated at inlet conditions of 330 °C and 1.45 MPa. The finished fuel product is 82 wt.% gasoline, 10 wt.% LPG and 8 wt.% fuel gas.

The second project is Green Gasoline from Wood Using Carbona Gasification and Topsoe TIGAS Processes, or Wood2Gasoline project [7]. It was developed in USA between 2010 and 2014. It demonstrated and validated a technology to convert woody biomass into gasoline and gathered industrial partners such as GTI, Andritz, Haldor-Topsoe, UPM, and Phillips 66, to cover the entire supply chain from the biomass to the drop-in gasoline product [7].

The pilot plant used Andritz-Carbonara technology for the gasification of woody biomass in a fluidized-bed reactor. It was operated at a pressure ca 10 bar and temperature of 850 °C to produce syngas. The syngas is pretreated, compressed and then sent to the TIGAS unit. This syngas has a H2/CO ratio close to 1.1. Thus, a combined MeOH/DME catalyst is appropriate at this stage to maximize the conversion of syngas into oxygenates, e.g. Topsoe DCK-10 catalysts. The syngas conversion reactor works at ca 70 bar and 220 °C. The conversion of syngas to DME is exothermic (ΔHr = 246 kJ∙mol⁻¹). Thus, a boiling water reactor design is convenient to guarantee efficient heat removal. The oxygenates stream is then mixed with a recycle stream that serves as a heat sink and contributes to regulate the temperature in the gasoline reactor. The recycle flow can be adjusted to regulate the reactor outlet temperature which is maintained in the range between 400 °C and 420 °C and uses a ZSM-5 catalyst to accelerate the conversion. A description of the TIGAS process is provided below in section 1.4.2.

In 2015 the United States Environmental Protection Agency (EPA) registered the green gasoline blend as an approved motor fuel. Moreover, it was estimated a reduction of approximately 74 % of greenhouse gas (GHG) emissions as compared with petroleum-based fuels, and the estimated cost per gallon 0.55 €/L $^{1}$ [7].

These research projects share similarities with BIOGO, including the use of ZSM-5 as an enabler material. Therefore, in the following section a brief description of zeolites and in particular of ZSM-5 is given.

$^{1}$ 2.56 US$/gallon. Conversion factors used: 1 US$ = 0.8161 €; 1 US gallon = 3.7854 L
1.2 Zeolites as enabler materials: ZSM-5 case

Zeolites are crystalline inorganic material, formed by \( \text{TO}_4 \) tetrahedra, with T representing atoms in tetrahedral position (such as Si, Al, P, Ge, etc.) bridged by oxygen ions. This means that the overall O/T ratio on the final framework is 2 [8, 9].

Pure silicate networks are neutral. If a Si\( ^{4+} \) within the framework is replaced with a trivalent cation, such as Al\( ^{3+} \), a negative charge is created which must be compensated by a charge balancing cation in extra-framework position [9]. The charge-balancing cation provides the zeolites with different properties of interest, such as ion exchange or catalytic activity. If the charge-balancing cation is a proton, the zeolite is conferred Brønsted acid properties and the acid site can be represented as a resonance structure as shown in Figure 1-3 (adapted from [10]).

Zeolite pores sizes are in the molecular range, varying from 0.3 nm to 1.5 nm. The pores of the zeolites are formed by 8, 10, 12 and up to 18-member rings (MR). In this case the MR refers to the T atom and one must consider the O ions that bridge the T atoms to account for the total number of atoms present in a ring. For example, a 10-MR would actually contain 20 atoms (10 T atoms + 10 oxygen atoms). A common classification of zeolites according to their pore size is: small (8-MR), medium (10-MR), large (12-MR) and extra-large (14-MR or more) pore size zeolites [8, 9].

Pores within zeolites can be arrange in a one-dimension (1D), two-dimension (2D) or three-dimension (3D) channel system configuration. The 2D and 3D channel configuration favors diffusion thus it is convenient for catalytic systems. Besides, the channels pattern can be straight, sinusoidal or zigzag [8, 9].

The Zeolite Socony Mobil – five (ZSM-5) was first synthesized by Mobil and reported in a US patent in 1972 [11]. It has a 3D channel pore system with straight and sinusoidal channels that intercept [12, 13] to create cages with a critical dimension of approximately 9 Å [13]. The pores are of elliptical shape with dimensions of 5.1 Å x 5.5 Å for the [100]-face and 5.3 Å x 5.6 Å for the [010]-face [14]. This is shown in Figure 1-4 (Adapted from [15]).

Since the pores are interconnected and have different dimensions, reactants can diffuse in by one type of pore, while products can diffuse out by the second type of pore. This is known as molecular traffic control (MTC) and provide the zeolite with shape selectivity [13]. This is represented in Figure 1-5 (reproduced from [13]). In addition, the MTC could prevent the occurrence of counterdiffusion which might be a limiting factor in catalytic conversions.

For the oxygenates conversion to hydrocarbons, topic of interest in this research, it has been reported that counterdiffusion does not affect the conversion rate, which could be explained by the 3D channel system present in ZSM-5 [13]. This translates into methanol and/or DME preferentially diffusing into the zeolite via the sinusoidal channels, while bulkier products (olefins, paraffins and aromatics) would diffuse out of the crystal by the straight channel.

The use of this zeolite in the methanol conversion to hydrocarbons found its first industrial application in New Zealand in 1984, where a commercial MTG plant was built and ZSM-5 was used as catalyst in the gasoline reactors. This process is described in detail in section 1.4.1.
Chapter 1

1.3 Chemistry of reactions

1.3.1 Methanol to dimethyl ether

The dehydration of methanol into dimethyl ether is a commercially available route for the production of this important material. It is carried out over an acidic catalyst, with γ-Al₂O₃ being commonly used in industry. The overall reaction is equimolar and exothermic with a standard enthalpy of reaction of $\Delta H_{r}^\circ = -23.0 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K [16]. The reaction is summarized in equation (1-1).

$$\text{2CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}; \Delta H_{r}^\circ = -23.0 \text{ kJ} \cdot \text{mol}^{-1}$$

(1-1)

Known processes use aluminum oxide catalysts, at relative high temperatures, to promote the reaction [17]. However, since the reaction is exothermic and the conversion is limited by the thermodynamic equilibrium, the use of high temperatures is unfavorable.

The mechanism of the reaction is still under debate [18] and two routes are considered likely. The first route supports the associative adsorption of methanol on the surface of the catalyst [19, 20, 21], while the second supports a dissociative adsorption of the alcohol [22]. A schematic representation of these two mechanisms is shown in Figure 1-6. This point will further be addressed in Chapter 3, where the kinetics of methanol to DME are discussed.

1.3.2 Oxygenates to hydrocarbons

First Carbon-Carbon bond formation

The MTH reaction have been extensively studied and more than 20 proposed mechanisms are described in literature for the formation of first carbon-carbon bond [23, 24]. However, these mechanisms have been rejected based on high activation barriers (> 210 kJ·mol⁻¹) obtained via DFT calculations [25, 26, 27, 28]. Other authors have proposed that the initiation of methanol conversion is caused by impurities in the feed [29, 30]. Although the effect of impurities has been shown [31], it was also proven that MTH reaction can proceed in the absence of such species [32].

Just recently, Liu et al. [33] have identified acetic acid and methyl acetate as the first intermediates containing C-C bonds. The authors propose that carbon-carbon bond is formed via CO carbonylation of methoxy groups, on the acid sites of the zeolite. This reaction is likely since methanol, DME and formaldehyde (HCHO) have electrophilic C atoms that could react with the nucleophilic carbon atom of CO, as has been reported previously for acidic zeolites [34, 35, 36]. Formation of CO and formaldehyde was observed by the authors even in silicalite (Na-ZSM-5) or γ-Al₂O₃. These results are also in accordance with that of Comas-Vives et al. [37], who observed formate surface species via IR and NMR, when DME was reacted on Al₂O₃ at 300 °C.
Chapter 1

An activation energy of 80 kJ mol⁻¹ was estimated for the carbonylation step [33], in accordance with a previous theoretical study on carbonylation of methanol and DME on Mordenite, where the activation energy was estimated to 84 kJ mol⁻¹ [38]. As early as 1998 [25] a reaction mechanism for the first C-C formation via: (i) methane and formaldehyde (see also [37]); or (ii) carbon monoxide, were considered likely.

Under MTH conditions, the authors estimated low rates of the carbonylation reaction. However, they indicate that this is enough to form traces of acetyl species (C-C bonds) and initiate the formation of the hydrocarbon pool [33], from which MTH products are formed via methylation, dealkylation, cyclization and hydrogen transfer reactions. The authors conclude that these low reaction rates could be the cause of the induction period commonly reported for this reaction [39, 40, 41, 42].

Furthermore, the authors showed the formation of C₂-C₄ alkenes from HOAc on ZSM-5, via surface reaction studies at increasing temperatures (50 – 500 °C). They indicated that acetic acid could undergo ketonization as reported by [43, 44, 45], to form CO₂ and acetone, followed by aldolization, cracking, cyclization and aromatization according to [43, 46, 47, 48].

Chowdhury et al. [49] have also identified surface acetate, methyl acetate and dimethoxymethane (DMM, CH₃OCH₂OCH₃) as the initial intermediates with C-C bonds. For this purpose, the authors used NMR, UV/Vis diffusive reflectance and mass spectrometry to evaluate the MTO process on H-SAPO-34. According to Chowdhury et al. [49], the mechanism may proceed as follows: first, methylation of a Brønsted acid site (ZeOH) forms a surface methoxy species (SMS) which interacts with another methanol or DME molecule. Then, formation of the first C-C according to an insertion reaction from SMS to the MeOH/DME molecule (Path I). Direct interaction of the SMS with methanol might also be possible (Path II), as originally proposed by [27]. Alternatively, carbonylation of the SMS can take place to form the first C-C bond, and further reaction with methanol results in MeOAc, supporting the results presented by Liu et al. [33].

**Reaction mechanism: The dual-cycle mechanism**

The dual-cycle mechanism is a derivation of the hydrocarbon pool mechanism originally proposed by Dahl and Kolboe [50, 51, 52, 53, 54]. Nowadays, it is that formation of hydrocarbons from these oxygenates (methanol and dimethyl ether) proceed in the hydrocarbon pool, via the dual cycle mechanism, as reported by Perez et al [55].

The dual-cycle mechanism was proposed by Bjørgen et al. [56]. As its name indicates, the mechanism consists of two cycles that run in parallel during the conversion of oxygenates to hydrocarbons. These two cycles are known as the aromatic cycle and the olefin (or alkene) cycle. A schematic representation of the two cycles is shown in Figure 1-7.

**Figure 1-7. Dual cycle mechanism.**

In the aromatic cycle, methylbenzenes represent the main species. The methylbenzenes are alkylated and dealkylated to produce ethylene and propylene [24]. According to Ilias and Bhan [57] ethylene does not participate (at least to a significant extend) in the olefin-based cycles. Therefore, it could be considered as a final product. The main reason is the low reactivity of ethylene in comparison to propylene or higher olefins. In this respect, Hill et al. [58, 59, 60] studied the methylation of C₂-C₄ olefins over different zeolites using DME as methylating agent and showed that the reactivity of ethylene is at least two orders of magnitude lower than that of propylene. The authors attribute this behavior to more stable intermediates resulting from more substituted olefins. A summary of the results obtained from Hill et al. [58, 59, 60] is included in Table 1-1.

In the olefin cycle, a chain growth reaction takes place where propylene is successively methylated to form higher olefins [61]. This reaction allows the incorporation of methyl
groups into olefins. If methylation is dominant, then C₅⁺ aliphatic compounds² are abundant in the MTH product distribution [62]. This has been reported by several authors [63, 64, 65, 66, 67] when using 10-member ring (10-MR) zeolites such as ZSM-22 and ZSM-23, where aromatic dealkylation and transport of cyclic species is hindered [62].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pre-exponential factor [k] (h⁻¹·bar⁻¹)</th>
<th>Apparent activation energy [Ea] (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>0.06</td>
<td>98</td>
</tr>
<tr>
<td>Propene</td>
<td>3.7</td>
<td>62</td>
</tr>
<tr>
<td>1-Butene</td>
<td>89</td>
<td>44</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>74</td>
<td>46</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>41</td>
<td>49</td>
</tr>
<tr>
<td>Isobutene</td>
<td>3509</td>
<td>56</td>
</tr>
</tbody>
</table>

Svelle et al. [68, 69] have studied the kinetics of zeolite-catalyzed methylation, by co-reaction of [¹³C]methanol with [¹²C]ethylene, [¹²C]propene or [¹²C]n-butene over H-ZSM-5 (Si/Al=45). These reactions were studied at 350 °C, low partial pressure of reactants (< 100 mbar), and low conversions to favor the methylation reaction. For all methylation reactions (any pair between methanol and ethene or propene or n-butene), the rate showed a first-order dependence on the olefin partial pressure and zero-order dependence on methanol partial pressure.

The cracking reaction shown in Figure 1-7 seems less relevant to our work considering that mild reaction conditions were used in this investigation. Sardesai et al [70] have shown that the cracking reaction increases significantly when the reaction temperature was increased from 400 to 640 °C, which are temperature conditions beyond our experimental settings.

1.4 Industrial perspective on the oxygenates conversion to hydrocarbons

Nowadays, several technologies coexist which offer opportunities to valorize waste and carbon-based material to reduce our carbon footprint. The two examples discussed in this section refer to industrial processes that target the conversion of carbon-based substances into fuels. These technologies are the MTG process by ExxonMobil and the TIGAS process by Haldor-Topsoe.

1.4.1 MTG process by ExxonMobil

ExxonMobil offers technologies for the conversion of methanol into gasoline, which include the use of fixed bed, fluidized bed or multitubular fixed bed reactors. Exxon’s original approach used a fixed bed reactor technology, and the first MTG plant was commercialized in the mid-1980’s [71]. After a decade of research on the conversion of oxygenates into gasoline [72, 73, 74, 75, 76, 77, 78], the commercialization was realized as an industrial facility in Motunui, New Zealand, as part of a gas-to-gasoline (GTG) complex [79]. In this facility, natural gas was first converted to methanol and then into gasoline, with a production capacity of approximately 570 000 ton/year of gasoline [80].

In the first stage of the process, methanol is vaporized, preheated and fed into a fixed bed reactor where MeOH is converted into a mixture of oxygenates (MeOH/DME/H₂O). This reaction is limited by an equilibrium conversion that decreases as temperature increases. The DME reactor contains alumina catalyst and the reaction is carried out at 310 to 320 °C and 21 to 27 bar of pressure [79, 80, 81, 82]. Around 15 to 20 % of the overall heat of reaction is released in this step [71, 80, 83]. This turns into a temperature increase across the reactor close to 90 °C [79]. Since the reaction is limited by equilibrium, it is considered that this part of the process is inherently stable [71].

In the second stage of the process, the stream of oxygenates is combined with recycle gas and fed to the MTG reactors. The recycle gas helps in controlling the temperature rise in the MTG reactor [80, 83, 84]. The recycle is set to a ratio of 9:1 [79, 85] to limit the temperature rise to 68 °C [85], and avoid additional problems related to reversible and irreversible deactivation [84]. The reaction occurs over a ZSM-5 catalyst and the oxygenates mixture is converted into hydrocarbons and water [84]. Approximately 90 % of the methanol is converted into hydrocarbons in the gasoline boiling point range [84].

² Aliphatic compounds: “Acyclic or cyclic, saturated or unsaturated carbon compounds, excluding aromatic compounds” [278]
Depending of the plant capacity, several reactors work in parallel to guarantee continuous operation, while one reactor is under regeneration or standby [80, 83]. The outlet of the MTG reactors is first cooled producing steam as byproduct [80], then it is split in two streams [71, 79]. The first one is sent to the reactor effluent/recycle gas heat exchanger, in order to manipulate the recycle gas temperature and, consequently, be able to control the inlet temperature of the MTG reactors. The inlet temperature of the MTG reactors is typically 350 to 370 °C and the pressure about 19 to 23 bar [80, 82]. The second stream is used to pre-condition (vaporize and preheat) the MeOH that is fed to the DME reactor. Then, these two streams are recombined and cooled down to 25 - 35 °C at 16 bar in a series of water cooled heat exchangers [84].

After cooling, the stream is sent to a splitter, where gas (light hydrocarbons, H₂, CO and CO₂), water and liquid hydrocarbons are separated. A schematic flow diagram of the process is illustrated in Figure 1-8 (prepared from [71, 79, 80]). The gas product is sent to the gas recycle compressor, and this stream is later on combined with the fresh feed and sent to the MTG reactor. Part of the stream leaving the separator is purged before entering the compressor and sent to the fuel gas header of the plant [86]. This is carried out to control the reactor pressure [83] and avoid build-up CO and H₂. The water, having approximately 0.1 to 0.2 wt.% of oxygenated organic compounds, is sent to treatment by conventional biological methods before disposal [84].

The liquid hydrocarbons are fed to a de-ethanizer. In this unit ethane and lighter compounds are removed by distillation. The bottom product of this column is fed to a stabilizer unit, where C₃ and C₄ compounds are removed by distillation. This overhead product is used as fuel gas [84]. The bottom product of the stabilizer is sent to the gasoline splitter to obtain light and heavy gasoline.

The heavy gasoline fraction (with a bubble point > 177 °C) has a high content of durene (1,2,4,5 tetramethylbenzene) [79, 80]. This component has a melting point of 79 °C; thus, further processing is required to improve drivability performance of the final product [71, 80, 83, 84]. Processing of this gasoline fraction occurs in the heavy gasoline treating unit (HGTU) over a multifunctional metal-acid catalyst [79, 80]. In this unit, hydrogen is used to reduce the durene content through isomerization, disproportionation, ring saturation, transalkylation, dealkylation and cracking [71, 80]. Finally, the heavy and light gasoline fractions are mixed together. This final product can be blended with the conventional gasoline produced in refineries or can be sold as final product [71].
Several improvements on the fixed bed reactor technology have been patented. These have translated into technologies based on fluidized and multitubular bed reactors. A brief description is presented below.

URBK-UHDE-Mobil MTG Process – Fluidized-bed reactor technology

To increase the efficiency of the process a second generation of the process was developed, and it is known as the URBK-UHDE-Mobil MTG Process – Fluid-bed reactor technology. The initial studies were carried out at Mobil by Liederman et al. [87], who evaluated the effect of process variables on the MTG reaction using a fluidized-bed reactor and demonstrated the feasibility of this technology.

The scale up process went from a laboratory equipment to a 4-bpd pilot plant, and to a demonstration plant of 100 bpd [80, 88]. The latter was built in Wesseling, Germany [82, 88], completed in 1985 and capacities of 130 to 200 bpd were proved [88].

The fluidized-bed MTG technology has an improved design derived from the experience gain with New Zealand’s fixed bed process [71]. Improvements include better heat integration, fewer and smaller heat exchangers, process optimization, as well as reduced compressor requirements. Other advantages included [80, 82, 83] direct steam generation in cooling coils immersed in the fluid bed reactor, continuous catalyst regeneration, uniform bed temperature, which translate into constant gasoline quality, the gasoline produced has a higher octane number with lower durene content (<5 wt.%), and the gasoline yield including alkylates increases at least by 7.5 %. The improvements achieved vs the fixed bed process could also translate into a reduction in capital cost around 15 to 20 % [71], and this is probably related to reduction of 6 reactors in the fixed bed technology to 1 reactor in the fluidized-bed technology [83].

In the first stage of the process methanol is vaporized, preheated and directly fed to the bottom of the MTG reactor [79, 80]. The reactor operates at low pressure, 4 bar [83], which contrasts with the fixed bed reactor technology, which operates at ca 20 bar. The heat released by the reaction is then used to produce high pressure steam via coils located inside the fluid bed [83]. The reactor design includes cyclones and a fluidized-bed regeneration reactor, similar in concept to well-known fluid catalytic cracking (FCC) units. In this design, catalyst is continuously extracted, regenerated (by coke burn off) and returned back to the fluid bed unit [79]. One general disadvantage of this type of reactor is that catalyst requires great mechanical strength [84].

Fractionation and treatment of the gasoline product are carried out in a similar way to the fixed bed reactor technology. However, a HGTU unit may not be needed, depending on the durene content requirements of the final product. In Table 1-2 (prepared from [79, 80, 83]) a summary of process condition is provided, together with a summarized product distribution and quality of the gasoline obtained. Based on this table, Tabak and Yurchak [79] pointed out that the second-generation Mobil process have better yield and increased gasoline quality when compared to the fixed bed reactor technology (first generation).

Lurgi-Mobil MTG Process – Multi tubular fixed bed reactor

One major disadvantage of the fixed bed process is the high cost related to large recycle flowrate of light hydrocarbons. If the control of temperature could be handled differently, then recycling gas could be minimized or even eliminated. Considering this, Lurgi AG proposed the use of a multitubular fixed bed reactor. This led to a joint venture between Lurgi and Mobil, that started cooperation in 1980 [83].

Considering that reported outlet temperature of the MTG reactor was 415 °C, it was unfeasible to use water as coolant. Thus, an approach using molten salts to remove the heat of reaction was suggested. The molten salt would circulate through the shell of a multitubular MTG reactor, to remove the heat generated by the reaction. The molten salt would also circulate through an external boiler to generate high pressure steam at 100 bar before returning to the shell of the reactor [83].

This new design of process allows the elimination of the DME reactor, which is a major advantage when compared to the base case process. In addition, the conversion of methanol to gasoline is accomplished in one reactor as is the case for the fluid-bed technology [89]. Also, the recycle flowrate of light hydrocarbons is reduced, although not completely avoided [83]. On the other hand, the major disadvantage is the high cost of multitubular reactors cooled by molten salts. MacDougall [83] indicates that the cost of this multitubular reactors could be one order of magnitude higher than a conventional fixed bed reactor. This author also explains that the fluid bed MTG technology is cheaper, simpler and has the same advantages of the multitubular technology. Therefore, it is doubtful that this technology would be commercialized [83].
1.4.2 Topsoe Integrated Gasoline Synthesis (TIGAS) process

Haldor-Topsoe licenses a two-stage process for syngas conversion into gasoline (STG). The first large-scale MTG plant with TIGAS technology was recently announced [90]. A summary of the technology is presented below with probable process conditions and operation philosophy. The information described is the result of an analysis of patents [84, 81, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104] and vast amount of data available in open literature. Haldor-Topsoe claims to avoid drawbacks from a two-stage process patented by Mobil [78] and to achieve additional improvements. A simplified diagram of the STG process is shown in Figure 1-10.

The feed of the first catalytic reactor is a mixture of fresh syngas and a recycle stream, which is obtained after separation of the product of the second reactor (second stage of the process); this produces a mixture with molar ratio of CO/CO₂ in the range of 5 to 20 [93, 94, 103]. Steam is added to this mixture to achieve a final CO/H₂ molar ratio close to 1. The flow of recycle stream is determined by the recycle ratio (recycle/fresh feed) used, which varies from 1 to 8 [103]. In this reactor, three main reactions take place [91, 93, 103]:

\[ CO + 2H₂ ↔ CH₃OH \]  \hspace{1cm} (1-2)

\[ CO + H₂O ↔ CO₂ + H₂ \]  \hspace{1cm} (1-3)

\[ 2CH₃OH ↔ CH₃OCH₃ + H₂O \]  \hspace{1cm} (1-4)

This catalytic reactor could comprise three types of catalyst: (i) a catalyst to synthesize methanol from syngas; (ii) a catalyst to further convert syngas to methanol and part of the methanol to DME; and (iii) a catalyst to further convert syngas, methanol and DME, with a desired production of C₅⁺ alcohols and ethers [84]. Suitable catalysts could be MK 121 and DMK-10 from Haldor-Topsoe A/S [84].

One reason to convert syngas to oxygenates is that pressure has a small influence on the conversion, as compared to the syngas to MeOH process where pressure plays a major role [103] and equilibrium conversion is tightly constraint [84]. Thus, the conversion of syngas to oxygenates is convenient if the desired working pressure is relatively low [96, 103], and when the H₂/CO ratio is low [91].

In Figure 1-9 a comparison between syngas to MeOH and syngas to MeOH/DME is shown. The data in this figure was obtained at 250 °C and pressure range from 1 bar to

<table>
<thead>
<tr>
<th>Table 1-2: Process conditions and product specifications.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed bed</strong></td>
</tr>
<tr>
<td><strong>DME Reactor</strong></td>
</tr>
<tr>
<td>Methanol/water charge (w/w)</td>
</tr>
<tr>
<td>Dehydration reactor inlet temperature (°C)</td>
</tr>
<tr>
<td>Dehydration reactor outlet temperature (°C)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td><strong>MTG Reactor</strong></td>
</tr>
<tr>
<td>Conversion reactor inlet temperature (°C)</td>
</tr>
<tr>
<td>Conversion reactor outlet temperature (°C)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Recycle ratio (mol recycle gas/mol fresh MeOH)</td>
</tr>
<tr>
<td>WHSV (h⁻¹)</td>
</tr>
<tr>
<td>Yields (wt.%) of methanol charged</td>
</tr>
<tr>
<td>Methanol+ether</td>
</tr>
<tr>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>CO, CO₂</td>
</tr>
<tr>
<td>Coke, other</td>
</tr>
<tr>
<td>Yields (wt.%) of methanol charged</td>
</tr>
<tr>
<td><strong>Hydrocarbon product (wt.%)</strong></td>
</tr>
<tr>
<td>Light gas</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Propylene</td>
</tr>
<tr>
<td>Isobutane</td>
</tr>
<tr>
<td>n-Butane</td>
</tr>
<tr>
<td>Butenes</td>
</tr>
<tr>
<td>C₄⁺ gasoline</td>
</tr>
<tr>
<td>Yields (wt.%) of methanol charged</td>
</tr>
<tr>
<td><strong>Fuel products (wt.%)</strong></td>
</tr>
<tr>
<td>Gasoline including alkylates (RVP-62 kPa)</td>
</tr>
<tr>
<td>LPG</td>
</tr>
<tr>
<td>Fuel gas</td>
</tr>
<tr>
<td>Yields (wt.%) of methanol charged</td>
</tr>
</tbody>
</table>
100 bar using Aspen Plus V7.2, with Peng Robinson as equation of state, as recommended by [15–17]. Results were validated with data presented by Erichsen et al. [18].

The removal of the product (methanol) shifts the equilibrium and allows higher conversion of syngas. This is exactly the case when syngas is transformed into MeOH/DME. The production of DME in this process depletes the methanol concentration in the system and, in consequences, the equilibrium is shifted and more syngas is converted to oxygenates. This improvement in equilibrium conversion is shown in Figure 1-9. At any set of conditions (P and T) the equilibrium conversion on syngas to MeOH/DME is much higher than the equilibrium conversion of syngas to MeOH.

![Figure 1-9. Syngas equilibrium conversion to Methanol (A) and Methanol/DME (B). Initial molar concentration: H₂ = 51%, CO = 48% and CO₂ = 1%](image)

The first reactor may be adiabatic or isothermal [103]. In the first case it must work at the lowest inlet temperature possible, to favor thermodynamics of the system. In the second case a multitubular fixed bed reactor with boiling water as coolant is preferred, since this allows recovery of heat generated by the reaction in the form of steam [91]. The reactor would probably operate at a pressure in the range of 30 bar to 50 bar. The pressure would vary depending on the pressure at which the syngas is obtained [103].

In reference to the temperature, the reactor would probably work in the range of 240 °C to 270 °C [84, 91, 97, 103]. Joensen et al. [84] indicated that formation of higher molecular weight alcohols (C₃⁺) is favored at temperatures above 250 °C. When these higher alcohols are converted to products they release less heat, which is a desired behavior to control the temperature of the reactor and the gasoline quality. Thus, temperature management demand is decreased (reduced recycle ratio [84, 96, 105]) and gasoline yield increased. The favorable effect of C₃⁺ alcohols on the gasoline synthesis section have been reported even at low concentrations, in the range of 0.05 wt.% to 1 wt.% of the total oxygenates [84, 96, 105].

The product from the first stage comprises unconverted syngas, MeOH and DME. It may also contain C₃⁺ alcohols that were formed in the first stage or added as a separate stream [84]. This stream is first combined with a recycle stream obtained from separation of the products of the second reactor [95], then, it is fed to the second reactor. This recycle stream helps to control the temperature rise caused by the heat released during the conversion process [103]. Also, its H₂ content reduces the coking of the gasoline catalyst, prolonging its cycle time, and allows the production of more stable gasoline (by reduction of olefin content) [95, 96].

In the second stage hydrocarbons are produced. This reactor works almost at the same pressure of the first step and with a feed inlet temperature preferably in the range of 320 °C to 330 °C [91, 94, 96, 103]. A conventional MTG reactor typically works at a minimum inlet temperature of 350 °C. With the improvement caused by the C₃⁺, the minimum inlet temperature can be reduced to 320 °C to 330 °C, which signifies a reduction of approximately 20 °C in the inlet temperature [84, 105]. This reduced inlet temperature would allow the use of an isothermal boiling-water multitubular reactor, which is almost prohibitive at conventional inlet temperatures (350 °C), since the boiling water pressure would raise above 165 bar, making the reactor excessively expensive [84, 105].

One thing to keep in mind is that low temperature in the MTG reactor reduces the deactivation rate but increases the durene content, lowering the quality of the final product [91]. Higher temperatures result in a better quality of gasoline, at the expense of faster deactivation of the catalyst [91]. The stability of the catalyst used to produce the gasoline is of utmost importance for the economy of the MTG process [92]. Deactivation of the catalyst depends on several factors, such type of reactants and products, process parameters and the formulation of the catalyst itself [92]. If the catalyst is deactivated by coke deposition, then the regeneration is done by burning off the coke with air or diluted air [92].
The outlet of the second stage is cooled down, e.g. to 15 °C and fed to a G/L/L separator. The gas phase stream is split in two sub-streams, one of them is purged, and the other is recycled to the inlet of the first stage, where it is mixed with the fresh syngas [103]. One liquid phase is mainly water, and the other is a hydrocarbon stream containing the desired product [91, 93]. The raw gasoline stream from the separator contains dissolved gases, C3s and C4s. This stream is sent to distillation to purify the gasoline stream [84].

The syngas that is recycled to the first stage of the process contains olefins and CO2. Part of the CO2 is removed before it is fed back to the oxygenates synthesis reactor [99, 100]. Removal of CO2 is achieved with physical or chemical solvents [94, 98]. In more recent patents [97, 99, 100] it is indicated that recycling of a specific amount of the raw effluent of the recycle reactors, without cooling and separation, has a positive effect on the final gasoline product. This final product will have a higher average value of C atoms. Additionally, this process is more energy efficient, since part of the stream that by-passes the separator does not require cooling down and subsequent heating to be included in the recycle stream [97, 99, 100].

The water content in the recycle stream must be limited to avoid dealumination [97, 99, 100]. It can be achieved by: i) removing water to a portion of the recycle stream; or ii) water gas shift (WGS) reaction where excess CO is used to convert water into H2 and CO2 [97, 99, 100]. The WGS option has the additional advantage of creating a H2 rich stream which reduces deactivation of the catalyst for gasoline synthesis by coking. The WGS catalyst should preferably have low selectivity of olefin hydrogenation, since the saturated compounds are stable, thus reducing gasoline yield [99, 100].

1.5 Compact gas to liquid technologies

At small scale, there are also technologies for synthesis of liquid fuels are available such as the project BIOGO which makes use of microreactor technology to put us a step closer to a carbon neutral economy. The technologies described below were identified via Process Economics Program Report from SRI-Consulting and Nexant Inc. [106, 107]. There are four leading technologies in the market for small scale gas-to-liquid production, these are: Velocys® microchannel GTL process, Compact GTL process, Greylock process and the Gas-to-Gasoline STG+® technology provided by Primus Green Energy. A short description of these technologies is provided below.
Velocys® microchannel GTL process using Fischer-Tropsch synthesis technology and microreactors to perform the gas-to-liquid conversion [108, 109]. They have achieved a single pass conversion close to 80% using a cobalt-based catalyst in fixed bed microchannel structures, which enables fast heat removal. Up to 95% CO conversion can be achieved if a tail-gas recycle is included in the process configuration. A schematic representation of an element of volume of Velocys’ microchannel structure is shown in Figure 1-11.

**Figure 1-11.** Schematic representation of an element of volume of Velocys’ microchannel unit. Reproduced from [108].

In addition, Velocys has shown that this technology can be easily scaled-up, since larger assemblies are formed from identical microstructures that retain their behavior during the scale-up process. They have shown a scale-up process in 4 steps from 1 microchannel to 276 process channels, showing in all cases similar reactor performance [110]. In the meantime, reactors have reached the dimension of meters.

Compact GTL, or CGTL, is a process to convert gas to liquids [111, 112]. It comprises four (4) key sections. In the first section, the feed gas is treated before the production of syngas takes place. In the second section, the treated gas is mixed with steam and syngas which is produced in a steam methane reforming (SMR) unit working in the range of 650 °C - 800 °C. Variants of the process generate syngas via partial oxidation (POX) or autothermal reforming (ATR) technology. The selection of the process depends in several factors including the scale of the unit and techno-economic aspects. The synthesis of hydrocarbons is carried out via Fischer-Tropsch (FT) using a cobalt-based catalyst, in a compact modular system working in two stages, which has been patented [112] and claimed to have lower reduced OPEX than conventional single-stage technology and longer catalyst life. This part of the process works in the range of 220 °C - 235 °C, and 25 bar. The final product is paraffinic and ultra clean (zero sulphur content) that can be further upgraded via conventional technologies provided by third parties.

In contrast to Velocys® microchannel GTL process, which uses microchannels diameter in the range of 1 mm, Compact GTL technology uses reactors with channels in the millimeter size, so-called mini-channels, usually in the range of 3 mm - 10 mm. According to company, this allows them to have a precise temperature control over the reaction.

One of the main disadvantages of FT technology is the production of waxes that must be process in order to obtain liquid fuel with higher value. This problem has been addressed by a process similar to FT developed by Greyrock Energy, Inc. [113] where the amount of waxes is greatly reduced to a cut with carbon number up to approximately 25.

Another technology for the conversion of gas into gasoline is provided by Primus Green Energy [114, 115, 116]. In contrast to the processes described above, the Gas-to-Gasoline STG+® technology provided by Primus Green Energy produces liquid hydrocarbons via the methanol route. The process has three main steps: (i) syngas production via steam methane reforming; (ii) syngas-to-gasoline; and (iii) gas/liquid separation. The syngas to gasoline step consists of four stages in series [114, 115] where part of the syngas is first converted to methanol, then methanol is converted to DME, gasoline is produced in the third stage via conversion of oxygenates, and the fourth stage targets the conversion of durene and polymethylbenzenes to high octane paraffins. These reactions take place in a closed loop. Unreacted syngas is returned to the first stage and the gasoline formed is extracted as a liquid from a separator.

**1.6 Research scope**

Dimethyl ether is a building block for the production of chemical and liquid fuels. It is commonly used as propellant in aerosol spray-cans, as transportation fuel or as intermediate for the production of liquid fuels. In the latter case, the use of DME as feedstock has advantages on the valorization of feed streams of low \( \text{H}_2/\text{CO} \) ratio, which are formed from feedstocks such as biomass or coal.
Considering the flexibility of this chemical, the focus of this research is centered on the production of DME and its further conversion into liquid fuels. This manuscript has been organized in two parts. The first part contains introductory information (Chapter 1), a discussion of the methods and initial tests (Chapter 2) and analysis of the DME production via dehydration of methanol (Chapter 3). Then on the second part, the research is focused on the use of DME as feedstock for green gasoline production. A brief description of the chapters is provided below.

Chapter 1 contains an introduction to the research topic and provides a technical description of the chemistry and technologies involved in the conversion of oxygenates to hydrocarbons.

Then, in Chapter 2 the material and methods used in this project are introduced. Attention has been given to the description of the reaction set-up and the analytical equipment used. Then a set of initial tests and results are introduced. Although these tests do not form part of the main results, they provide the necessary foundation for the analysis of results shown in subsequent chapters.

In Chapter 3, the discussion is centered around the methanol dehydration reaction, using a commercial ZSM-5 catalyst. The selection of this catalyst is done in contrast to the conventional methanol to DME technology that uses γ-alumina as dehydration catalyst. Experimental studies and mathematical modelling were used to develop and identify a suitable kinetic model, that proved to be robust under different reaction conditions, including such with a high-water content in the feed. Kinetic parameters of the different models were calculated and evaluated against physicochemical constraints and guidelines on entropy values. The evaluation of entropies was the key factor to differentiate between rival models. The results presented in this section has been published in the Chemical Engineering Journal, vol. 347 (2018) 741-753.

The second part of this research focuses on the use of DME as intermediate for hydrocarbon synthesis. In Chapter 4 the DME to hydrocarbon (DhH) reaction is evaluated using different ZSM-5 catalysts. The effect of process parameters (temperature, pressure, feed composition and weight hourly space velocity) on conversion and selectivity are analyzed. A drawback of this reaction is that the catalyst deactivates relatively fast due to coke formation. This deactivation phenomena and its effect on DME conversion and product selectivity is addressed in Chapter 5. Some of the results presented in this section are in preparation for publication.

A more detail examination of the DhH reaction is given in Chapter 6. The evaluation is approached in the form of an intrinsic kinetic analysis. The development of the kinetic model considered main steps of the established reaction mechanism, namely the dual cycle mechanism. In this process, the kinetic parameters of the new model were estimated from regression analysis using kinetic data measured under gradientless conditions. The results presented in this section has been published in the Chemical Engineering Journal, vol. 354 (2018) 21-34.

In the final section, Conclusions and Outlook, a synopsis of the main finding of this research and insight into future prospects of research are provided.
“If we knew what it was we were doing, it would not be called research, would it?”

Albert Einstein (1879-1955)
2.1 Introduction

It is well-known that there is an increasing concern in regards to reproducibility in scientific research. In spite of its importance, there is probably some resistance from researchers to work while to account for it. How do we approach the problem of poor reproducibility? The resistance to change walks together with different allegations including the diversity and/or novelty of the work that is being done and to what extent reproducibility can be “truly measured”, after all Albert Einstein said “If we knew what it was we were doing, it would not be called research, would it?”.

Reproducibility is difficult to achieve because many factors coexist that could alter someone’s work [117], which include error/measurement ratios, heterogeneity of experimental results, complex experiments and/or experimental set-ups among others. However, there is a trend to make research more reproducible. In this context, Goodman [117] indicates that it is important to clearly describe methods, results and inferences made. Therefore, in this chapter a thorough description of the materials used is included. These include catalysts, inert materials and gases. Then, we provide a description of analytical equipment and the test rig. We also provide details on the analytical methods used and the testing protocols. At the end of the chapter, a set of initial tests and results are introduced. Although these tests do not form part of the main results, they provide the necessary foundation for the analysis of results shown in subsequent chapters.

2.2 Materials

2.2.1 Catalysts

Three samples of catalyst were used in this research:

i. Commercial sample of ZSM-5 (ammonium form) with SiO$_2$/Al$_2$O$_3$ ratio of 58, obtained in powder form from Alfa Aesar (Lot no. W04B025).

ii. Commercial sample of ZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio of 23; and

iii. ZSM-5 synthesized by the University of Warwick with SiO$_2$/Al$_2$O$_3$ = 100.

All samples were received in powder form. Before their use in activity tests, the samples were pelletized in a manual hydraulic press, for 2 min and 10 T of pressure; then, the samples were crushed in an agate mortar; and finally, the samples were sieved to the desired particle diameter size (160 µm to 250 µm).

2.2.2 Silicon Carbide

Silicon carbide (SiC) was used as inert material to physically dilute the catalyst bed. The SiC was obtained from Alfa Aesar (Lot no. 10187470) with an average particle size of 355 µm. This material was sieved, and different particle size fractions were obtained. The fraction with particle size of 160 µm to 250 µm was used for the dilution purpose during kinetic tests. The dilution facilitates isothermal operation mainly by reducing the heat release per unit volume in the bed and enhancing heat conduction in the bed [118, 119]. The amount of SiC was selected to keep a weight ratio catalyst/SiC of 1/10.

The particle size fraction larger than 250 µm was used to pack inert SiC beds on top and bottom of the catalytic bed. The top packing works a preheating zone (gas flow downwards), increases the surface area available for heat transfer and ensures that the gas flow reaches the desired temperature before entering the catalytic bed. The bottom packing allows the gas flow to exit the catalytic bed with a uniform flow pattern, without a sharp change from a packed section to an empty-tube section.

This material is chemically inert [120, 121] and has been used as foam support in the methanol dehydration [120] reaction. Inertness of the material (including quartz wool) was tested in experiments at 375 °C and 425 °C. No conversion or decomposition of DME was observed. A chemical analysis of the commercial SiC is reported elsewhere [122].

2.2.3 Gases and reagents

Reagents and auxiliary gases used during experimental tests were:

- Methanol HPLC grade from Merck (LiChrosolv®), with a purity greater than 99.8 % and less than 0.03 % water content;
- Dimethyl ether (DME 3.0) supplied by LINDE with a purity greater than 99.9 %;
- Dried compressed air;
- Pressurized nitrogen from a liquid N$_2$/evaporator system. Purity > 5.0;
- Argon used in physisorption analysis with purity >5.0;
- 2.96 % NH$_3$/He supply by LINDE. Gas used in TPD analysis;
- Synthetic air (33 % O$_2$ in He) used in TGA analysis.
2.3 The MTG Set-up

The evaluation of process parameters on reaction performance and the kinetic measurements were performed in a semi-automated set-up. This system is flexible in regards to its operation capabilities. The set-up can be operated in one pass mode up to a pressure of 6 bar abs, or in recycle mode to a pressure up to 1.5 bar abs. Process regards to its operation capabilities. The set-up can be operated in one pass mode up to measurements were performed in a semi-automated set-up. This system is flexible in chapters.

Feeding section

This section consists of Bronkhorst mass flow controllers (MFCs). They were used to regulate the flow of liquid methanol, gaseous dimethyl ether, nitrogen and auxiliary gases during catalyst pre-treatment and kinetic tests. The MFCs are shown in Figure 2-1 with tags MFC-01 to MFC-06.

During the evaluation of the methanol to DME reaction (Chapter 3), liquid methanol was fed using a Coriolis mass flow meter (Model Series: CORI-FLOW, part number: M12V14I-PAD-21-K-S). This liquid feed was sent to an evaporator and the vapor phase product was sent undiluted to the reactor or mixed with other gases such as nitrogen and/or DME. To control the gas feed, mass flow controllers using a thermal conductivity principle were used (Model Series: EL-FLOW Select, part number: F-201CV-100-TAD-21-K). In the evaluation of the DME conversion to hydrocarbons, only gaseous species were used.

Reaction section

This section is constituted by three main devices: a reactor, a split-tubular furnace and a recycle pump. In reference to the reactor, three different types were used. Quartz tubular reactors were used for kinetic measurements at atmospheric pressure (Chapter 3 and Chapter 6). Titanium tubular reactors were used during catalysis performance testing at 2 – 5.5 bar (Chapter 4). Titanium was used instead of stainless steel to avoid secondary reactions on the reactor wall during experiments at high temperature. The dimensions of the tubular reactors are shown in Table 2-1. Finally, the third type of reactor was a stainless steel microstructured reactor. A microstructure reactor of this type was built by laser welding two plates containing 14 microchannels of 25 mm length, 500 μm width and 400 μm depth (further details in [123]). Before fixing the two plates together, the microchannels were wash-coated with the catalyst under investigation. During this process, approximately 10 mg of catalyst were incorporated. The complete preparation of the reactor, including catalyst incorporation, was done by Fraunhofer ICT-IMM Mainz.

Table 2-1. Tubular reactor characteristics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Length (mm)</th>
<th>Outside diameter (mm)</th>
<th>Inside diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>390</td>
<td>7.8</td>
<td>13.1</td>
</tr>
<tr>
<td>Titanium</td>
<td>390</td>
<td>9.53</td>
<td>7.75</td>
</tr>
</tbody>
</table>

The tubular reactors were installed with a thermowell (1 mm OD) concentric to the reactor. The thermowells were coated by Silcoat® with a silicon layer (SilcoNert®) to passivate their surface and avoid decomposition of oxygenates while kinetic runs took place.

During catalytic tests, the catalyst was packed in the annular space between the thermowell and the reactor. In kinetic measurements the catalyst sample was diluted with SiC, in a weight ratio catalyst:SiC of 1:10. The temperature of the catalytic bed was monitored by three K-type thermocouples placed within the thermowell. The location of each thermocouple (within the thermowell) was adjusted to measure the temperature in the top, middle and bottom part of the catalytic bed. These are indicated in Figure 2-1 by instruments TI-33, TI-34 and TI-35. The temperature difference between any two thermocouples was kept below 2 °C during the kinetic experiments. Heating of the reactor was done by means of a split-tubular furnace with a maximum temperature of 900 °C and a power output of 1100 W (series 3210, from Applied Test Systems).

The set-up also contains a diaphragm pump which can be used to recycle a major part of the reactor outlet stream to its inlet. This pump was supplied by KNF Verder, model N 012 ST.26E. The pump had a variable speed motor that indirectly controlled the recycle flow rate. The recycle flow could be varied from 1 L∙min⁻¹ to 10 L∙min⁻¹. Kinetic measurements were done with a recycle flow of 5 L∙min⁻¹. Also, this pump could work at 180 °C, which was necessary to avoid condensation of water and other species in the recycle stream.
To regulate the pressure during single pass operation at elevated pressure, a high-
temperature diaphragm back pressure regulator (BPR) was used. The BPR model was
supplied by Pressure Control Solutions (model LF1SN12-NSMP5 00T30054KKB). During
all tests, it was heated to 180 °C and kept at this temperature to avoid condensation of
heavy compounds. The desired pressure was set with PR-22, as depicted in Figure 2-1.
After an experimental test, the pressure in the dome of the BPR was released via the
three-way valve V-100.

In addition, all lines and valves conducting the flow of gas were also heated by means of
heating cords, thus avoiding undesired condensation. The heated lines were divided in
divided into four sections to enhance the robustness of the system and increase flexibility. These are
shown in Figure 2-1 with dashed-lines of colors red, green, blue and purple. The red and
green lines were kept at 180 °C to avoid condensation of water and/or hydrocarbons. The
blue-dashed line was kept at 110 °C. This section only transported DME and/or methanol.
Thus, a higher temperature was not required. The purple-dashed line heated the line that
was connected directly to the reactor. Therefore, its temperature varied in accordance
with the experimental settings. It is worth noting that all instruments, valves and
equipment located in the recycle loop were carefully selected to allow operation at high
temperature and avoid condensation of species during experimental runs.

A by-pass was included to evaluate the feed before carrying out the reaction. This means
that the catalyst could be pretreated and stabilized to the correct reaction conditions
while the feed was fed to the sample loops of the GC via a by-pass. That allowed
continuous operation and feed preparation.

In addition, the signals from the safety sensors were incorporated in an inter-lock
sequence. The inter-lock would shut down the system in case of dangerous situation, such
as high temperature, high pressure, high DME concentration inside the set-up, failure in
the ventilation of the system or if the Emergency push-down button would be pressed.

Analytical section

The product stream of the Reaction section was fed to the Analysis section via a heated
line to keep all compounds in the gas phase (see Figure 2-1). In the analysis section, a
heated multiposition valve system captured part of the product stream and injected this
sample into the gas chromatograph (GC) by means of an on-line injection valve. In
addition, a total of 15 product samples could be collected (in gas phase) at any moment.
during the catalyst testing sequence. Each sample loops had a volume of 250 µL and the samples trapped there could be injected in the GC during off-line operation.

The GC (model 7890B - Agilent Technologies) and the heated valve system were supplied by Technical Knowledge Solutions GmbH (Teckso). A schematic representation is shown in Figure 2-2. The GC was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), a capillary 50-m PONA column and a 30-m Plot-Q column.

![Figure 2-2. Gas chromatograph configuration.](image1)

Finally, the set-up also had a thermal conductivity detector (TCD) and power control unit for binary gas analysis. The assembly, model 24-527-077-4, was provided by Gow-Mac Instruments CO. This detector could be used to monitor the pretreatment or regeneration process of the catalyst. This instrument is defined with the tag CI-71 in Figure 2-1.

![Figure 2-3. Schematic representation of a pycnometer.](image2)

### 2.4 Experimental procedures

#### 2.4.1 Catalyst Characterization

A short description of the analytical techniques used for catalyst characterization is provided below. In addition, characteristics of all equipment are summarized in Table 2-2.

**Absolute solid density**

The catalyst absolute density was only measured for the commercial ZSM-5 catalysts with SiO₂/Al₂O₃ ratio of 58. This catalyst was used in kinetic measurements and determination of its density is important to accurately estimate the effect of heat and mass transport phenomena on the reaction rate observed.

The absolute density was measured by helium pycnometry, using the He Pycnometer described in Table 2-2. In a typical test, 100 mg of catalyst were used for the analysis. A schematic representation of the equipment is shown in Figure 2-3. In the first stage of the analysis, the sample is prepared by filling and evacuating the sample chamber with helium. This step removes undesired gases form the system. Then, in the second stage of the analysis, the sample chamber is filled with He and the pressure is recorded. Then, the valve connecting both chambers is opened. Helium expands into the expansion chamber and the pressure is recorded. Then, the outlet valve is opened and the system is evacuated. This cycle is repeated until the deviation of three consecutive measurements is less than 0.1 %.
Finally, the absolute density of the sample ($\rho_s$) is calculated from equation (2-1) [124], where $W_s$ is the sample weight and $V_s$ is the sample volume defined by equation (2-2). The latter equation is defined from calibration measurements in the pycnometer with $V_c$, $V_x$, $P_6$, and $P_5$ representing the volume of the empty sample chamber, the volume of the expansion chamber, the initial pressure in the sample chamber during analysis, and the final pressure in the system when He has been released into the expansion chamber, respectively.

$$ \rho_s = \frac{W_s}{V_s} \quad (2-1) $$

$$ V_s = \frac{V_c - \frac{V_x}{1 - \frac{P_6}{P_5}}}{(2-2)} $$

**Bulk density**

The bulk density was measured via mercury intrusion porosimetry. The sample was placed in a penetrometer, then this sample holder was filled with mercury. This is schematically represented in Figure 2-4. The bulk density ($\rho_b$) can then be calculated with equation (2-3), knowing the weight of the sample ($W_b$), the volume of the empty penetrometer ($V_p$), and the volume of mercury required to fill the sample tube.

$$ \rho_b = \frac{W_b}{V_p - V_{HG}} \quad (2-3) $$

**Figure 2-4.** Schematic representation of a penetrometer containing a porous sample and filled with mercury.

### Table 2-2. Summary of equipment used during research project.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Supplier</th>
<th>Model</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bruker AXS diffractometer</td>
<td>Bruker</td>
<td>D2 PHASER</td>
<td>Determine diffraction pattern of catalyst sample</td>
</tr>
<tr>
<td>Analytical balance</td>
<td>Mettler Toledo</td>
<td>XS 150 (dual range)</td>
<td>Weigh catalyst sample for kinetic measurements</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max = 41 g / 120 g d = 0.01 mg / 0.1 mg</td>
</tr>
<tr>
<td>Analytical balance</td>
<td>Sartorius</td>
<td>BP 210S</td>
<td>Weigh catalyst samples for characterization tests</td>
</tr>
<tr>
<td>Quadrupole mass spectrometer (QMS)</td>
<td>ESS</td>
<td>QMS Genesys 422</td>
<td>Characterize the fluid dynamic behavior of the recycle reactor</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>FEI</td>
<td>Quanta™ 3D FEG</td>
<td>Electron beam resolution. 1.2 nm at 30 kV (SE). Accelerating voltage: 200 V – 30 kV</td>
</tr>
<tr>
<td>Chemisorption analyzer</td>
<td>Micromeritics</td>
<td>AutoChem II</td>
<td>NH3-TPD tests</td>
</tr>
<tr>
<td>Injection valve</td>
<td>Inacom Instruments</td>
<td>V-541</td>
<td>RTD measurements</td>
</tr>
<tr>
<td>Helium pycnometer</td>
<td>Quantachrome</td>
<td>Ultrapyc 1200e</td>
<td>Determine density of catalyst particles</td>
</tr>
<tr>
<td>Surface area analyzer</td>
<td>Micromeritics</td>
<td>ASAP 2020</td>
<td>Argon used during measurements</td>
</tr>
<tr>
<td>Mercury intrusion analyzer</td>
<td>Micromeritics</td>
<td>Autopore IV 9505 (228 MPa)</td>
<td>Measurement of pore size (&gt; 5 nm) and macro pore volume</td>
</tr>
<tr>
<td>Thermogravimetric analysis</td>
<td>Mettler Toledo</td>
<td>TGA/DSC 1 STARRe System</td>
<td>Used to quantify coke in spent catalyst samples</td>
</tr>
</tbody>
</table>
Surface area, pore size and volume

All catalysts were characterized by physical adsorption of argon (Ar) in an ASAP 2020, from Micromeritics (see Table 2-2). In a typical test, 50 mg of catalyst were used. The catalyst is placed in a U-shaped tube, where it was dried and physisorbed species were removed from its surface by outgassing at high vacuum.

Once the sample was dried and free from surface species, a U-shaped tube is submerged in liquid argon at -186 °C, until stabilization. The catalyst is kept at this temperature during the whole experiment. Then known amounts of Ar was admitted into the chamber containing the catalyst. That create an increase in pressure that followed by a decreased, caused by Ar adsorption on the surface of the catalyst. Once the pressure has reached equilibrium, its value is recorded and a new amount of Ar is send to the catalyst chamber, repeating the procedure just described. This is repeated until the pressure inside the chamber equals 1 bar. At this point the isothermal adsorption curve is completed and estimation of surface area, pore size and volume are carried out by the equipment. The results of these physicochemical tests are included in chapters 3 and 4.

X-ray diffraction spectroscopy

The XRD pattern from the catalyst sample was measured with a Bruker AXS diffractometer (D2 PHASER A26-X1-A2B0D3A) using a Cu anode ($\lambda_{XRD} = 1.54184$ nm). The 2θ analysis was performed in the range of 5° 2θ to 55° 2θ. The scanning speed and step width were set to 2°∙min$^{-1}$ and 0.032°, respectively.

Temperature programmed desorption of ammonia (NH3-TPD)

Ammonia (NH$_3$) TPD profiles of the ZSM-5 catalysts were measured in a chemisorption analyzer from Micromeritics. In a typical test, 50 mg to 200 mg of the sample were loaded in a test tube. The sample was calcined at 550 °C for 2, under synthetic air flow (the temperature program is described in 2.4.2). After the oxidation pretreatment, the temperature of the sample was lowered to a specific adsorption temperature ($T_{ads}$) under helium flow. Then, saturation of the sample with NH$_3$ was carried out at this temperature, followed by flushing with He for at least 1 h, or until the signal of the thermal conductivity detector (TCD) stabilized. The adsorption temperatures were 100 °C and 230 °C. After the saturation with NH$_3$, the sample was flushed in He flow for 1h. Then, the sample temperature was lowered to 50 °C. This temperature was kept for 30 min followed by TCD sensor stabilization. After stabilization, the TPD was started and evolution of desorbed ammonia was monitored via the TCD. The TPD analysis was performed at heating rates of 10 °C·min$^{-1}$, 15 °C·min$^{-1}$, and 20 °C·min$^{-1}$.

Electron microscopy

Scanning electron microscopy (SEM) (Quanta™ 3D FEG, from FEI) was used to determine the average crystal size. For this purpose, the open source software ImageJ 1.51k, developed by the National Institutes of Health (USA), was used.

Thermogravimetric analysis (TGA)

In a typical test, 25 mg of sample were placed in ceramic crucible. The TGA analysis was done by heating the sample from 50 °C to 750 °C under air flow of 50 cm$^3$·min$^{-1}$. The weight loss and the heat flow were recorded.

2.4.2 Catalyst Oxidizing Treatment – Regeneration

Before and after any activity test, an oxidizing pretreatment (regeneration) was carried out. The catalyst was calcined under a flow of synthetic air (30 cm$^3$·min$^{-1}$). The calcination took place with a temperature program at three levels: 300 °C, 400 °C and 550 °C. From one level to the other, the temperature was increased at a rate of 5 °C·min$^{-1}$. Once each level was reached, it was kept constant for 2 h.

The oxidizing pretreatment accomplished two purposes: (i) when a fresh catalyst was used, then the ammonium form of the catalyst (NH$_4$-ZSM-5) was transformed into the proton form (H-ZSM-5); and (ii) for a catalyst loading used in several experiments, the oxidizing temperature treatment removed adsorbed water and any coke deposits that could have formed under reaction conditions. The step-wise temperature increase was selected to control the amount of water (steam) formed during the regeneration process and avoid permanent deactivation of the zeolite during the treatment [125, 126]. These particular temperatures (300 °C, 400 °C and 550 °C) were selected in accordance to observations made by Sorensen [127]. This author performed a series of temperature programmed oxidation (TPO) analysis on coked ZSM-5 samples used in the methanol-to-gasoline reaction. The author observed that combustion of the carbonaceous deposits starts at approximately 300 °C, showing a first peak just below 400 °C and a maximum in the vicinity of 550 °C. Different combustion stages are associated with different types of coke having various H/C ratios. These observations are also in accordance with Bibby et. al [128]. In addition, it has been observed that slight amount of coke might remain after an oxidizing treatment at 550 °C but this coke has little to no effect on the catalyst
performance [126, 129]; therefore, the value of 550 °C has been set as the limit temperature for regeneration.

### 2.4.3 Methanol to DME – Kinetic tests

In a typical experiment, 25 mg to 50 mg of catalyst with a particle diameter in the range of 160 µm to 250 µm were used. The catalyst was mixed with SiC of the same size in a weight ratio SiC:catalyst of 10:1. The dilution facilitates isothermal operation mainly by reducing the heat release per unit volume in the bed and enhancing heat conduction in the bed [118, 119]. The catalytic bed was placed in a quartz tubular reactor, fixed between two quartz wool packings. At the bottom and on top of the catalytic bed, two additional layers of pure SiC were packed. The SiC was used to dilute the bed and contributed to dissipate the heat released by the reaction, leading to a quasi-isothermal behavior of the catalytic bed. These pure SiC layers helped to preheat the feed (by increasing the surface area), before it entered the catalyst bed, and to maintain a uniform flow profile upstream and downstream of the catalyst bed.

The fixed bed reactor was then connected to the set-up. The system was flushed with nitrogen (N2) at a flow rate of 30 Ncm³·min⁻¹. Then, the N2 flow was switched to compressed air (CA) and the oxidation treatment described in section 2.4.2 was performed. Then, the catalyst was cooled down to reaction temperature under N2 flow (30 cm³·min⁻¹). This condition was kept for at least 30 min before a kinetic test was started.

In a typical kinetic test, pure MeOH or a mixture of 70 wt. % MeOH / 30 wt. % H2O was fed via a Bronkhorst Cori-Flow meter. The liquid feed was evaporated in a microstructured evaporator heated by electricity. Then, the vapor-phase MeOH feed could be further mixed with N2 to lower the partial pressure of the reactant and evaluate its effect during the kinetic testing. A summary of experimental conditions is presented in Table 2-3. Finally, the outlet of the recycle reactor was sent to an on-line GC in which methanol, dimethyl ether and nitrogen were quantified.

During tests of the methanol dehydration to DME, the methanol and DME were analyzed in the FID, while N2 was measured in the TCD. In a typical experiment, process parameters (temperature, space velocity, and partial pressures of methanol in the feed) were set at the desired values; then, the product stream was analyzed in at least seven (7) consecutive GC injections. Each GC analysis took approximately 5 min plus 1 min for stabilization of the GC before the following analysis; therefore, the total analysis time for a particular experimental setting was approximately 40 min.

<table>
<thead>
<tr>
<th>Process variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure (bar)</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>140 – 190</td>
</tr>
<tr>
<td>WHSV (h⁻¹)</td>
<td>15 – 100</td>
</tr>
<tr>
<td>Water content (wt.%)</td>
<td>0 – 30</td>
</tr>
<tr>
<td>Partial pressure of MeOH in feed</td>
<td>0.33 – 1</td>
</tr>
</tbody>
</table>

### 2.4.4 DME to Hydrocarbons – Evaluation of process parameters

In a typical experiment, 100 mg to 250 mg of catalyst were used. The catalyst was placed in a quartz or titanium tubular reactor, fixed between two quartz wool packings. At the bottom and on top of the catalytic bed, two layers of pure SiC were packed. These pure SiC layers helped to preheat the feed (by increasing the surface area), before it entered the catalyst bed, and to maintain a uniform flow profile upstream and downstream of the catalytic bed.

The fixed bed reactor was then connected to the set-up. The system was flushed with nitrogen (N2) at a flow rate of 30 Ncm³·min⁻¹. Then, the N2 flow was switched to compressed air (CA) and the oxidation treatment described in section 2.4.2 was performed. Then, the catalyst was cooled down to reaction temperature under N2 flow (30 Ncm³·min⁻¹). This condition was kept for at least 30 min before the reaction test was started.

Pure DME or a mixture of 16 % DME in N2 was fed via a Bronkhorst mass flow controller. A summary of experimental conditions is presented in Table 2-4. The product stream at the outlet of the reactor was sent to an on-line GC in which methanol, dimethyl ether and hydrocarbons were quantified. See section 2.3 for details.

The process parameters were evaluated in two types of tests. In the first type, long test runs (24 h) were performed in single pass mode, with different catalysts, and using pure DME as feed. The aim was to understand the behavior under quasi-adiabatic conditions...
that would allow some inferences in regards to product selectivity and stability of the catalysts used. In these tests, only online injections of product samples were performed.

**Table 2-4. Process variables used in DTH conversion.**

<table>
<thead>
<tr>
<th>Process variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure (bar)</td>
<td>1 – 5.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>325 – 375</td>
</tr>
<tr>
<td>WHSV (h⁻¹)</td>
<td>25 – 125</td>
</tr>
<tr>
<td>Molar fraction of DME in feed</td>
<td>0.16 – 1</td>
</tr>
</tbody>
</table>

In the second type of experiment, short runs of 3 h were made. These tests allowed better understanding of the effect of pressure on the behavior of the system. In these experiments, the feed was 16 % DME in N₂. The product stream was analyzed via online injection in the GC. Also, product samples were collected during the test. A total of 15 samples were collected in this period and analyzed in off-line mode.

In addition, a series of tests were carried out under recycle mode. The recycle operation showed the same fluid dynamic behavior as that of continuous stirred tank reactor (CSTR); in consequence, the design equation of an ideal CSTR can be used in the interpretation of results. This is shown in equation (2-4), where \( W_{\text{cat}} \), \( F_{\text{AD}} \), \( x_A \), and \( -r_A \) represent weight of catalyst, inlet molar flow rate of reactant, oxygenates conversion and rate of oxygenates’ conversion, respectively.

\[
\frac{W_{\text{cat}}}{F_{\text{AD}}} = \frac{x_A}{-r_A}
\]  

Equation (2-4) can solve for \( -r_A \), and written as function of WHSV to yield equation (2-5). The units used in this equation follow the International System of Units (SI), and the term (1 h / 3600 s) has been added for dimensional consistency of the equation.

\[
-r_A = x_A \cdot \frac{\text{WHSV}}{M_W} \cdot \left( \frac{1 \text{ h}}{3600 \text{ s}} \right)
\]

The weight hourly space velocity is a measure of how fast a stream is processed. The larger the value the shorter the time a fluid of element spends in the reactor. For the conversion of oxygenates to hydrocarbons, this translates into a set of conversions and selectivities that depend on contact time or 1/WHSV.

In all GC measurements, DME and C₄⁺ hydrocarbons (except isobutane) were analyzed in the FID, while N₂, methanol, C₂-C₃ hydrocarbons and isobutane were measured in the TCD. The GC run took 70 min, and another 10 min were required for the oven too cool down from 210 °C (final GC oven temperature) to 30 °C (initial GC oven temperature); therefore, the total time from one injection to the next was 80 min.

### 2.4.5 DME to Hydrocarbon – Kinetic tests

In a typical experiment, 10 to 50 mg of catalyst were used. It was diluted with SiC, packed in the reactor, and treated under oxidizing conditions as described in 2.4.3. Kinetic measurements were carried out at atmospheric pressure and using pure dimethyl ether as feed. In each test, 18 samples were analyzed, and the composition of 30 different species or groups of compounds was recorded.

A full factorial design was used to define the experimental grid. Two factors (Temperature and WHSV) were evaluated at five levels each. Details are provided in Table 2-5. The limits of the temperature and WHSV were defined after an initial exploratory set of experiments. Reactions at temperatures higher 375 °C and WHSV lower than 25 h⁻¹ led to almost full conversion and mass transfer limited conditions. The product stream was analyzed in a GC that operated both in on-line and off-line mode. Details of the analytical method were given in the previous section.

**Table 2-5. Factors and levels used in the experimental program.**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Temperature (°C)</th>
<th>Weight hourly space velocity (WHSV) (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levels</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>337</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>362</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>375</td>
<td>125</td>
</tr>
</tbody>
</table>
2.5 Initial tests

2.5.1 Recycle reactor – evaluation of fluid dynamic behavior

The fluid dynamic behavior of the recycle system was evaluated by measuring the residence time distribution (RTD) via the pulse tracer experiments [130, 131]. In a typical experiment, nitrogen (N₂) was used as carrier gas and Helium (He) as tracer. The tracer was manually injected in the inlet of the recycle reactor (RR) by means of an injection valve (Inacom instruments, model V-541). The volume of tracer injected was $6.27 \times 10^{-8}$ m³ ($62.7 \, \mu$L). This accounted for the volume of the injection loop ($50.0 \, \mu$L) and the internal volume of the valve ($12.7 \, \mu$L). The experimental conditions are summarized in Table 2-6.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
<td>N₂</td>
</tr>
<tr>
<td>Tracer compound</td>
<td>He</td>
</tr>
<tr>
<td>N₂ flow (STP m³/s)</td>
<td>$1.67 \times 10^{-6}$ (100 STP cm³·min⁻¹)</td>
</tr>
<tr>
<td>Volume of tracer injected [V_inj] (m³)</td>
<td>$6.27 \times 10^{-8}$ (62.7 µL)</td>
</tr>
<tr>
<td>Volume of the recycle loop [V] (m³)</td>
<td>$8.11 \times 10^{-5}$ (81.1 cm³)</td>
</tr>
</tbody>
</table>

Table 2-6. Experimental conditions during RTD measurements.

The concentration of He in the outlet of the RR was measured with a quadrupole mass spectrometer (QMS) from ESS. Then, the He concentration was used to determine the experimental RTD function, which was compared to a perfect continuous stirred tank reactor (CSTR) fed with an imperfect pulse of tracer, in contrast to the Dirac delta function used under ideal conditions [131]. The result is shown in Figure 2-5.

In this figure, the experimental data are represented by black circles with 95 % confidence interval (CI) bars. The continuous line denotes the model of an ideal CSTR fed with an imperfect pulse of tracer. The excellent agreement between the experimental data and the model confirms that the recycle reactor behaves as a well-mixed CSTR reactor. Thus, the design equation of a CSTR can be used in the interpretation of conversion and rate data obtained from this system.

2.5.2 Fixed bed recycle reactor vs Microstructure reactor

The performance of the fixed bed recycle reactor (FBRR) and a microstructure reactor (MSR) was compared under similar reaction conditions (T, P, WHSV and feed composition) and using the commercial ZSM-5 catalyst with SiO₂/Al₂O₃ ratio of 58 described in section 2.2.1. Some characteristics of both reactors are given in Table 2-7.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Fixed bed</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation mode</td>
<td>Recycle</td>
<td>Single pass</td>
</tr>
<tr>
<td>Bed or channel diameter (mm)</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>Bed or channel length (cm)</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>Catalyst particle size</td>
<td>160-250 µm</td>
<td>NA</td>
</tr>
<tr>
<td>Catalyst thickness</td>
<td>NA</td>
<td>ca. 10 µm</td>
</tr>
<tr>
<td>Number of channels</td>
<td>NA</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 2-7. FBRR and MSR characteristics.

For clarity, only one out of ten data points has been plotted in this figure.
Methanol conversion ($x_{\text{MeOH}}$) was used as a measure of performance. It is defined by equation (2-6), where $F_{\text{MeOH},0}$ and $F_{\text{MeOH}}$ represent the inlet and outlet molar flow rates of methanol. In addition, the conversion was limited to values lower than 15 % to decouple kinetics and reactor type, i.e. the material balance in an element of volume of a MSR is similar to that of a plug-flow reactor (PFR), but the same analysis in the recycle reactor render the CSTR design equation. A fair comparison of performance requires similar operating conditions and similar working regime.

$$x_{\text{MeOH}} = \frac{F_{\text{MeOH}} - F_{\text{MeOH},0}}{F_{\text{MeOH},0}} \quad (2-6)$$

Two performance comparisons were carried out. Experimental details are shown in Table 2-8. The first comparison was carried out with pure methanol in the feed. The results are shown in Figure 2-6. Graph (A) shows results when the WHSV was 70 h⁻¹. As expected, the conversion of methanol increases with the temperature, and this can be related to the reaction rate dependence on $T$ according to the Arrhenius equation. No significant difference is observed in any of the experimental settings. However, the mean of conversions shifts more from one another as the temperature increases. In fact, this is expected. As the conversion increases, the performance of the reactor is affected by the kinetics and the reactor configuration itself. Also, an increase in temperature could lead to mass transfer limited conditions, where the MSR performs better than a fixed bed recycle reactor.

Two performance comparisons were carried out. Experimental details are shown in Table 2-8. The first comparison was carried out with pure methanol in the feed. The results are shown in Figure 2-6. Graph (A) shows results when the WHSV was 70 h⁻¹. As expected, the conversion of methanol increases with the temperature, and this can be related to the reaction rate dependence on $T$ according to the Arrhenius equation. No significant difference is observed in any of the experimental settings. However, the mean of conversions shifts more from one another as the temperature increases. In fact, this is expected. As the conversion increases, the performance of the reactor is affected by the kinetics and the reactor configuration itself. Also, an increase in temperature could lead to mass transfer limited conditions, where the MSR performs better than a fixed bed recycle reactor.

Table 2-8. MSR vs RR. Experimental details.

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Comparison 1</th>
<th>Comparison 2</th>
<th>Comparison 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>140 – 190</td>
<td>140 – 190</td>
<td>140 – 190</td>
</tr>
<tr>
<td>WHSV</td>
<td>70</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>Feed (wt.%%)</td>
<td>100 % MeOH</td>
<td>100 % MeOH</td>
<td>70 % MeOH / 30 % H₂O</td>
</tr>
</tbody>
</table>

Graph (B) shows results when the WHSV was 100 h⁻¹. A similar behavior to Figure 2-6 (B) is observed, with higher conversions as temperature increases. Again, the conversions observed for any temperature for both the MSR and FBRR are not significantly different. Comparing data from Figure 2-6 (A) with Figure 2-6 (B) at the same temperature, it is possible to observe a decrease in the conversion with an increase in the WHSV. An increase in WHSV is translated into a shorter residence time, and in consequence the overall conversion observed is reduced.

In Figure 2-7 results are shown for the reactor performance using a feed of 70 wt.% MeOH / 30 wt.% H₂O. Once again, a typical increase in conversion with higher temperatures is observed. Water does not affect the measurements between FBRR and MSR. Conversion results in both reactors are not significantly different. However, there is a clear difference between pure MeOH feed (Figure 2-6 (A)) and mixed feed (Figure 2-7). This is clearly observed as a reduction of the conversion when the content of water in the feed is 30 %, and this is independent of the reactor. It will be shown in Chapter 3 that this effect is caused by water inhibition (kinetic effect), and not by thermodynamics.

It is worth noting that both the FBRR and the MSR were operated under isothermal conditions. In the case of the FBRR, low conversion per pass is achieved and the heat released by the reaction is quickly transported out of the system by convection. A recycle flow rate of ca 5 L·min⁻¹ were used during the recycle operation and temperature was monitored in the top, middle and bottom of the catalytic bed as explained in Section 2.3. The MSR also worked under isothermal conditions. In this case, the heat is removed by conduction through the reactor wall. That is actually one of the main advantages of the MSR used in this research. In fact, the heat transfer capabilities of a MSR could be better used if the methanol conversion reaction is carried out to completion (for example, in an
industrial setting). This reaction is exothermic, of positive order with respect to reactants (see Chapter 3) and limited by equilibrium, meaning that a plug-flow isothermal operation is desired to minimize footprint and maximize conversion per pass.

Figure 2-7. Performance comparison of microstructure reactor vs fixed bed recycle reactor using a mixed feed of 30 % wt. H₂O / 70 % wt., and WHSV = 70 h⁻¹.

On the other hand, there are also drawbacks or limitations in the use of microreactors. First, at high flow rates the flow in each channel of the MSR might deviate from one another. This will depend on the flow rate and the design of the MSR, e.g. if a flow distributor is available in the inlet of the reactor. In addition, selection of the reactor material plays an important role (this applies for any reactor). This was the case in this research project, in which the initial idea was to use stainless steel MSR to perform the kinetic evaluation of the dimethyl ether to gasoline (DtG) reaction. The microreactors were supplied by one of our partners (Fraunhofer ICT-IMM). It turned out that methanol decomposes on stainless steel at temperatures above 250 °C, as we saw from experimental measurements.

2.5.3 Stability tests during methanol conversion to DME

Long test run

In the stability test under reaction conditions, the activity of the catalyst was measured for a period of 20 h, to detect signs of catalyst deactivation. Conversion of methanol (\( \chi_{\text{steady}} \)) was used as an indicator of the catalyst performance. The test was done at 190 °C, feeding pure methanol at a weight hourly space velocity (WHSV) of 20 h⁻¹, and the reactor configuration was single pass. This condition was selected to operate the system at a conversion level of around 30 %, far from equilibrium, to avoid biased results that might be obtained at high conversions.

The stability of the catalyst under reaction conditions is shown in Figure 2-8 as a plot of methanol conversion vs time on stream (TOS). The activity of the catalyst remains constant, in accordance to results reported by Alharbi et al. [18]. Some variability in the conversion was observed but this was caused by fluctuations in the MeOH feed system. This result assures the steadiness of catalyst activity during the kinetic test measurements, which lasted at most 8 h.

Figure 2-8. Methanol conversion during a test run of 20 h.

The upper (UL) and lower (LL) natural limits were calculated from the moving range, according to the expression (2-7) and (2-8), where \( \overline{MR} \) is the mean of the difference between data point \( i \) and \( i - 1 \) [132].

\[
\text{UL} = \bar{x} + 2.66 \cdot \overline{MR} \tag{2-8}
\]

\[
\text{LL} = \bar{x} - 2.66 \cdot \overline{MR} \tag{2-7}
\]

Reaction / regeneration cycles

In particular experiments the same catalyst loading was used. However, in-between experiments the oxidizing pretreatment, named hereafter regeneration, was carried out. Oxidizing treatments at high temperature can cause permanent deactivation on zeolite
catalysts, thus a series of tests working on reaction/regeneration cycles was carried out. After each cycle, the activity of the catalyst was measured and compared to the activity of the fresh catalyst.

In some experiments, the same load of catalyst was used in a series of reaction-regeneration cycles. The regeneration consisted of a temperature treatment as described in section 3.2.5. To determine if a significant degree of irreversible deactivation was taking place due to reaction/regeneration cycles, the activity of a load of ZSM-5 was monitored over 4 cycles. The results indicate that there is not a significant difference between activity of the catalyst in the 1st and 4th cycle. The details of average conversion and 95% confidence intervals (CI) for the 1st and 4th cycles are shown in Table 2-9.

Thus, it is concluded that the same catalyst sample can be used reliably at least during four (4) regeneration cycles.

<table>
<thead>
<tr>
<th>Regeneration Cycle</th>
<th>1st (fresh sample)</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>0.081</td>
<td>0.079</td>
</tr>
<tr>
<td>LL 95% CI</td>
<td>0.079</td>
<td>0.078</td>
</tr>
<tr>
<td>UL 95% CI</td>
<td>0.082</td>
<td>0.080</td>
</tr>
</tbody>
</table>

Evaluation of recycle flow rate

To assess the effect of the recycle flow on catalyst performance a series of tests were carried out at 140 °C, WHSV of 100 h⁻¹, feeding methanol at a flow rate of 2.5 g h⁻¹, and a recycle flow rate from 2 L min⁻¹ to 5 L min⁻¹.

Experimental results are shown in Figure 2-9 as methanol conversion with 95% CI bars versus pump output (%). The pump output is varied from 20 % to 50 %, which corresponds to gas flow rates of 2 L min⁻¹ to 5 L min⁻¹. After statistical analysis of the results, no significant difference in methanol conversion was observed with change in recycle gas flow rate. In these experiments, the WHSV is constant but the superficial gas fluid velocity changes, which does have an effect on the mass transfer coefficient \( k_L \) [133, 134]. Since the conversion had little to no variation, it is concluded that external mass transfer limitations are absent, in accordance to [134, 135]. Mass transfer limitations were also assessed by testing criteria shown in the next section.

2.6 Summary and Conclusions

In this chapter, the experimental set-up and the testing protocols have been described. Considering the nature of the two reactions studied (methanol to DME, and DME to hydrocarbons), and experimental set-up was designed and built. The design of the system allowed flexible operation under a wide range of experimental conditions.

In spite of the fast deactivation process observed during the conversion of oxygenates to hydrocarbons, which is uneven and has been compared to a “burning cigar” [136], we have shown that it is possible to design an equipment that can perform reaction tests under homogenous conditions. The system was designed to operate as a continuous stirred tank reactor (CSTR), and its fluid dynamic behavior was confirmed by measurements of residence time distribution during pulse-tracer experiments.

The overall design challenge was even more interesting when the fast deactivation system was combined with typical slow analytical response (a detail analysis of hydrocarbons via GC). We explained in this chapter that the analysis of one (1) sample of product could take up 80 min (including cooling of GC oven). This slow process was compensated by addition of gas sampling loops that work synchronized with the reaction, taking samples while the catalyst deactivated and performing the GC analysis in off-line mode. This allowed close monitoring of the product stream in the initial instants of the reaction.
It was also shown for the methanol dehydration reaction to DME, that a microstructure reactor performed similar to the recycle fixed bed reactor. The inspection of results seems to indicate that the MSR performs better. In principle it is true, although there was no statistical difference between results of the MSR and the recycle fixed bed reactor. Also, under the same conditions for a positive order reaction, a CSTR (in this case the recycle reactor) shows less conversion than a PFR (equivalent to the MSR). This is a plausible reason for the constant bias observed in the experimental measurements.

The good performance of the MSR draws us to conclude that the high heat transfer capacities of MSRs make them suitable for kinetics testing of highly exothermic reactions. It was also shown for the methanol dehydration reaction, that the catalyst used for these test (ZSM5-SAR58) was stable under the operating conditions and showed no signs of deactivation after 20 h of analysis. In addition, this catalyst is resistant to heat treatment under oxidizing conditions and this was demonstrated by testing protocols with reaction-regeneration cycles.
An experiment is a question which science poses to Nature, and a measurement is the recording of Nature’s answer

Max Planck (1858 - 1947)

CHAPTER 3

Methanol dehydration to DME over a ZSM-5 catalyst
3.1 Introduction

Dimethyl ether (DME) is an environmentally-friendly, multimarket chemical that can be easily liquefied and used as an intermediate or end product. Its applications range from aerosol propellant to intermediate in olefins or liquid fuel synthesis [16, 137]. Additionally, it has a notable potential as clean fuel in power generation or in automotive applications [137], with commercial examples already available [137]. In 2011, DME demand was close to 3 million metric tons (T) [137] and by 2014 was almost 4 million T [138], which demonstrate the importance of this emerging fuel.

The dehydration of methanol (MeOH) is largely used for the production of DME. The process is known as the indirect route of DME synthesis [139], and several companies such as Uhde, Lurgi and Toyo provide technologies to carry it out [16]. Since the reaction is limited by equilibrium, the unreacted methanol must be recirculated to the inlet of the reactor, thus a high conversion per pass is desired. The overall reaction and the standard enthalpy of reaction, at 298.15 K, are given by equation (3-1).

\[
2\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}; \Delta H_f^0 = -24.03 \text{ kJ} \cdot \text{mol}^{-1}
\] (3-1)

Known processes use aluminum oxide catalysts, at relative high temperatures, to promote the reaction [17]. However, since the reaction is exothermic and the conversion is limited by the thermodynamic equilibrium, the use of high temperatures is unfavorable. It is also known that the reaction can be performed at a lower temperature by using ZSM-5 as catalyst, as Tavan et al. [20] have shown by direct comparison of reaction performance on commercial γ-Al_2O_3 and HZSM-5 catalysts. The ability of ZSM-5 to perform the reaction at lower temperatures originates from the increased acid strength of ZSM-5 over Al_2O_3. For an acid catalyzed reaction, increased acidity of the catalyst would render higher activity [140]. This has been particularly described by Alharbi et al. [18] for the methanol dehydration to DME.

Compared to aluminum oxide catalysts, the use of lower temperature with ZSM-5 favors the thermodynamic equilibrium of the system and higher conversions per pass, could be achieved. The conversion of methanol to DME on aluminum oxide catalysts have been well investigated, and several kinetic studies are reported in literature [20, 141, 142, 143, 144]. Less work has been done with ZSM-5 catalysts, although it has recently gained more attention and few publications are available [18, 19, 20].

The reaction mechanism of the methanol dehydration reaction on ZSM-5 is still under debate [18]. Some authors support a mechanism in which associative adsorption of methanol takes place (associative pathway) [19, 20, 21], while others support a mechanism with dissociative adsorption of methanol (dissociative pathway) [22]. This debate also leads to disputes on the suitability of kinetic expressions.

In consequence, this chapter focuses on analyzing the validity of kinetic models proposed in literature and their modifications, with the purpose of determining an intrinsic rate equation for the methanol dehydration to DME over a commercial ZSM-5 catalyst, that is valid in a wide range of operating conditions, including feeds with high water content (up to 30 wt.%). The importance of this assessment lays in the consequence it brings to reactor design [145]. First, ZSM-5 is a more acidic catalyst than γ-Al_2O_3, and in consequence has higher activity, thus, it could be possible to perform the dehydration reaction at lower temperature than in a conventional industrial unit and using a smaller reactor or at least one of similar size. Second, we evaluate the effect of water at a level of 30 wt.% which is in the range of crude methanol (methanol obtained from a production facility without purification). It means that it would be possible to design a reactor to operate with not only pure methanol as feed but with crude methanol as well.

3.2 Experimental summary

Material and methods

A detailed description of the materials and methods discussed in this chapter was provided in Chapter 2. Therefore, only a short description is provided below.

The catalyst used in this chapter was a commercial ZSM-5 sample with a SiO_2/Al_2O_3 of 58. The physicochemical properties of the catalyst were evaluated by different techniques, including argon physisorption, helium pycnometry, XRD, SEM and temperature program analysis. The results are shown in section 3.3.1.

The kinetic tests were carried out in a semi-automated set-up. A simple diagram of the set-up is shown in Figure 3-1.
Figure 3-1. Simplified scheme of reaction apparatus. Red line indicates heated lines.

Definition of basic equations

The conversion of methanol ($x_{\text{MeOH}}$) after a certain amount of time compared to the conversion of the fresh catalyst was used as an indicator of the catalyst activity. It was also used in the calculation of reaction rate data from the recycle reactor. The conversion of methanol is defined by equation (3-2), where $F_{\text{MeOH},0}$ and $F_{\text{MeOH}}$ represent the inlet and outlet molar flow rates of methanol in mol·s⁻¹.

$$x_{\text{MeOH}} = \frac{F_{\text{MeOH},0} - F_{\text{MeOH}}}{F_{\text{MeOH},0}} (3-2)$$

The experimental reaction rate of methanol conversion ($-r_{\text{MeOH}}$) can be estimated from equation (3-3) [130], where $W_{\text{cat}}$ represents the weight of catalyst in kg, $\mathcal{R}$ is the recycle ratio, and the other variables as defined above.

$$W_{\text{cat}} = (\mathcal{R} + 1) \int_{0}^{x_{\text{MeOH}}} \frac{dx_{\text{MeOH}}}{n_{\text{eff}} x_{\text{MeOH}}} - r_{\text{MeOH}} (3-3)$$

If $\mathcal{R}$ is high enough the recycle reactor behaves as a well-mixed continuous stirred tank reactor (CSTR) [130]. In our case, this approach is also supported by the results of the fluid dynamics analysis, which are explained in Chapter 2, section 2.5.1. The resulting expression is given by equation (3-4).

$$W_{\text{cat}} = \frac{x_{\text{MeOH}}}{1 - r_{\text{MeOH}}} (3-4)$$

In the calculation process, equation (3-4) was solved for $-r_{\text{MeOH}}$ and adapted to allow the use of measurable quantities in their original units. The resulting equation to calculate the rate of methanol conversion is given by equation (3-5), where $WHSV$ is given in h⁻¹ and the molecular weight of methanol ($MW_{\text{MeOH}}$) is given in kg·mol⁻¹.

$$-r_{\text{MeOH}} \text{ mol kg}^{-1} \text{s}^{-1} = \frac{WHSV}{MW_{\text{MeOH}}} \left( \frac{1\text{h}}{3600\text{s}} \right) (3-5)$$

Testing criteria: exclusion of heat and transport limitations

Internal and external mass transfer limitations were evaluated via the Weisz-Prater criterion and the Mears criterion, respectively. Internal and external heat transfer limitations were tested using Anderson’s criterion and Mears’ criterion, respectively. These testing criteria were selected because their application only depends on known or measurable quantities. The equations describing the criteria are summarized in Table 3-1 [146, 147, 148, 149].

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Equation</th>
<th>Eq. N°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass transfer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weisz-Prater [150]</td>
<td>$N_{WP} = \frac{r_{b} \cdot r_{obs}}{D_{g} \cdot C_{g}} \leq 0.3$</td>
<td>(3-6)</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>$\omega = \frac{r_{obs} \cdot \rho_{b} \cdot r_{p} \cdot n}{k \cdot C_{g}} \leq 0.15$</td>
<td>(3-7)</td>
</tr>
<tr>
<td>Heat transfer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anderson [151]</td>
<td>$\psi = \left( \frac{E_{app}}{R \cdot T} \right) \left( \frac{\Delta H_{r} \cdot r_{obs} \cdot r_{p}^{2}}{k_{eff} \cdot T} \right) &lt; 0.75$</td>
<td>(3-8)</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>$\chi = \left( \frac{\Delta H_{r} \cdot r_{obs} \cdot \rho_{b} \cdot r_{p} \cdot E_{p}}{h_{p} \cdot T^{2} \cdot R} \right) &lt; 0.15$</td>
<td>(3-9)</td>
</tr>
</tbody>
</table>

Kinetic analysis

Estimation of kinetic parameters was performed in MATLAB®, by means of the function ‘*nlinfit*’. This function uses the Levenberg-Marquardt algorithm [152] during the minimization process of the objective function (OF). The OF is given by equation (3-10), where $r_{\text{exp}}$ and $r_{\text{cat}}$ are the experimental and calculated reaction rates of methanol dehydration to DME, respectively, at the experimental setting $j$.

$$OF = \sqrt{\sum_{j} \left( \frac{r_{\text{exp}} - r_{\text{cat}}}{M_{\text{MeOH}}} \right)^{2}} (3-10)$$
\[ OF = \sum_{j=1}^{N_{\text{exp}}} (y_j^{\text{exp}} - y_j^{\text{cat}})^2 \]  

(3-10)

Kinetic expressions were written as function of a kinetic factor \((k_i)\) and adsorption constants of species \(i\) \((K_i)\). The kinetic factors were expressed as a reparametrized Arrhenius function, in accordance with the description given by [153, 154, 155], with apparent activation energy \(E_{\text{app}}\), as depicted in equation (3-11). Adsorption constants were expressed as function of the standard entropy of adsorption \(\Delta S_{\text{ad,i}}^0\) and standard enthalpy of adsorption \(\Delta H_{\text{ad,i}}^0\), according to equation (3-12) [156]. A reparameterization is required to minimize the correlation between the pre-exponential factor and the argument of the exponential function, thus simplifying the convergence during the minimization process [154, 155].

\[ k = k_{\text{ref}} \cdot \exp \left[ -\frac{E_{\text{app}}}{R} \left( \frac{1}{T} - \frac{1}{T_p} \right) \right] \]  

(3-11)

\[ K_i = \exp \left[ \frac{\Delta S_{\text{ad,i}}^0}{R} \right] \cdot \exp \left[ -\frac{\Delta H_{\text{ad,i}}^0}{RT} \right] \]  

(3-12)

Estimated values of kinetic parameters were tested against physicochemical constraints. These are shown in Table 3-2 [156, 157, 158, 159, 160]. In addition, the entropies of adsorption were checked against a guideline shown in equation (3-13). This relation was suggested by Vannice et al. [160] and was empirically determined from entropies of chemisorption and the linear correlation between entropy and enthalpies of adsorption detected by Everett [161]. In this equation, entropy is given in J mol\(^{-1}\) K\(^{-1}\) and enthalpy is given in J mol\(^{-1}\).

\[ -\Delta S_{\text{ad,i}}^0 < 51.1 - 0.0014 \cdot \Delta H_{\text{ad,i}}^0 \]  

(3-13)

In addition, the kinetic models were evaluated considering: (a) parity plots of experimental rate versus calculated rate of reaction; (b) predicted value plots, to analyze residual [153]; and (c) Akaike’s information criterion [162] to make a relative rank of the model that performed well. The predicted value plots, to analyze residuals, was supplemented with the one-sample t-Test [163]. This test is used to test a hypothesis on a sample’s mean, when the sample comes from a normally-distributed population with unknown variance. In the case of residuals, the mean of the population is assumed to be zero (0), and the variance is unknown, thus the test can be applied. The evaluation was done by using the MATLAB® function “ttest” which will return a value of zero (0) if the mean of the residuals is zero (0) and the sample is normally distributed. The calculation was done at a significance level of 5 %.

**Table 3-2. Physicochemical constraints.**

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exponential factor ([k_{\text{ref}}]) (mol kg(^{-1}) s(^{-1}))</td>
<td>(k_{\text{ref}} &gt; 0)</td>
</tr>
<tr>
<td>Apparent activation energy ([E_{\text{app}}]) (J mol(^{-1}))</td>
<td>(E_{\text{app}} &gt; 0)</td>
</tr>
<tr>
<td>Enthalpy of adsorption for species (i) ([\Delta H_{\text{ad,i}}^0]) (J mol(^{-1}))</td>
<td>(-\Delta H_{\text{ad,i}}^0 &gt; 0)</td>
</tr>
<tr>
<td>Entropy of adsorption for species (i) ([\Delta S_{\text{ad,i}}^0]) (J mol(^{-1}) K(^{-1}))</td>
<td>(0 &lt; -\Delta S_{\text{ad,i}}^0 &lt; \gamma_{p,i})</td>
</tr>
</tbody>
</table>

In reference to the Akaike’s information criterion [162], it allows to rank models according to their performance, relative to each other. The AIC, equation (3-14), depends on the number of experimental measurements \((N)\), the residual sum of squares of the regression analysis \((OF)\), as defined above, and the number of parameters \((k)\).

\[ AIC = N \cdot \ln \left( \frac{OF}{N} \right) + 2k \]  

(3-14)

**True activation energy and reaction order**

The true activation energy \(E_{\text{true}}\) and the order of the reaction with respect to methanol \((n_m)\) and water \((n_w)\) were estimated for the kinetic model that performed best. The relation between \(E_{\text{app}}\) and \(E_{\text{true}}\) is given by the partial derivative of the forward reaction rate \((r^+\)) with respect to the temperature. The general definition is given by equation (3-15) [164, 165].

\[ E_{\text{app}} = RT^2 \frac{\partial}{\partial T} \ln (r^+) \]  

(3-15)

Finally, the order of the reaction with respect to methanol \((n_m)\) and water \((n_w)\) is considered. In a power law kinetic, the reaction order is given by the power of the concentrations or partial pressures present in the kinetic expression. However, for a LHHW kinetics the order of the reaction is somewhat more complex and the order of the reaction is given by the partial derivative of the forward reaction rate with respect to the partial pressure of the species in consideration [164], as shown in equation (3-16).
\[ n_i = p_i \frac{\partial}{\partial p_i} \ln (r^i) \]  

(3-16)

3.3 Results and Discussions

3.3.1 Catalyst characterization

**Absolute and bulk density**

Absolute and bulk density are used to estimate the real catalyst porosity. The absolute density of the catalyst was determined via helium pycnometry, while the bulk density was measured via mercury intrusion porosimetry. The techniques and equipment used for the measurements are described in Chapter 2, section 2.4.1. The measured values of absolute and bulk density were 1640 kg·m\(^{-3}\) and 1016 kg·m\(^{-3}\), respectively.

**Surface area, pore size and volume**

Textural properties were measured by Argon (Ar) physisorption and mercury intrusion porosimetry (see equipment details in Chapter 2). The measured surface area was 452 m\(^2\)·g\(^{-1}\), and the total pore volume was 0.251 cm\(^3\)·g\(^{-1}\). These results are in good agreement with the certificate of analysis provided by the supplier [166]. The argon (Ar) adsorption/desorption isotherms are shown in Figure 3-2.

The physisorption isotherm showed characteristics of both microporous and macroporous structure. Its behavior can be explained by two Ar filling stages. In the first one, micropore filling occurs [167, 168, 169]. Thus, a steep increase in adsorbed volume is observed at low relative pressure (p/p\(_0\)), followed by a plateau. In the absence of other pore structures the resulting isotherm would be of Type I, according to IUPAC nomenclature [167]. In the second one, unconstrained adsorption in mono- and multilayers occurs, evident by a steep increase (without plateau) at p/p\(_0\) close to 1. In the absence of other pore structures, a Type II isotherm would be observed, distinctive of macroporous or non-porous solids [167]. The microporous characteristic is caused by the intrinsic microporous structure of ZSM-5, with pore dimensions of ca 5 Å, while the macroporous characteristic was probably caused by the intercrystalline structure of the material created during the pelletization process, similarly to observations made by other authors [170].

The dual behavior was confirmed by the bimodal pore size distribution observed, which is shown in Figure 3-3. On graph (A), it is shown the differential pore volume (DPV) as function of pore diameter (d\(_{\text{pore}}\)) in the microporous region (d\(_{\text{pore}} < 2\) nm), determined from Ar isotherms. The main peak is centered at 0.5 nm, in accordance with the MFI structure, it originates from capillary condensation of the nitrogen in the micropores. On graph (B), the plot of Log(differential intrusion volume) as function of d\(_{\text{pore}}\) is shown. It was determined from the intrusion cycle of a mercury intrusion porosimetry test. In this case, the peak is centered at 55 nm, in the macroporous region (d\(_{\text{pore}} > 50\) nm), in accordance to the observation previously made on the Ar-isotherm behavior.

**Figure 3-2.** Ar adsorption/desorption isotherm of catalyst sample.

**Figure 3-3.** Pore size distribution. (A) Micropore region from physisorption analysis; (B) Meso- and macropores region from mercury porosimetry.
Chapter 3

X-ray diffraction spectroscopy

It is known that ZSM-5 is a microporous material [14]. The diffractograms of the catalyst sample and the simulated reference material (Figure 3-4) were compared following the procedure described by [8, 169]. The good correlation between diffractograms confirmed the mordenite framework inverted (MFI) structure of our zeolite sample. The data of a simulated reference material was obtained from the International Zeolite Organization [171, 172], and it was taken in the range 0° to 55° 2θ degrees, step size of 0.0323° 2θ, wavelength of CuA1 (1.54056 Å), and scaled to 50 000.

The MFI structure was also confirmed by the strong characteristic peaks at low 2θ reflection, namely at 7.94° and 8.90°, corresponding to Miller indices \([hkl]\) of [011] and [200] of calcined ZSM-5, respectively [170, 172].

![Figure 3-4. XRD spectra: (a) ZSM-5 catalyst sample used; (b) Reference material.](image)

Electron microscopy

SEM images are presented in Figure 3-5. Determination of crystal size was done by manually measuring crystals in micrographs with resolution of 500 nm. An average crystal size of ca 300 nm was determined.

![Figure 3-5. Scanning electron micrographs.](image)

Temperature program desorption of ammonia (NH\(_3\)-TPD)

Temperature program desorption of ammonia (NH\(_3\)-TPD) was used to characterize the acidity of the zeolite [173]. Results are shown in Figure 3-6. Graph (A) shows the NH\(_3\)-TPD results when adsorption temperature was 100 °C. Two peaks can be identified. The first one at ca 170 °C attributed to medium acidity. Another one at higher temperature, ca 330 °C, corresponding to strong acid sites. These results are in accordance with results from other authors [169, 170, 174, 175].

Graph (B) shows three additional TPD results. This were carried out after adsorption at 230 °C and with desorption at three different heating rates 10, 15 and 20 °C min\(^{-1}\). Results are plotted as TCD signal vs time, and these plots were used for integration and determination of strong Brønsted acidity. The results agreed well with theoretical calculation of Brønsted acidity based on the SiO\(_2\)/Al\(_2\)O\(_3\) ratio of the zeolite.

3.3.2 Testing criteria: exclusion of heat and transport limitations

Results of testing criteria on mass and heat transfer limitations are shown in Table 3-3. It can be observed that all testing criteria have been met. Thus, it is concluded that the reaction is neither mass nor heat transfer limited, and that all measurements were performed in the kinetic regime. The procedure followed in the calculations of these criteria and the estimation of different properties are discussed in detail in Appendix A.
The absence of internal mass transfer limitations was verified through the calculation of the Weisz-Prater number ($N_{\text{WP}}$) [131, 176]. If the diffusion through the catalyst particle is considered, a $N_{\text{WP}}$ of 0.15 is obtained. Also, $N_{\text{WP}}$ becomes $1.7 \cdot 10^{-3}$ when diffusion through a catalyst crystal is considered. In both cases the criterion is fulfilled ($N_{\text{WP}} < 0.3$).

The external mass transfer limitation was evaluated by means of the Mears criterion [131, 146]. Here attention is paid to the Reynolds number, since the criterion is valid only in a certain range of the $Re$. Under our experimental conditions, the particle Reynolds number ($Re_p$) was approx. 38. At this low value, the correlation of Petrovic and Thodos [177] must be used, which is valid for $3 < Re_p < 2000$. A value of $2.2 \cdot 10^{-4}$ was obtained, which is much lower than 0.15. Thus, the Mears’ criterion is met, and it can be concluded that under the experimental conditions of this work, the reaction was not limited by mass transfer. These results agree with the steady conversion observed at increasing recycle gas flow rates.

Here, a summary of the testing criteria results is presented. The calculations were performed at the experimental conditions where the observed reaction rate was the highest, i.e. $T = 190 \, ^\circ\text{C}, \text{WSHV} = 100 \, \text{h}^{-1}$, and $y_{\text{MeOH},0} = 1$.

The intraparticle heat transfer limitation was evaluated by means of the Anderson’s criterion [151]. The criterion is fulfilled when temperature gradients within the catalyst particle can be neglected. The criterion was derived considering a maximum deviation between observed rate and the rate in an isothermal pellet to be less than 5%. To proceed with the calculation, the effective thermal conductivity of the particle ($\lambda_{\text{eff}}$) was estimated from experimental data of other authors [178, 179] and Woodside’s correlation [180]. Anderson’s criterion was satisfied, with a value of $2.7 \cdot 10^{-2}$ ($< 0.75$).

\textbf{Table 3-3. Results from testing criteria to neglect heat and mass transfer limitations.}

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Result from this investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weisz-Prater [150]</td>
<td>$N_{\text{WP}} = 1.6 \cdot 10^{-2} \leq 0.3$</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>$\omega = 5.6 \cdot 10^{-5} \leq 0.15$</td>
</tr>
<tr>
<td>Anderson [151]</td>
<td>$\psi = 6.7 \cdot 10^{-3} \leq 0.75$</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>$\chi = 1.0 \cdot 10^{-3} \leq 0.15$</td>
</tr>
</tbody>
</table>

Mears also proposed a criterion to exclude external heat transfer limitations [131, 146]. If the criterion is fulfilled, it indicates that the temperature in the bulk fluid phase and in the external surface of the catalyst is basically the same. Correlations from Chilton and Colburn [181], and from Gupta and Thodos [182] were used to estimate the gas phase to particle heat transfer coefficient ($h_p$), which is then used to verify the criterion. The Mears’ criterion was satisfied and a value of $2.4 \cdot 10^{-1}$ was obtained ($< 0.15$).

From these results, it is concluded that the reaction is neither mass nor heat transfer limited, and that the measurements were performed in the kinetic regime.

\subsection*{3.3.3 Activity tests - Effect of reactants and products}

It has been shown that methanol dehydration to DME is insensitive to the total system pressure [144]. However, the methanol molar fraction in the feed might have an influence on the kinetics. To this end, a series of tests were carried out at WHSV of 100 h$^{-1}$, temperature between 140 °C and 190 °C, and partial pressure values of methanol of 0.33, 0.67 and 1.0 bar. Results are shown in Figure 3-7. The conversion was kept low, to minimize the effect caused by the products.

The results show that at temperature of 165 °C and lower, where the conversion was less than 2 %, the reaction rate of methanol consumption is insensitive to the partial pressure of methanol, indicating zero order reaction on methanol partial pressure, similar to the behavior observed by Alharbi et al. [18] over an heteropoly acid catalyst. Since the conversion is low, effects of the reverse reaction can be neglected [183]. Under these conditions, the reaction rate can be approximated by the zero order rate law, which is:

\[ r = -\frac{dC_{\text{MeOH}}}{dt} = k \cdot C_{\text{MeOH}} \]

where $r$ is the reaction rate, $C_{\text{MeOH}}$ is the methanol concentration, and $k$ is the overall rate constant.

\[ k = \frac{2.7 \cdot 10^{-2}}{5.6 \cdot 10^{-5} \cdot 1.0 \cdot 10^{-3}} = 75.2 \, \text{h}^{-1} \]

\textbf{Figure 3-6. NH3-TPD profiles of ZSM-5 sample.} (A) TCD signal vs temperature and NH3 adsorption at 100 °C; (B) TCD signal vs time, with NH3 adsorption at 230 °C.
conditions, the desorption of a product is the rate-controlling step, and the surface of the catalyst might be considered completely saturated with methanol. On the other hand, at temperatures of 177 °C and 190 °C, the reaction rate slightly increases as the methanol partial pressure rises. In this case, the rate determining step (RDS) could be: (i) adsorption of the reactant; (ii) surface reaction with, or without dissociation of methanol; and (iii) desorption of a product [183].

Figure 3-7. Effect of methanol partial pressure on reaction rate; WHSV = 100 h⁻¹.

The effect of water has been widely reported. Water adsorbs on active sites and inhibits the reaction [141, 184], thus lower reaction rates are observed. In addition, the inclusion of water in the feed exerts an effect on the equilibrium of the reaction and reduces the maximum conversion that can be attained. This effect has been analyzed by determining how the equilibrium conversion changes with temperature and water content in the feed. Equilibrium data were obtained from a sensitivity analysis performed in Aspen Plus V7.2 at 1 bar and temperature in the range of 100 °C to 400 °C. An RGibbs reactor was used in the modeling process and the Peng-Robinson equation of state was used as thermodynamic method, in accordance to studies made by other authors [185, 186]. The results are shown in Figure 3-8.

Plot (A) shows how the equilibrium conversion of methanol changes with water molar fraction in the feed. The increase in feed water content reduces the methanol equilibrium conversion that can be attained, since it favors the reversible reaction (DME+H₂O → MeOH). This is shown for different reaction temperatures. As the temperature increases, the equilibrium conversion suffers a further decrease and this is caused by the reduction of the equilibrium constant with an increase in temperature. This behavior was expected since it is characteristic of exothermic reactions. An isotherm at 350 °C has been included to illustrate the typical outlet temperature of an industrial DME reactor working with Al₂O₃ as catalyst [187]. As can be observed, a significant improvement on the equilibrium conversion is achieved by using ZSM-5 as catalyst, which operates at lower temperature and would allow an increased conversion per pass of approximately 5 - 10 %. In an industrial plant, the higher attainable conversion would easily translate into lower power composition since less unconverted methanol would need to be recycle to the inlet of the DME reactor.

Figure 3-8. (A) Methanol equilibrium conversion versus molar fraction of water in the feed for different temperatures; and (B) Methanol equilibrium conversion versus temperature (°C) for different water content in the feed.

The effect of temperature is further illustrated in Figure 3-8 (B). In this plot, three curves representing fixed water quantities in the feed are shown. When pure methanol is fed, then the higher equilibrium conversion can be achieved. If 30 wt.% of water is added to the feed, then the equilibrium conversion that can be reached decreases. However, if the operating temperature is low, it would still be possible to achieve methanol conversions close to 90 %, and this exalts the benefit of the use of ZSM-5 as catalyst, which can work at lower temperature than the Al₂O₃ catalyst commonly used in industrial practice. The higher the amount of water, the stronger the effect on equilibrium conversion, as shown by the dotted line in graph (B), which represent 70 wt.% of water in the feed.
In the case of DME, it has been reported that this species does not adsorb on the catalyst; thus, it doesn’t compete for adsorption on active sites and doesn’t inhibit the reaction. This observation was experimentally confirmed for sulfonic resins [184, 188], but to our knowledge, there is no experimental evidence on ZSM-5. To determine the effect of DME on the methanol conversion, two sets of experiments were performed at \( T = 190 \, ^\circ\text{C} \), \( \text{WHSV} = 100 \, \text{h}^{-1} \), and partial pressure of methanol in the feed of 0.33 bar. In the first set of experiments, nitrogen was used as gas balance; in the second set, nitrogen was substituted by DME. The results showed that in both cases the conversion was 6%, thus, the effect of DME is similar to that of an inert gas, for example nitrogen, at least as long as the conversion is sufficiently small and the reverse reaction is negligible. Tests were limited to low conversion also to avoid effects of water adsorption that might bias the interpretation of the results.

According to Satterfield [189] the reaction regime can be determined from a plot of \( \log(\text{rate}) \) vs inverse of absolute temperature. Exemplary results are shown in Figure 3-9 for a feed of pure methanol at \( \text{WHSV} = 100 \, \text{h}^{-1} \), graph (A), and for a mixed feed of 70 wt.% methanol / 30 wt.% water and methanol \( \text{WHSV} = 14 \, \text{h}^{-1} \), graph (B). It can be observed that the experimental data fall in straight lines, and the slopes are different from zero (0). This strong temperature dependence of the rate is another indication for the assumption that the reaction regime is not limited by external mass transfer.

![Figure 3-9. Arrhenius plot. (A) Pure methanol feed and WHSV = 100 h^{-1}, (B) Mixed feed of 70 wt.% methanol and 30 wt.% water, and WHSV = 14 h^{-1}.](image-url)

### 3.3.4 Kinetic analysis

Kinetic tests were performed in the temperature range from 140 °C to 190 °C. At these temperatures, only the desired products were observed. Negligible amounts of side products, hydrocarbons smaller than \( \text{CH}_3 \), could be detected at temperatures higher than 200 °C.

#### Kinetic models

Nineteen kinetic models were evaluated. A summary of the kinetic models tested in this investigation are included in Table 3-4 [141, 142, 190, 191]. The models were both of power law and Langmuir-Hinshelwood-Hougen-Watson (LHHW) type. The LHHW models were obtained from literature [20, 141, 142, 184, 190, 191]. They were used as proposed by the authors or modified by the inclusion of a driving force term, as described by [183]. Also, these models were developed for the methanol to DME reaction on acid catalysts such as \( \gamma - \text{Al}_2\text{O}_3 \), sulfonic acid ion exchange resins and HZSM-5, considering various RDS, e.g. methanol adsorption with dissociation, without dissociation, surface reaction, among others.

The models that performed best during the kinetic analysis are described below and their equations are shown in Table 3-5. The first model in Table 3-5 corresponds to a modified version of the model of Gates & Johanson [184]. The model was modified to include a driving force term, as explained by Yang and Hougen [183]. The original model was developed for methanol dehydration over a sulfonic acid ion exchange resin. The authors considered non-dissociative adsorption of methanol, and the RDS was the combination of two molecules of methanol adsorbed in adjacent sites. Also, the authors assumed that DME was weakly adsorbed on the catalyst. This means that DME adsorption constant \( K_d \) was negligible compared to the adsorption constants of methanol \( K_m \) and water \( K_w \). Thus, it was removed from the adsorption term of the equation.

The second model was developed from Klusáček & Schneider [190], to explain the dehydration of methanol on sulphonated styrene-divinylbenzene copolymer used as catalyst. The authors assumed that only one type of active center was involved in the dissociative adsorption of methanol, and the RDS is a surface reaction. They observed that \( K_d \rightarrow 0 \), after fitting their experimental data; thus, \( K_d \) was considered negligible in the model. As in the previous case, the original model was modified, to include a driving force term, as explained by Yang and Hougen [183].
Table 3-4. Summary of kinetic models tested.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r = k$</td>
<td>$r = \frac{k(K_m p_m)^2(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
</tr>
<tr>
<td>$r = k \cdot p_m$</td>
<td>$r = \frac{kK_m p_m(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
</tr>
<tr>
<td>$r = k \cdot p_m^2$</td>
<td>$r = \frac{kK_m p_m^2(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
</tr>
<tr>
<td>$r = \frac{k \cdot p_m}{p_w}$</td>
<td>$r = \frac{kK_m p_m(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
</tr>
<tr>
<td>$r = \frac{kK_m p_m}{(1 + K_m p_m)^2}$</td>
<td>$r = \frac{k \cdot p_m}{p_w}$</td>
</tr>
<tr>
<td>$r = \frac{kK_m p_m}{(1 + K_m p_m)^2}$</td>
<td>$r = \frac{kK_m p_m^2(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
</tr>
<tr>
<td>$r = \frac{kK_m p_m^2}{(1 + K_m p_m + K_w p_w)^2}$</td>
<td>$r = \frac{k \cdot p_m}{(1 + k_3 p_h^2 + k_4 p_w)^4}$</td>
</tr>
<tr>
<td>$r = \frac{kK_m p_m(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})}$</td>
<td>$r = k \cdot p_m^2(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + K_m p_m + K_w p_w)$</td>
</tr>
<tr>
<td>$r = \frac{kK_m p_m(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + 2/\sqrt{K_m p_m + K_w p_w})^2}$</td>
<td>$r = k \cdot p_m(1 - p_d p_w/(p_m^2 K_{eq}))}{(1 + K_m p_m + p_w/\sqrt{K_{eq})}$</td>
</tr>
</tbody>
</table>

The last model was recently developed by Ha et al. [19]. They proposed new reaction pathways for the dehydration of methanol over metal-modified ZSM-5 catalysts. The mechanisms included the adsorption of two methanol molecules and their activation, and the presence of adsorbed methyl carboxonium ion (CH$_3$OH$_2^+$). Each individual step in the mechanism was assumed as RDS in order to derive the kinetic expressions. The equation that performed best is included in Table 3-5, and it considers the dehydration of the methyl carboxonium ion (CH$_3$OH$_2^+$) into a methoxy species and adsorbed water as RDS.

Model fitting and discrimination

Before the fitting procedure, kinetic constants were reparametrized using equation (3-11), and a reference temperature ($T_0$) of 438.15 K. After evaluation of the kinetic models, three of them fulfilled the physicochemical constraints shown in Table 3-2. Also, the kinetic parameters were significantly different from zero (0). The models and their OF values are shown in Table 3-5.

As described in the previous subsection and shown in Table 3-5, the modified models of Gates & Johanson and Klusáček & Schneider contain the driving force term. This term is included within the square brackets in the corresponding equations. It is determined from partial pressures of reactants and products in the gas phase and the equilibrium constant ($K_{eq}$). The equilibrium constant was calculated from the standard Gibbs energy of formation ($\Delta G^o$). Correlations and constants used in the determination of $\Delta G^o$ can be found in [157, 192, 193].
Also, it must be noted that the adsorption constant for DME ($K_a$) was omitted from the models. This is known to be valid for reaction systems including sulfonic acid ion exchange resin as catalyst [184, 188]. In the present study, the catalytic system was different; thus, the assumption had to be confirmed, as described in section 3.3.3. After confirmation, the $K_a$ was set to zero (0) in all the kinetic models. This is also supported by the work of Ding et al. [194], who found an enthalpy of adsorption of dimethyl ether ($\Delta H_{ad,d}$) on H-ZSM-5 of -18 kJ·mol$^{-1}$. This value is below the commonly cited limiting energy between physisorption and chemisorption [195], -40 kJ·mol$^{-1}$, thus indicating that DME might be physisorbed on the surface but not chemisorbed. Although it is not possible to distinguish physisorption from chemisorption only by the heat of adsorption [168, 195], low values of $\Delta H_{ad,d}$ favor the decision of neglecting the adsorption constant of DME when compared to the adsorption constants of water ($\Delta H_{ad,w}$) or methanol ($\Delta H_{ad,m}$). It is worth mentioning that theoretical studies in literature show values of DME enthalpy of adsorption on ZSM-5 as high as -98 kJ·mol$^{-1}$ [196], and the authors claim that experimental evidence shown by [197] supports their calculation. However, this is only true when the number of molecules per unit cell is less than two (2). At higher concentration values the enthalpy of adsorption quickly decays reaching a plateau value ca -40 kJ·mol$^{-1}$ when the concentration per unit cell of molecules is equal to or greater than three (3) [197].

From the OF results (Table 3-5), it seems that the modified model of Klusáček & Schneider is the best. However, difference between the objective function values is too small to be used as a clear indicator for discrimination. Therefore, the rival kinetic models were further evaluated via parity plots of experimental versus calculated reaction rates as well as residual analysis plots. These are shown in Figure 3-10.

The parity plots of the three models (graphs A1, A2, and A3) show good agreement between experimental and predicted rates. Experimental measurements are shown with 95 % confidence interval bars. They are all on top or close to the line $y = x$ (continuous-red line), and within the simultaneous 95 % confidence bounds, confirming the good agreement between experimental data and calculated results. The good agreement was already expected from the low OF results, shown in Table 3-5.

The reaction rates observed in this investigation varied in the range of 0.001 to 0.07 mol$_{\text{MeOH}}$kg$_{\text{cat}}^{-1}$s$^{-1}$. These observations agree well with those of Ha et al., who evaluated the methanol dehydration reaction using pure methanol in their feed (without dilution with inert gas) and an alkali-modified ZSM-5 with SiO$_2$/Al$_2$O$_3 = 80$. On the contrary, lower reaction rate values were reported for the same reaction and type of catalyst by Migliori et al. [191]. This discrepancy could be caused by a combination of low partial pressure of methanol in the feed used by these authors and the use of a catalyst with higher SiO$_2$/Al$_2$O$_3$ ratio, thus less acidic, as has been reported by Alharbi et al [18].

Zhang et al. [144] also reported similar intrinsic methanol reaction rates but on γ-Al$_2$O$_3$ catalysts working at higher temperatures, in the range of 240 °C to 340 °C. These results can be explained by the lower acidity of γ-Al$_2$O$_3$ with respect to ZSM-5 [20]. It is concluded that by carrying out the reaction on a ZSM-5 catalyst, it is possible to work at a lower temperature than with γ-Al$_2$O$_3$ catalysts (typically used in industry) but maintaining similar reaction rates levels. Therefore, the use of ZSM-5 catalyst could allow the reduction of the size of the equipment required to achieve a certain productivity, and it would also allow a higher conversion per pass since the equilibrium conversion is favored at lower temperature.

The residuals were evaluated via predicted value plots as described by Kittrell [153]. The analysis helps to identify non-random variations in the data, which can be used to further discriminate among the remaining models. These plots are presented on the right side of Figure 3-10, in graphs C1, C2, and C3. According to these results, all models seem to perform equally well, with residuals randomly distributed above and below zero (0). As described in section 3.2 (Kinetic analysis), the residuals were also tested using the MATLAB® command “ttest”. Results showed that all models fulfilled the null hypothesis, i.e. all residual samples are normally distributed and their mean is zero (0). Also, it is concluded that systematic errors are not present in the measurements, but only random experimental error, which is intrinsic to the reaction tests and measurements, as explained by [153]. All models seem equally adequate. Further discrimination was achieved by close analysis of the kinetic parameters shown in Table 3-6.

It is shown that activation energy ($E_a$) for all models are around 106 kJ·mol$^{-1}$, within 10 % of the value reported by Alharbi et al. [18] of 95 kJ·mol$^{-1}$ on HZSM-5 with Si/Al=10. However, other authors [19, 20] have found values in the range of 52 to 69 kJ·mol$^{-1}$. The source of the discrepancy is unknown. It could be caused by a compensation relation (see Constable-Cremer in [198]), which is a linear correlation between observed frequency factors and apparent activation energies for a series of catalysts and a particular reaction, or one catalyst and a series of similar reactions [198, 199].
In this comparison, the compensation effect could be related to changes in the acid strength of the catalysts, produced by the metal modifications implemented by these authors. Likewise, Alharbi et al. [18] have shown a linear correlation between turnover frequency and acid strength for different catalysts, including HZSM-5 with different Si/Al ratios. Another plausible explanation is related to kinetic measurements affected by internal mass transfer limitations, which we consider possible, considering the large particle size these authors used during experimentation (420 µm to 841 µm). If pore diffusion limits the reaction, the measured activation energy is the mean of the activation energy measured in the kinetic regime and the activation energy for pore diffusion ($E_D$) [176, 189]. Considering that $E_D$ of methanol on HZSM-5 is 12.3 kJ·mol$^{-1}$ [200], and the activation energy measured in the kinetic regime is ca 106 kJ·mol$^{-1}$ (reported in this study) the mean value results in an activation energy of ca 59 kJ·mol$^{-1}$, which is in close proximity to the values reported by [19, 20].

Different values of enthalpy of adsorption of methanol on ZSM-5 are reported in literature, with values ranging from -26 kJ·mol$^{-1}$ to -115 kJ·mol$^{-1}$ [194, 196, 201, 202]. Results presented in Table 3-6 show that $\Delta H_{\text{ad,m}}^0$ varies from -45 kJ·mol$^{-1}$ to -70 kJ·mol$^{-1}$, in accordance with values reported elsewhere [197, 201, 203]. In particular, the $\Delta H_{\text{ad,m}}^0$ determined from the model of Klusáček & Schneider [190] is in close agreement with the value of -65 kJ·mol$^{-1}$ reported by [204], determined via density functional theory (DFT).

In the case of enthalpy of adsorption of water ($\Delta H_{\text{ad,w}}^0$), the results vary from -73 kJ·mol$^{-1}$ to -93 kJ·mol$^{-1}$, also in good agreement with values reported by Lee et al. [202] for heat of adsorption of water in zeolite. These authors showed that heat of adsorption varied with coverage, starting at ca -100 kJ·mol$^{-1}$, and varying to approximately -80 kJ·mol$^{-1}$ at high coverage of water (400 µmol/g). These high values of enthalpy of adsorption reveal the exothermic nature of water interaction with the zeolite structure, as Zhang et al. [205] suggested.

It is important to note that the above comparisons correspond to experimental results determined in this investigation with those reported by other authors using ZSM-5 with a wide range of Si/Al ratios, meaning that different acidic and hydrophilic properties are in play. However, the direct comparison of adsorption enthalpies of water and methanol in ZSM-5 with different Si/Al is appropriate, considering that the isosteric heats of adsorption are fairly independent of the Si/Al ratio once a certain number of molecules had been adsorbed in the zeolite [205, 206].
Chapter 3. Methanol Dehydration to DME over a ZSM-5 Catalyst

Table 3-6. Summary of kinetic parameters.

<table>
<thead>
<tr>
<th>Model</th>
<th>(k_{T_0} \cdot 10^2)</th>
<th>(E_{\text{app}}) ((\text{kJ} \cdot \text{mol}^{-1}))</th>
<th>(-\Delta S_{\text{ad},m}^0) ((\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}))</th>
<th>(-\Delta H_{\text{ad},m}^0) ((\text{kJ} \cdot \text{mol}^{-1}))</th>
<th>(-\Delta S_{\text{ad},w}^0) ((\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}))</th>
<th>(-\Delta H_{\text{ad},w}^0) ((\text{kJ} \cdot \text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Gates &amp; Johanson</td>
<td>1.69 ± 8·10^{-2}</td>
<td>103.4 ± 3.1</td>
<td>73 ± 2</td>
<td>44.5 ± 0.7</td>
<td>182 ± 2</td>
<td>89.6 ± 0.3</td>
</tr>
<tr>
<td>Modified Klusáček &amp; Schneider</td>
<td>8.16 ± 0.51</td>
<td>109.3 ± 3.7</td>
<td>137 ± 12</td>
<td>70.3 ± 5.4</td>
<td>153 ± 26</td>
<td>73.1 ± 12.0</td>
</tr>
<tr>
<td>Ha et al. [19]</td>
<td>1.70 ± 7·10^{-2}</td>
<td>104.4 ± 2.9</td>
<td>91 ± 2</td>
<td>49.5 ± 0.6</td>
<td>189 ± 2</td>
<td>93.3 ± 0.3</td>
</tr>
</tbody>
</table>

These models also obey the entropy constraints shown in Table 3-2. The standard entropies of adsorption, of both methanol and water, are negative and fall below the gas phase values, for methanol \(\Delta S_{g,m}^0 = 240\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) and water \(\Delta S_{g,w}^0 = 189\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\), reported by [192]. In the case of the Ha et al. model [19], the value is actually at the limit of an entropy constraint. The predicted value of \(-\Delta S_{\text{ad},w}^0\) is 189 ± 2\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\, and it lays just at the boundary of the maximum value that \(-\Delta S_{\text{ad},w}^0\) should reach. It is not possible to conclude that the value is significantly greater than 189\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\, thus this model is still considered satisfactory, and included in the further analysis.

Vannice et al. [160] suggested a guideline to make use of the entropy of adsorption on the discrimination process, see eq. (3-20). The upper limit of this recommendation was empirically determined from entropies of chemisorption and the linear correlation between entropy and enthalpies of adsorption detected by Everett [161]. In this equation, entropy is given in J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} and enthalpy is given in J \cdot \text{mol}^{-1}.

\[
-\Delta S_{\text{ad},w}^0 < 51.1 - 0.0014 \cdot \Delta H_{\text{ad},w}^0
\]

The results obtained in the modified model of Gates & Johanson and Ha et al. [19] are significantly greater than the limit determined by the recommendation [160], also shown in Table 3-7. These results give strong indication that the models should be discarded or just at the boundary of the maximum value that \(-\Delta S_{\text{ad},w}^0\) should reach. It is not possible to conclude that the value is significantly greater than 189\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\, thus this model is still considered satisfactory, and included in the further analysis.

\[
-\Delta S_{\text{ad},w}^0 < 51.1 - 0.0014 \cdot \Delta H_{\text{ad},w}^0
\]
considered with great caution, since it may indicate that one of the parameters lacks of physical meaning. The modified model Klusáček & Schneider [190] has a different interpretation. It is not possible to conclude that the value obtained of $\Delta S_{act,w}^{0}$ is significantly higher than the recommendation, thus it is considered satisfactory.

To discriminate further, the Akaike’s Information Criterion (AIC) was used, and the results are shown in Table 3-8. The modified model of Klusáček & Schneider showed the lowest AIC; thus, it is considered the best among the rival models.

After careful evaluation of the kinetic models, assessment of the physicochemical constraints, consideration of the entropy recommendation from Vannice et al. [160], and the results of AIC, it is concluded that the modified Klusáček & Schneider kinetic model is the best to describe the methanol to DME conversion over ZSM-5. Moreover, the selection of this model supports a mechanism in which methanol experiences dissociative adsorption and the RDS is a surface reaction, in accordance to the work of Klusáček & Schneider, and more recently Moses et al. [22].

**Table 3-8. Akaike’s information criterion.**

<table>
<thead>
<tr>
<th>Model</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Gates &amp; Johanson</td>
<td>-341</td>
</tr>
<tr>
<td>Modified Klusáček &amp; Schneider</td>
<td>-353</td>
</tr>
<tr>
<td>Ha et al. [19]</td>
<td>-346</td>
</tr>
</tbody>
</table>

**Model Validation**

The validation of the model was performed by comparing the performance of the model vs data taken at atmospheric pressure, WHSV = 50 h⁻¹, partial pressure of methanol in the feed of 0.67. These data were not used during the regression analysis. The results of model performance with these new data is shown as a parity plot in Figure 3-11. The agreement between experimental data and model is remarkable, with all data points falling within the ± 5 % boundaries. In addition, calculation of the residuals means squared resulted in a value of $6 \times 10^{-6}$, which represents an average deviation between model and experimental data of ca 0.01 %. This confirms the good performance of the model and its validity.

![Figure 3-11. Parity plot of experimental versus calculated reaction rate. Validation data. Dashed lines represent ± 5 % deviation from the line y = x.](image)

### 3.3.5 True activation energy and reaction order

The apparent activation energies, determined from regression, may differ from the true activation energy of the process, and this is evidenced below. It has been indicated that the $E_{app}$ changes with experimental conditions, since the surface coverage of the reactants may change within the experimental spectrum evaluated [164, 198]. In fact, Bond et al. [198] have explained that in the absence of mass transfer limitations the relation between $E_{app}$, $E_{true}$ and $\Delta H_{m}$ may lead to a decrease in the slope of an Arrhenius plot.

Application of the definition provided in section 3.2 (True activation energy and reaction order) for the kinetic expression developed by Klusáček & Schneider [190] leads to equation (3-21).

$$E_{app} = E_{true} + \Delta H_{m} - 2 \cdot \left( \frac{\Delta H_{m} K_{m} P_{m} + \Delta H_{w} K_{w} P_{w}}{1 + 2 \sqrt{K_{m} P_{m} + K_{w} P_{w}}} \right)$$  (3-21)

The evaluation of this equation, using the experimental conditions of this research and the estimated kinetic parameters, indicates that the true activation energy is in the range between 80 and 130 kJ·mol⁻¹, the upper limit being within 15 % of the value reported by Blaszkowski and van Santen [21, 204]. This is considered as a good agreement, provided that the accuracy of DFT calculations are in the range of ± 10 kJ·mol⁻¹ [207].
Finally, the orders of reaction with respect to methanol ($n_m$) and water ($n_w$) were determined by application of equation (3-17) to the kinetic expression proposed by Klusáček & Schneider and modified in this work. The results are shown in equations (3-22) and (3-23).

$$n_m = 1 - 2 \cdot \frac{\sqrt{K_mp_m}}{1 + 2\sqrt{K_mp_m + K_wp_w}}$$  \hspace{1cm} (3-22)

$$n_w = -2 \cdot \frac{Kwpdbw}{1 + 2\sqrt{Kmpm + Kwpw}}$$  \hspace{1cm} (3-23)

This evaluation yields $n_m$ in the range between 0.07 and 0.45, which indicates a slight influence of methanol partial pressure on the reaction rate. This is in good agreement with the experimental results shown in Figure 3-7 and the reaction order of 0.23 reported by Alharbi et al. [18]. Additionally, $n_w$ is in the range between -0.80 and 0, in agreement with the observation that water has an inhibiting effect on the reaction rate, as reported by different authors [141, 184].

3.4 Conclusions

The present studied focused on the kinetic analysis of methanol to dimethyl ether conversion on a commercial ZSM-5 zeolite. The MFI structure of the commercial zeolite was confirmed via XRD, and its textural properties were determined via gas physisorption and mercury intrusion porosimetry. NH$_3$-TPD analysis allowed the identification of two types of acid sites with medium and high strength. Also, crystal size (used in the preliminary calculations) was measured from SEM images, and an average value of ca 300 nm was determined.

Previous to the kinetic analysis, a series of preliminary studies were performed. It was demonstrated that the recycle reactor had a fluid dynamic behavior equivalent to a CSRT. Also, from long term runs and reaction/regeneration cycles, it was proven that ZSM-5 is an effective and stable catalyst to convert MeOH to DME. Moreover, it is highly selective when operated under appropriate conditions ($T < 190$ °C). By-products were not detected during the experimental work of this investigation. Moreover, the effect of heat and mass transfer, inside and outside the catalyst particle, were evaluated using Weisz-Prater number, and criteria from Mears and Anderson. All criteria were met; thus, it was concluded that experimental tests were done in the kinetic regime.

In reference to the kinetic models, there wasn’t a significant difference between the performance of the modified models of Gates & Johanson, Klusáček & Schneider, and the model of Ha et al. [19]. The kinetic parameters estimated with these models had physical and statistical significance. However, on the basis of the analysis made in this study, by means of a recommendation from Vannice et al. [160] on adsorption entropies and Akaike’s information criterion [162], it is concluded that the modification applied to the model of Klusáček & Schneider results a kinetic equation that is robust and provides excellent performance in the description of methanol to DME conversion over ZSM-5. This supports a mechanism with dissociative adsorption of methanol and a surface reaction as rate determining step. It should be emphasized that kinetic and adsorption parameters, from the modified model of Klusáček & Schneider, fulfilled all physicochemical constraints and recommendations, and the enthalpies of adsorption were in good agreement with independent data of adsorption on ZSM-5 and DFT studies.

Finally, the effect of operating conditions was considered to determine the true activation energy and order of the reaction with respect to methanol and water. It was shown that the true activation energy, calculated in this work, comes close to the value estimated by [207] via DFT calculations. Moreover, it was shown that the order of the reaction with respect to methanol is positive, whereas the order with respect to water is negative. The latter agrees with the reported inhibiting effect of water on the MeOH to DME conversion.
A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales.

Marie Curie (1867-1934)
4.1 Introduction

The conversion of DME to hydrocarbons has gained attention in recent years because of the advantages that DME provides in the valorization of feed streams of low H₂/CO ratio, which are formed from feedstocks such as biomass or coal. Also, this process is relevant because the reaction rate of DME to hydrocarbons is significantly higher than that of methanol and this could reduce the footprint necessary to achieve the same conversion [208]. In fact, in the conventional fixed bed technology that uses methanol as feed, the methanol is first converted to DME in a dehydration reactor, which is followed by the gasoline synthesis reactors (see section 1.4.1). This means that in the conventional fixed bed technology DME is the main component of the feed that is sent to the gasoline synthesis units, hence its importance.

In addition, Martinez et al. [208] have shown that under isothermal conditions, the deactivation rate of the catalyst used for the conversion of DME to hydrocarbons is much slower than the deactivation rate observed when methanol is used as starting material, which could bring further benefits from the operational point of view.

In this chapter, the aim is to study the effect of process variables on the conversion of DME to hydrocarbons. In the conversion process, water is released, which further reacts with DME to form methanol in an endothermic process. The overall reactions of DME to hydrocarbons and to methanol are shown in equations (4-1) and (4-2).

\[
\begin{align*}
\text{CH}_3\text{OCH}_3 & \rightarrow C_2 - C_5 \text{ olefins} + H_2O \rightarrow \text{Paraffins} + \text{Aromatics} \\
\text{CH}_3\text{OCH}_3 + H_2O & \leftrightarrow 2\text{CH}_3\text{OH}
\end{align*}
\]

The evaluation of process variables was carried out on three catalysts with different acidity. By the end of this chapter, it will be shown that acidity, and process parameters such as reaction temperature, pressure, and space velocity play simultaneous roles that define catalyst performance.

This chapter provides initially a physicochemical characterization of the three catalysts used in the process parameter evaluation followed by the analysis of the performance of these catalysts analyzed under quasi-adiabatic conditions. It is shown that heat effects in the catalytic bed play a major role on catalyst performance and might falsify the true effect of process parameters. It will be shown how quasi-isothermal operation could be achieved and how the effect of rapid catalyst deactivation was addressed, which allowed an assessment of the effect of process parameters in the absence of catalyst deactivation by extrapolation of experimental data to time zero on stream (details are provided in Chapter 5).

4.2 Experimental summary

Materials and methods

A detailed description of the materials and methods discussed in this chapter were presented in Chapter 2. Therefore, only a short explanation is provided below.

Three catalysts were investigated below: a commercial ZSM-5 catalyst with a SiO₂/Al₂O₃ of 23, a commercial ZSM-5 sample with a SiO₂/Al₂O₃ of 58 and a ZSM-5 catalyst supplied by the University of Warwick with a SiO₂/Al₂O₃ of 100. Hereafter, these solids are referred as ZSM5-SAR23, ZSM5-SAR58 and ZSM5-SAR100, respectively. The physicochemical properties of the catalyst were evaluated by different techniques, including argon physisorption at 87 K, X-ray diffraction spectroscopy XRD, and temperature programmed desorption of ammonia.

Performance tests were carried out in the semi-automated equipment, which could be operated in singles-pass or recycle-pass mode. Process variables such as temperature, pressure, flow rate of reactants, flow rate of auxiliary gases and pump speed were monitored and controlled via PID controllers and LabVIEW, from National Instruments Corporation. A schematic representation of the experimental set-up is shown in Figure 4-1. A P&ID and details of the equipment are provided in Chapter 2.

![Figure 4-1. Set-up for the conversion of MeOH and DME to hydrocarbons.](image-url)
Definition of basic equations

The conversion of DME to hydrocarbons can be interpreted by equations (4-1) and (4-2). In the first equation, DME is converted to hydrocarbons and in that process, water is released. Once water is present in the medium, it can react with DME to form methanol, according to equation (4-2).

As explained in Chapter 1, both DME and methanol are decomposed in the surface of the zeolite to form methoxy species which react further to produce the hydrocarbon species. Therefore, the discussion of methanol conversion or DME conversion alone is not constructive. In general, the conversion of a lump species (Oxygenates) is considered as the preferred way to account for both methanol and DME simultaneously. This is given in equation (4-3).

\[
\frac{\text{Total MeOH equivalent} - \text{Hydrocarbons MeOH equivalent}}{\text{Total MeOH equivalent}} = (4-3)
\]

4.3 Results and Discussion

4.3.1 Catalyst characterization

Textural properties

Textural properties were determined via Ar physisorption analysis at 87 K. Calculation of surface area, pore volume and pore size distribution were determined from nonlocal density functional theory (NLDFT) \[209, 210, 211\]. The results are shown in Figure 4-2 for the three samples under consideration. It can be observed on graphs A1, B1 and C1 that all three catalysts show isotherms of Type I, characteristic of microporous materials \[167, 168\]. In the case of materials ZSM5-SAR58 and ZSM5-SAR100, a mixed behavior is observed, since the adsorption/desorption curves also show a slight similarity to type II isotherms, characteristic of macroporous solids \[167, 168\].

The mixed behavior is explained by two Ar filling stages, as was explained in Chapter 3. In the first stage, micropore filling occurs and a steep increase of adsorbed volume is observed through capillary condensation at low relative pressure (p/p₀), followed by a plateau \[167, 168, 169\].
In the second stage, unconstrained adsorption in mono- and multilayers occurs, evident by a steep increase at \( p/p_0 \) close to 1. In the absence of other pore structures, a Type II isotherm behavior would be observed, distinctive of macroporous or non-porous solids \[167\]. This behavior is observed for the ZSM5-SAR58, which is depicted in graph B1. For the ZSM5-SAR100 catalyst, the increase in adsorbed volume close to \( p/p_0 = 1 \) is not so pronounced, and it is related to mesoporosity present in this sample. Thus, a smoother transition is observed between the microporous and macroporous behavior.

In these plots, the hysteresis loops (desorption isotherm) almost overlap with the adsorption isotherms. They show an H4 loop type, characteristic also of microporous materials \[167\]. In addition, on graphs A2, B2 and C2 it is clearly shown that the average pore diameter in the three zeolites is 5 Å, in agreement with known channel diameter of MFI type zeolites, in the range of 5.1 to 5.6 Å \[14\].

A summary of the textural properties, surface area and pore volume, of the three catalysts is presented Table 4-1. It is worth noting that the material with lowest aluminum content (highest SiO\(_2\)/Al\(_2\)O\(_3\)) had the highest BET surface area and the highest pore volume. These results are used in section 4.3.2 for the interpretation of the experiments, when the catalyst stability is related to its acidic properties and mesoporosity.

### Table 4-1. Textural properties of catalyst.

<table>
<thead>
<tr>
<th>Property</th>
<th>ZSM5-SAR23</th>
<th>ZSM5-SAR58</th>
<th>ZSM5-SAR100</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m(^2)·g(^{-1}))</td>
<td>323.6</td>
<td>262.4</td>
<td>330.8</td>
</tr>
<tr>
<td>DFT pore area (m(^2)·g(^{-1}))</td>
<td>527.9</td>
<td>452.0</td>
<td>502.9</td>
</tr>
<tr>
<td>DFT pore volume (cm(^3)·g(^{-1}))</td>
<td>0.18309</td>
<td>0.18145</td>
<td>0.24023</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) spectroscopy

The catalysts were analyzed via XRD spectroscopy to confirm the MFI structure. The results are shown in Figure 4-3, for the samples ZSM5-SAR23 (curve a), ZSM5-SAR58 (curve b), ZSM5-SAR100 (curve c) and a simulated reference material (curve d), see \[42, 43\]. The good correlation between the diffractograms of the samples with the reference material indicates that all catalyst samples have an MFI structure. This inference is in fact confirmed by the strong characteristic peaks at low 2\( \theta \) reflection, namely at 7.94\(^\circ\) and 8.90\(^\circ\), corresponding to Miller indices [hkl] of [011] and [200] of calcined ZSM-5, respectively \[40, 43\].

Temperature program desorption of ammonia (NH\(_3\)-TPD)

Acidity of the solid materials was characterized via temperature programmed desorption of ammonia (NH\(_3\)-TPD) \[173\]. In the conversion of oxygenates to hydrocarbons, the acidity is a key property that affects the catalyst activity and stability.

In Figure 4-4, profiles of NH\(_3\)-TPD for the ZSM5-SAR23 catalyst are shown. Graph (A), shows the TPD profile as function of temperature. In this case, the adsorption of NH\(_3\) was carried out at 100 °C. After saturation, the temperature was lowered to 50 °C and the TPD was started using a heating rate of 10 °C·min\(^{-1}\). Experimental details were provided in Chapter 2. The results are characteristic for ZSM5 zeolites \[212\], with two peaks clearly identified. One peak is found at ca 195 °C (low temperature peak \[174\]), attributed to Lewis acidity and/or weak Brønsted acidity \[168\], and another one at higher temperature, ca 395 °C, corresponding to strong Brønsted acid sites, and not Lewis acid sites \[168, 174\]. A shift in the base line is observed above 600 °C which can be partially attributed to desorption of ammonia from strong Lewis acid sites \[174\]. These results are in accordance with literature \[169, 170, 174, 175\].

In graph (B) of Figure 4-4, the desorption of ammonia from the sample is plotted versus time. In this case, the saturation of the sample with ammonia was carried out at 230 °C,
to favor the adsorption of the base only on strong acid sites. These plots were used in the calculation of experimental acidity. In this respect, Niwa et al. [213] showed that the area below the TPD curve expressed as NH$_3$ concentration ($C_{NH_3,g}$) versus temperature depends on the heating rate ($\beta$), the carrier gas flow ($F$), the sample weight ($W$) and the acid concentration ($A_0$) in accordance to equation (4-4)

\[ C_{NH_3,g} = \beta \cdot A_0 \cdot W \cdot \frac{d\theta}{dT} \]  

In consequence, quantitative calculations can be made from TPD curves expressed versus time or versus temperature if the heating rate is considered. The experimental and measured acidity values for the ZSM5-SAR23 sample are reported in Table 4-2. Similar results are shown in Figure 4-5 and Figure 4-6 for the catalysts ZSM5-SAR58 and ZSM5-SAR100. Characteristic peaks at low and high temperature were observed (170 °C and 330 °C for ZSM5-SAR58, and 187 and 364 °C ZSM5-SAR100), when the adsorption of ammonia took place at 100 °C.

The low temperature peak almost vanished when the adsorption of ammonia took place at 230 °C (Graph (B) in Figure 4-5 and Figure 4-6), similar to the behavior observed for the ZSM5-SAR23 catalyst. The TCD signals measured as function of time were used to determine the acidity value and to compare with theory, as shown in Table 4-2. Good agreement is observed between experimental and theoretical values, with deviations of less than 10 %, similar to those reported by Al-Dughaither et al. [170].
Table 4-2. Theoretical and calculated acidity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular weight [MW] (g mol⁻¹)</th>
<th>Acidity (µmol NH₃/g HZSM-5)</th>
<th>Acidity ratio measured/ theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM5-SAR23</td>
<td>1485</td>
<td>693</td>
<td>673</td>
</tr>
<tr>
<td>ZSM5-SAR58</td>
<td>3588</td>
<td>251</td>
<td>279</td>
</tr>
<tr>
<td>ZSM5-SAR100</td>
<td>6111</td>
<td>181</td>
<td>164</td>
</tr>
</tbody>
</table>

4.3.2 Catalyst performance

Overview of reaction and product distribution

In this section, an overview of the phenomena observed initially for the DME-to-hydrocarbons (DtH) reaction is provided for the three catalysts with different SiO₂/Al₂O₃ ranging from 23 to 100. The catalysts were tested for a period of 24 h, in a single-pass mode, under quasi-adiabatic conditions. In this period, 19 samples of the reactor product stream were analyzed via GC, in intervals of 80 min. Details of the experimental procedure are provided in section 2.4.4.

Under quasiadiabatic conditions, temperature profiles developed in the catalytic bed. Therefore, the interpretation of results also accounts for heat effects as reported by Yarulina et al. [118]. The results of catalyst performance are reported as conversion of oxygenates (x₀ₓᵧᵧᵧ) and mass fraction of the hydrocarbon product stream (hydrocarbon distribution). The latter means, that the desired mass fraction of component/lump (Xᵢ) is calculated dividing its mass flow rate (mᵢ) by the total mass flow rate of hydrocarbons in the product stream (m_HC), as shown in equation (4-5). This is a typical approach applied frequently in the literature [214, 215, 216]. Therefore, neither oxygenates nor water are considered in the calculation of the mass fractions. This allows a direct comparison of results based only on the hydrocarbon product stream.

\[
Xᵢ = \frac{mᵢ}{m_HC} \tag{4-5}
\]

In Figure 4-7 the results as obtained for the ZSM5-SAR23 catalyst are shown. The composition of the hydrocarbon fraction is described by four lumps: (i) C₁-C₄; (ii) C₅-C₇; (iii) C₈-C₁₁; and (iv) C₁₁⁺. In the first three hours of the reaction we can observe a drastic change in product composition that is related to the temperature profile that develops on the catalytic bed and the dramatic deactivation of the catalyst. In the first 15 min of the reaction, the catalytic bed temperature raised from an initial temperature of 350 °C to 426 °C (see Figure 4-8). This high temperature favored the formation of light hydrocarbons, in accordance with observation made by [217, 218], which translated into an initial C₁-C₄ fraction of almost 55 %, measured 20 min after the reaction started.

As the reaction proceeds, the catalyst deactivates due to coke formation and this translates into a decrease in the conversion with time [219, 220, 221]. In fact, it has been established in literature that coke forms in the initial part of the catalytic bed (close to the inlet of reactants), and a “coke front” develops and travels through the bed [222, 223]. Then, deactivation gets more obvious also in the product composition when the coke front reaches the end of the bed and unconverted oxygenates are observed. In the case of the ZSM5-SAR23 sample, the coke builds up so fast that even in the initial stage of the reaction (t < 3 h), the conversion of oxygenates dropped from approximately 90 to 22 % (Figure 4-7). In this same period, the temperature of the bed dropped from 426 °C to ~360 °C. This decrease in temperature originates from a reduction of the heat released by the reaction (less conversion). Irreversible deactivation via dealumination was not further considered for discussion, since it has been reported to be insignificant at reaction temperatures below 500 °C [224].

![Figure 4-7. Quasiadiabatic test reaction in a single-pass test of 24 h. ZSM5-SAR23, WHSV = 10 h⁻¹, Tᵢₙᵢ = 350 °C, Pᵣᵢ = 1 bar, pure DME in feed.](image-url)
The sharp temperature decrease translated also into a dramatic change of the product distribution. The light fraction (C_1-C_4) concentration dropped from 55 % to 40 %, while the C_5-C_7 fraction increased from 13 % to 27 %. The higher fractions C_8+ did not show significant changes in this initial period.

In the period 3 h ≤ TOS ≤ 10 h, the conversion of oxygenates drops from 22 % to ~3 %. This reduction of oxygenates conversion translated into a decrease in bed temperature from ~360 °C to ~352 °C. In this period, the product distribution remained relatively stable, where C_1-C_4 represented close to 40 % products, while the C_5+ accounted for the remaining 60 %.

After 15 h, the conversion of oxygenates drops below 1 %. Light hydrocarbons (C_1-C_4) are the main products formed with a continuous increase in selectivity that reached more than 90 % after 20 h of reaction. The increase in the C_1-C_4 hydrocarbons occurs at the expense of the heavier fractions, which rapidly decrease after 15 h of TOS. The sudden change in selectivity with small further change in conversion could be related to the progressive deactivation of the catalytic bed. After 15 h, probably all the catalyst was deactivated by coke formation. The coke that builds up in the zeolite blocks the pores and limits diffusion [225], which has a bigger impact on larger molecules. Owing to these diffusion limitations the formation of small hydrocarbons is favored [226].

The dynamic behavior of this zeolite is related to its acidic properties. The use of a less acidic catalyst leads to a more stable behavior. The product composition over ZSM-5 catalyst with SiO_2/Al_2O_3 = 58, and SiO_2/Al_2O_3 = 100 are shown below.

In Figure 4-9, the results of hydrocarbon product distribution and the oxygenates conversion are shown for the catalyst ZSM5-SAR58. The mass fractions of the different product lumps show slight changes over time, in contrast to the behavior observed on the ZSM5-SAR23 catalyst. In the initial stage of the experiment a sharp increase of the bed temperature is observed (see Figure 4-10), which originates from the heat released by the reaction. The high temperature in the catalytic bed favored the formation of the C_1-C_4 fraction, which represented ~50 wt.% of the initial hydrocarbon product.

As the reaction proceeds, the catalyst deactivates and the conversion of oxygenates progressively decreases. This decrease reduces the heat released in the bed and as a consequence the temperature inside the reactor also decreases. This also affected the product distribution, causing a reduction in the C_1-C_4 fraction to ~40 wt.%, while the C_5-C_7 hydrocarbons increased from ~20 to ~30 wt.%.

However, the ZSM5-SAR58 catalyst was more stable than the ZSM5-SAR23 sample. The oxygenates conversion in the ZSM5-SAR58 catalysts was > 95 % for at least 4 h, while in the same period the conversion of the ZSM5-SAR23 decreased to 22 %. This slower decrease in conversion also translates into a slower decrease in catalyst bed temperature as shown in Figure 4-10.

The different behavior the two catalysts is also related to their different textural properties. In the case of ZSM5-SAR23 only microporosity was observed. Therefore, as soon as coke starts to form, it will block pores and limit diffusion of reactants into the zeolite crystallites.
Chapter 4

In contrast the ZSM5-SAR58 catalyst showed indications of macroporosity which facilitates the transport of reactants, in spite of coke formation, and allows higher conversions over time.

![Figure 4-10. Catalytic bed temperature profile. Catalyst ZSM5-SAR58.](image)

The best catalytic performance was observed for the sample ZSM5-SAR100. The observed product distribution and oxygenates conversion are shown in Figure 4-11. The product distribution was even more stable compared to ZSM5-SAR58. In a period of 24 h, the C1-C4 fraction slightly decreased from 42 wt.% to 39 wt.%, while the C5-C7 fraction increase from 29 wt.% to 33 wt.%. In the same period, the C8-C11 fraction showed a slight decrease of ca 2 wt.%.

As can be expected from the changes of product distribution this catalyst showed the best performance with regard to stability. In a period of 24 h, the oxygenates conversion decreased from 100 % only to 74 %.

The stable conversion also translates into a more stable reactor bed temperature which is shown in Figure 4-12. As in the previous cases, the catalyst bed temperature at the inlet rapidly increases initially but only from 350 °C to 400 °C, well below the ca 420 °C observed for the other two catalysts. The lower temperature increase results in longer lifetime owing to slower deactivation rates at lower reaction temperatures [118, 227].

The lower temperature increase could be partially related the lower acidity and to the ~30 % higher pore volume of the ZSM5-SAR100 sample, (see Table 4-1). The higher pore volume translates into lower catalyst density and this turns into a lower heat released per unit volume (the same mass of catalysts was used in each experiment), which can influence catalyst lifetime [118].

![Figure 4-11. Quasiadiabatic test reaction in a single-pass test of 24 h. ZSM5-SAR100, WHSV = 10 h⁻¹, Tini = 350 °C, P = 1 bar, pure DME in feed.](image)

Similar to the analysis shown above, the different behavior of the ZSM5-SAR100 originates from its mesoporosity which was induced during the synthesis procedure (catalyst supplied by University of Warwick) to produce a hierarchically structure zeolite [228]. The hierarchically structure is given by a combination of the micropores of the MFI structure and induced mesopores which facilitate the transportation of reactants and products [228]. Improved transport properties also render better accessibility and consequently longer lifetime in accordance with observations made by other authors [227].

In spite of different acid strength of the active sites (see Table 4-2), similar selectivities were observed for ZSM5-SAR58 and ZSM5-SAR100, which is in accordance with Michels et al. [227].

The performance of the samples described above was also compared by the coke content in the spent catalysts (samples obtained after the 24 h runs). In Figure 4-13 the results of thermogravimetric analysis (TGA) for the fresh and spent samples are shown. The fresh samples present different weight losses related mainly to water released during the temperature treatment of the TGA, while the weight losses observed for the spent samples relates to coke removed by oxidation during the analysis. The spent ZSM5-SAR23 and ZSM5-SAR58 catalysts showed similar TGA profiles, see Figure 4-13 (A) and (B). The analysis indicates that both samples contained comparable amounts of coke, ca 12 wt. % each, which is similar to values found for fully deactivated ZSM-5 samples elsewhere [222,
In spite of the similar coke content, the ZSM5-SAR58 catalyst showed lower loss of activity than the ZSM5-SAR23 sample which could originate from the higher macroporosity and improved accessibility of the active sites of this sample as discussed above [118, 228].

Figure 4-12. Catalytic bed temperature profile. Catalyst ZSM5-SAR100.

As shown above, the sample ZSM5-SAR100 showed the best performance with regard to lifetime and a more stable product distribution during the 24 h test. The TGA analysis shows that this samples contained ca 8 wt.% coke after the 24 h test. A lower amount of coke was expected, since this catalyst remained active during the 24 h test, and because a higher SAR ratio is known to generate less coke under similar reaction conditions [226]. The lower reaction temperature observed for ZSM5-SAR100 (see Figure 4-12) is also in favor of lower deactivation rate [118].

Figure 4-13. Thermogravimetric analysis of fresh and spent samples (TOS = 24 h). Samples tested at WHSV = 10 h⁻¹, Tini = 350 °C, P = 1 bar, pure DME in feed.

Effect of overall pressure on product distribution

In this section, we provide an evaluation of the effect of the reaction pressure which was changed from 2.5 bar to 5.5 bar. The three samples analyzed in the previous subsection (ZSM5-SAR23, ZSM5-SAR58 and ZSM5-SAR100) were tested in single pass mode, at 350 °C, WHSV = 10 h⁻¹ and DME concentration in the feed of 16 mol %. The total reaction time was limited to 3 h and the results are shown in Figure 4-14, each graph displaying information on product distribution and oxygenates conversion.

The effect of pressure was investigated at a pressure not higher than 5.5 bar due to constraints of the experimental set-up. The results as observed for catalyst ZSM5-SAR23 are shown in Figure 4-14, graphs A1 and B1. At 2.5 and 5.5 bar reaction pressure, the catalyst ZSM5-SAR23 showed a similar decay of the conversion from ~70 % to ~30 %. Again, the fast deactivation is related to coke formation on the zeolite [219, 224]. The amount of coke was measured via TGA and the results are shown in Figure 4-15, graph (A) indicating similar coke build-up. The major changes are observed in the product distribution. In particular, the selectivity to C1-C4 fraction decreased while the C5+ increased as the pressure was increased from 2.5 bar to 5.5 bar, in accordance with observations made by other authors [216].

The catalysts ZSM5-SAR58 and ZSM5-SAR100 showed somewhat different behavior than the ZSM5-SAR23 sample. The results are shown in Figure 4-14, graphs A2 to B3. In agreement with the results shown in the previous section the samples ZSM5-SAR58 and ZSM5-SAR100 are more stable than the ZSM5-SAR23 catalyst.

The TGA results for the catalyst ZSM5-SAR23 after 24 h on stream (Figure 4-13) and 3 h on stream (Figure 4-15) are remarkably similar. According to Rojo-Gama et al. [230], once breakthrough of oxygenates is observed, the coke content only increases slightly. Therefore, it is concluded that for this catalyst almost all the coke is formed in the first three hours of reaction. A different behavior is observed for the samples ZSM5-SAR58 and ZSM5-SAR100, which showed a larger coke content when the reaction was carried out for a longer period of time (3 h vs 24 h).
Chapter 4: DME Conversion to Hydrocarbons

In addition, in Figure 4-15 we observe the effect of pressure on the amount of coke that accumulates on the catalyst. It is clearly shown for graphs (B) and (C) that the amount of coke increases with an increase in operating pressure, in accordance with results presented by other authors [222]. This effect cannot be observed for the ZSM5-SAR23 sample, because the faster deactivation translates into a catalyst blocked with coke [230].

It worth noting that the conversion and product distribution discussed here vary from those shown in the previous section. The changes observed mainly originate from the differences of temperature in the catalyst bed. In the quasi adiabatic tests (previous section) temperature rise were in the order of 50 °C to 70 °C, while the tests shown in this section presented only a slight increase in temperature and the reactions were kept at 350 °C with a maximum deviation of 4 °C. It is quite obviously that the reaction temperature strongly affects the stability of the catalyst and the selectivity towards the products [118].

In single pass mode the catalytic bed is subject to certain temperature and well-developed concentration profiles with at least two reaction fronts inside the catalyst bed. The first profile is related to the dehydration of oxygenates and the second profile reflects the reaction of the intermediate products [223]. As typical for an integral reactor, only the integral performance of the catalyst can be observed at the reactor outlet.

To overcome these issues, tests in recycle operation were performed. The recycle operation allowed gradientless reaction conditions; thus, the catalyst is tested under a well-defined temperature and concentration. The following investigations were performed only with the ZSM-5 SAR58, since this catalyst was used for kinetic analysis (see Chapter 6).
4.3.3 Effect of process parameter on product distribution at t = 0

Several factors can induce changes in yield and selectivity during the conversion of oxygenates to hydrocarbons. The observations discussed in this section utilize data which have been obtained at three different molar fractions of DME in the feed (0.1, 0.5 and 1) and a total pressure of 1 bar. The data have been extrapolated to time = 0. That means, that deactivation effects are not considered. The extrapolation of data was carried out for each particular experiment by means of second order polynomials. In Chapter 5, details will be provided to justify this procedure.

Figure 4-16 shows the partial pressure of MeOH and DME as determined at different temperatures and space velocities.

It can be seen that independent of the partial pressure of DME in the feed, as soon as the reaction proceeds (conversion of oxygenates > 0), the partial pressure of DME dramatically decreases and that of MeOH increases. The result is in accordance with the work of Chang et al. [73] and originates from the reaction of DME with H₂O to form MeOH. The behavior is equally observed for all reaction conditions and it seems to be independent of the partial pressure of DME in the feed.

In the discussion below, we only consider hydrocarbon product distribution, since the main goal was to understand the effect of process variables on product selectivities.

Effect of temperature on product distribution

The effect of temperature on product distribution is shown in Figure 4-17. The data shown in this figure were obtained at a WHSV = 25 h⁻¹, a total pressure of 1 bar, and temperatures of 325 °C, 350 °C and 375 °C. In addition, graphs (A), (B) and (C) correspond to experiments made with a molar fraction of DME in the feed of 0.1, 0.5 and 1.0, respectively.

In Figure 4-17 results are reported as mass fraction of the different product lumps (Xᵢ), which are calculated according to equation (4-5). That means, neither oxygenates nor water are considered in the calculation. The product distribution is represented in three main cuts: C₂⁻⁻C₄⁺ fraction (ethylene, propylene and butenes), LPG (liquefied petroleum gas) fraction that groups propane and butanes, and C₅⁺ fraction that represents the liquid hydrocarbons cut. A fourth fraction was initially considered in the analysis which represented light gases (methane and ethane). This light gas fraction was not considered since it was below 0.1 wt. % for all cases.

At the lowest temperature the predominant fraction are the light olefins (ethylene, propylene and butylenes). This is in accordance with previously reported results [73]. Under these conditions, the mass fraction of oxygenates in the product stream was 0.74. When the temperature was increased from 325 °C to 350 °C and to 375 °C, the reaction rates increased and the mass fraction of oxygenates in the product decreased from 0.74 to 0.27 and 0.13.

With increasing conversion of oxygenates, the C₂⁻⁻C₄⁺ fraction decreased, while an increase in the saturated C₃⁻⁻C₄⁺ compounds and of the in the C₅⁺ fraction was observed, in agreement with results reported by Chang and Silvestri [73, 218]. Dehertog and Froment [218] explained that the maximum amount of C₂⁻⁻C₄⁺ olefins can be obtained over zeolites with high Si/Al ratio in the range of 250. At lower Si/Al, which is the case in this study, the acid site density is too high and intermediates products (small olefins) easily react further to form higher alkanes, by hydrogen transfer [217, 218], and aromatics. The increase in the C₃⁻⁻C₄⁺ fraction is related to an acceleration of the hydrogen transfer reactions. of the kinetic analysis of the reaction rates is provided in Chapter 6.
The reaction temperature was limited to 375 °C here. At higher temperatures, other authors [70, 214, 231] have observed an increase in olefins C\textsubscript{2}−C\textsubscript{4} formation. This indicates that, depending on the WHSV, acid site density, and partial pressure of reactants, the ethylene/propylene concentration goes through a minimum in the range of 325 °C – 375 °C, which is obviously the optimum temperature range to maximize the selectivity towards C\textsubscript{5+} hydrocarbons, when the target product are species in the gasoline boiling range.

In Figure 4-17 (B) and (C) results are shown for experiments carried out with DME partial pressure in the feed of 0.5 bar and 1 bar. The results show similar trends compared to Figure 4-17 (A). Only slight differences in the behavior are observed for the different partial pressure of the reactant in the feed.

**Effect of WHSV on product distribution**

Using equation (2-5), it is possible to make a clear interpretation of the effect of WHSV on product distribution, which has been depicted in Figure 4-18. In this figure, the effect of space velocity on product distribution is shown at 25 h\textsuperscript{-1}, 75 h\textsuperscript{-1} and 125 h\textsuperscript{-1}, which corresponds to graphs (A), (B) and (C) respectively. The product distribution is represented in the three main fractions as described in the previous section.

In Figure 4-18 experiments obtained at a partial pressure of DME in the feed of 0.1 bar are shown. We can observe that the C\textsubscript{2}−C\textsubscript{4} fraction increases as the WHSV changes from 25 h\textsuperscript{-1} to 125 h\textsuperscript{-1}, at the expense of the LPG and C\textsubscript{5+} fraction, which is in agreement with results from other authors [70, 73, 232]. The behavior is characteristic of intermediate species in a set of reactions in series, and it agrees with the reaction scheme shown in equation (4-1). In a simplistic form, equation (4-1) could be reformulated as equation (4-6), with A, B and C as the oxygenates, olefins and rest of hydrocarbons fraction, respectively. Given that B is an intermediate (the olefins cut), its concentration in the system depends on the two kinetic constants k\textsubscript{1}, k\textsubscript{2}, and the residence time. For a CSTR this is described by equation (4-7) [130]. In this equation, the residence time is a quadratic term in the denominator; therefore, a decrease in its value (shorter contact time = larger WHSV) translates into an increase of the intermediate product.
\[
A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{4-6}
\]

\[
\frac{C_B}{C_A_0} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \tag{4-7}
\]

The same conclusions can be drawn for graphs (B) and (C) of Figure 4-18. Similar trends were observed for other sets of conditions that involved lower and higher temperatures (from 325 °C to 375 °C) and WHSV values from 33 h\(^{-1}\) to 100 h\(^{-1}\). The plots under analysis correspond to a temperature of 350 °C, which is a typical inlet temperature of an industrial oxygenates to hydrocarbons reactor (see section 1.4).

**Effect of reactant (DME) feed partial pressure on product distribution**

The effect of DME partial pressure in the feed \(p_{\text{DME,0}}\) on product distribution is shown in Figure 4-19. The data shown in this figure were obtained at a WHSV = 25 h\(^{-1}\), a total pressure of 1 bar, and temperatures of 325 °C, 350 °C and 375 °C, corresponding to graphs (A), (B) and (C), respectively. Similar to the previous plots, the species quantities are shown as mass fraction of the different lumps \(X_i\), which are calculated according to equation (4-5).

Figure 4-19 (A) shows that the light olefin fraction \((C_2^- - C_4^-)\) is favored at the lowest partial pressure of DME in the feed \(p_{\text{DME,0}}\) (0.1 bar), in agreement with results shown by other authors [70, 216, 218] for the conversion of methanol to hydrocarbons. At 325 °C, the light olefins represent almost 60% of the hydrocarbon product. This value quickly decays to values below 50% as \(p_{\text{DME,0}}\) increases to 0.5 bar and 1 bar. It has been reported that an increase in partial pressure increases the gasoline yield \((C_5^+\) by favoring the formation of higher hydrocarbons via oligomerization and aromatization reactions [232, 233]. Inoue [234] has attributed these changes to shifts in chemical kinetics and favored thermodynamics for oligomerization reactions at higher partial pressures.

From these results we conclude that similar effects on the product distribution are observed when the partial pressure of DME in the feed is decreased and when the reaction temperature is increased, in accordance with observations made by other authors in the conversion of methanol to hydrocarbons [218].
4.4 Conclusions

In the conversion of DME to hydrocarbons, the performance of the catalyst can be greatly affected by process parameters, reactor operation mode (adiabatic or isothermal, differential or integral) and the intrinsic physicochemical properties of the catalyst.

We showed that catalysts tested under quasi-adiabatic conditions are greatly affected by the temperature profiles that developed in the catalytic bed (heat effects). A dramatic impact was observed on catalyst stability and selectivity. The magnitude of these effect varied from one catalyst sample to the other, which mainly differed in their acidic properties. The most acidic catalysts deactivated the fastest than the least acidic one showed the slowest deactivation.

We conclude that assessment of the effects of process parameters on highly exothermic reactions and fast deactivating catalysts cannot be assess with simple tests in an integral reactor. A catalyst tested under these conditions will be subject to different simultaneous processes happening at once, that make it cumbersome to discern the real effect of process variables. Therefore, our approach was to test the catalyst under isothermal conditions, in a differential reactor and extrapolate the measured values to time on stream zero (0), when deactivation effects are negligible.

Our observations allow us to conclude that deactivation of the catalysts occurs faster if the reaction temperature is high, if the reactor operates in single pass mode as integral reactor, if the reactor operates under adiabatic or quasiadiabatic conditions, at low space velocities (long contact times), and at high partial pressure of reactant in the feed.

In addition, the formation of C₅⁺ was favored when the reaction temperature was relatively high (up to 375 °C), the molar fraction of DME in the feed was 1, and the space velocity was slow, i.e. at long contact times. These observations agreed with expected results for a set of reactions that occur in series, and when the desired product is not an intermediate, but the final product of the reaction sequence.
CHAPTER 5

Catalyst deactivation during DME conversion to hydrocarbons

“All models are wrong but some are use full”

George Box (1919-2013)

Robustness in the Strategy of Scientific Model Building, Technical summary rept. (1979)
5.1 Introduction

A catalyst may deactivate by different mechanisms including poisoning, leaching or coking, some of them having a reversible or permanent effect \[235, 236, 237, 238, 239\]. During the conversion of oxygenates to hydrocarbons, the ZSM-5 catalyst could suffer from permanent deactivation via dealumination, and reversible deactivation due to coke formation \[84, 125\]. Understanding the catalyst stability is of critical importance, since it affects the economics of the process \[92\] by decreasing product yield and shifts in selectivities \[92\].

In this chapter, our goal is to understand how deactivation affects selectivity and how to properly extrapolate data to time zero (t = 0), so that information on the fresh catalyst is obtained, as explained by \[240, 241, 242\]. These data will then be used in Chapter 6 to perform a kinetic analysis of the DME conversion to hydrocarbons. For this reason, we have performed tests in a gradientless recycle reactor, in short test runs of 3 h and the data have been extrapolated to time zero (0) on stream. For the extrapolation process a best choice was selected out of several deactivation functions and polynomials.

5.2 Experimental summary

**Materials and methods**

A detailed description of the materials and methods discussed here were provided in Chapter 2. Therefore, only a short explanation is provided below.

One catalyst was used in the analysis and discussion that follows, namely the commercial ZSM-5 catalyst with a SiO\(_2\)/Al\(_2\)O\(_3\) of 58 named hereafter ZSM5-SARS8. The physicochemical properties of the catalyst were evaluated by different techniques, including argon physisorption at 87 K, X-ray diffraction spectroscopy XRD, and temperature program desorption of ammonia. The results of this characterization were shown in section 4.3.1.

The reaction tests were carried out in a semi-automated equipment, which operated in the recycle mode. A schematic representation of the experimental set-up was shown in Figure 4-1 (Chapter 4), and a P&ID was included in Chapter 2.

It must be highlighted that for each catalytic test, 18 samples of the product stream were analyzed using a gas chromatograph (GC) equipped with a multiposition valve system. It is common practice that these reactions are carried out for several hours and only few data points are obtained at the initial stage of the reaction \[219, 220, 224, 243\]. The limitation of this approach is that the behavior of the catalyst can significantly change in the initial reaction period. With our approach using a multiposition valve system, we were able to collect data relatively fast; thus, we could capture the initial behavior of the catalyst and be confident in the extrapolation process to time zero (0) on stream.

In a typical test, the outlet stream was analyzed from time 5 min onwards. However, for extrapolation purposes the data points taken at 5 min and 10 min have been neglected. The reason is that a transient behavior was observed in the initial period of the reaction \(t \leq 10\) min. This transient state is caused by N\(_2\) initially present in the recycle reactor which is progressively displaced by reactant feed, and by an initial temperature increase which was observed at the start of the experimental runs. The extrapolation of data, avoiding initial transient conditions has been previously reported by other authors \[244, 245\].

5.3 Results and Discussions

5.3.1 Catalyst deactivation

**Deactivation process – Decay in oxygenates conversion**

Permanent deactivation via dealumination of the zeolite could occur during reaction if the temperature is high enough \[84, 118\] or during regeneration of spent catalyst by coke combustion \[229\]. In both cases, steam is generated which can lead to dealumination of the catalyst \[229, 246\]. In this study, this mechanism is not considered, since all experiments were carried at \(T \leq 375\) °C, and the effect of steam on catalyst activity can be neglected when the temperature is below 500 °C \[224\].

With regard to deactivation by coke formation, it has been reported that ZSM-5 catalysts are more resistant than other zeolites, mainly because the small pore size limits aromatics condensation \[224\] and pore blockage is limited due to the 3D interconnectivity of the zeolite pores. However, the deactivation process is still rapid. This affects oxygenates conversion and the product distribution even in the initial instant of the reaction \[242\]. Changes in selectivity can be related to different coking rates on acid sites with different
Chapter 5

Acid strengths. In fact, Aguayo et al. [247] have shown that the strong acid sites are more affected by deactivation than weaker acid sites. According to their research it seems that coke forms and builds up much faster on the strong acid sites, and once these are deactivated, coke forms at a slower rate [247].

The decay of oxygenates conversion (mentioned above) is shown in Figure 5-1. The data shown were collected at WHSV of 25 h⁻¹, 75 h⁻¹ and 125 h⁻¹, and five (5) temperatures in the range of 325 °C to 375 °C (see plot for details). It can be observed that under different operating conditions the decrease in oxygenates conversion shows different patterns, in agreement with observations made by Perez et al. [219]. This makes the extrapolation of data to \( t = 0 \) non-trivial, and the problem is addressed in a subsequent section.

Figure 5-1 shows that higher temperatures lead to faster decrease in oxygenates conversion, which translates into faster deactivation. Zaidi and Pant [232] have attributed this behavior to an increase of cracking and oligomerization reactions during the conversion of oxygenates to hydrocarbons with increasing temperature. This observation is also in agreement with results presented by other authors [232, 248]. An exception to this behavior is observed in graph (A) at WHSV = 25 h⁻¹ and \( T \geq 362 \) °C. At these conditions, the conversion was too high (\( > 90 \% \)) to gain relevant data for kinetic analysis.

\[ \text{Figure 5-1. Conversion of oxygenates versus time. Molar fraction of DME in the feed is 1 and the WHSV corresponds to (A) 25 h}^{-1}, (B) 75 h}^{-1} \text{ and (C) 125 h}^{-1}. \]

In addition, if data at the same temperature are compared (same marker in graph (A), (B), and (C)), we can clearly notice that an increase in WHSV results in a decrease in conversion in accordance with [249]. This result was expected since the contact time between reactants and catalyst is reduced as WHSV is increased. The decrease in conversion is observed from the initial instants of the reaction, in contrast to the constant plateau observed by Breken et al. [249]. The reason for the discrepancy is associated to the operation mode. Breken et al. [249] worked on a single pass fixed bed reactor, while our work was done in a gradientless recycle reactor.

Comparing data on all graphs, it seems that conversion of oxygenates decays faster at lower WHSV, in accordance with observation made by [248] for the conversion of methanol to hydrocarbons on SAPO-34. It is important to realize that deactivation of the catalyst is caused by coke formation. Coke is formed as a side product in a set of reaction in series. Therefore, longer contact times (or shorter WHSV) favors the formation of these species which deactivate the catalyst. A schematic diagram of the reaction and including coke formation is shown in Figure 5-2 (adapted from [208]).

\[ \text{Figure 5-2. Schematic diagram of the reaction.} \]

Change of lumps composition over time

The conversion of methanol/DME into hydrocarbons is characterized by a continuous catalyst deactivation. As shown above, the deactivation of the catalyst results in a decrease in conversion, see Figure 5-1, in accordance with results presented by Benito et al. [220]. The decrease of the mass fractions of the products is shown in Figure 5-3 for the light olefin fraction (ethylene, propylene and butenes), in Figure 5-5 for a fraction named LPG
and composed of propane and butanes, and in Figure 5-7 where the hydrocarbons C5+ are lumped.

![Figure 5-3](image)

**Figure 5-3.** Evolution of mass fraction of C2+-C4= olefins with time. Data collected at yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹; and (C) 125 h⁻¹.

In Figure 5-3 (A) it is possible to observe that the highest temperatures (> 362 °C) the concentration of light olefins goes through a maximum, in accordance with observation made by other authors [220, 249, 250]. The behavior is characteristic of an intermediate species. However, these data cannot be used for the kinetic analysis as mentioned above.

An interesting observation can be made from Figure 5-4, where the mass fraction of the C2+-C4= lump it is plotted versus the conversion of oxygenates. It is possible to observe that the mass fraction of the lump is independent of the space velocity and the temperature of the experiment, and it seems that the degree of conversion of oxygenates can be used a parameter to characterize the amount of small olefin that are produced in the system. Small divergencies are observed at high conversions, which again questions the applicability of these data for kinetic analysis. As will be shown in Chapter 6, under these conditions (high T and low WSVH), the reactions were in the mass transfer limited regime. Under these conditions the product distribution is also affected by the diffusion of the different species.

Figure 5-5 shows the behavior of the LPG lump, which is composed of propane and butanes. It is clearly visible that the concentration of this lump decreases with time on stream under all experimental conditions, which agrees with the observation made by Pop et al. [250]. The LPG fraction is formed by hydrogen transfer reactions, and consequently the same behavior as observed for the C2+-C4= olefins would be expected in all cases.

![Figure 5-4](image)

**Figure 5-4.** Mass fraction of C2+-C4= versus conversion of oxygenates. Experiments were performed at WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min.

However, when the data generated at low WHSV and high temperature are compared, it is observed that the olefins fraction passes through a maximum, while the LPG fraction constantly decreases with time, which allows the assumption that the hydrogen transfer reactions have little effect on the formation of light olefins.

![Figure 5-5](image)

**Figure 5-5.** Evolution of mass fraction of the LPG lump with time. Experimental conditions: yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹; and (C) 125 h⁻¹.
When all the data of the mass fraction of the LPG lump are plotted versus conversion of oxygenates (Figure 5-6), again a single curve is observed independent of reaction temperature and contact time. It is important to mention that this figure contains data of experiments performed in a period of three hours; thus, product mass fractions obtained at different catalyst activity are shown in Figure 5-6.

![Figure 5-6](image)

Figure 5-6. Mass fraction of the LPG lump versus conversion of oxygenates. Experimental conditions: WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min.

The data measured for the C₅⁺ lump is shown in Figure 5-7. The decreasing mass fraction of this lump is expected, owing to the catalyst deactivation as the reaction proceeds. It is in accordance with observations made by other authors [220, 224].

![Figure 5-7](image)

Figure 5-7. Evolution of mass fraction of the C₅⁺ lump with time. Experimental conditions: yDME in feed of 1.0, and WHSV of (A) 25 h⁻¹; (B) 75 h⁻¹; and (C) 125 h⁻¹.

Finally, the mass fraction of the C₅⁺ lump versus oxygenates conversion is presented in Figure 5-8. As in the previous cases, all measured data points form a single curve independent of process parameters such as temperature, space time or the time on stream of the sample.

![Figure 5-8](image)

Figure 5-8. Mass fraction of C₅⁺ fraction versus conversion of oxygenates. Experimental conditions: WHSV from 25 h⁻¹ to 125 h⁻¹, temperature from 325 °C to 375 °C, and time on stream of 15 min to 180 min.

Two different patterns can be observed in figures 5-3, 5-5 and 5-7. At conversions higher than 90 %, a relatively slow decrease of the mass fraction of the products LPG and C₅⁺ fractions, and an increase in the fraction of light olefins that passes through a maximum is visible. When conversion was lower than 90 %, the decay in conversion (indicated by the increasing mass fraction of oxygenates) was accompanied by a decay in product composition of all lumps, including the light olefins fraction. It seems that in this lower range of conversion, the product distribution was independent of deactivation, and in consequence of coke formation, in accordance to results presented by [249].

The high mass fraction of the C₅⁺ lump (compared to the intermediate light olefins and LPG) is assumed to originate from the DME feed used in the current investigation. At the short contact times (high space velocities) applied the C₅⁺ content in the product stream was expected to be considerably lower. However, the high C₅⁺ fraction could originate from a shifted contribution of the two synthesis cycles that operate in the dual cycle mechanism (See Chapter 1 and Chapter 6). According to Martinez-Spin et al. [208] the reaction rate of DME to hydrocarbons is faster than the methanol conversion to hydrocarbons. In addition, these authors claim that the olefin cycle could be favored when DME is used as feed.
At a high degree of conversion as observed at the highest temperatures it can be assumed that product selectivity pattern is affected by transport processes inside the zeolite which become even more dominant when coke is formed and decreases even more the size of the diffusion paths. In fact, an increase in the C2= -C3= fraction, see Figure 5-3 (A), is to be expected for species which are small enough to diffuse easily in and out of the zeolite crystals.

**Deactivation functions and extrapolation to time zero on stream**

Several empirical descriptions of the deactivation can be found in literature. These depend mainly on the deactivation mechanism observed [157]. In the case of zeolites', the decay of activity by coke formation strongly depends on the acidity and pore structure of the catalyst [251].

A quantitative description of the effect of coke content on a catalyst activity was initially provided by Voorhies [252]. This author developed an empirical equation to relate the coke content deposited on the catalyst \( C_c \) to the contact time \( t_c \), using two empirical constants \( b \) and \( n \), see (5-1). In the original work [252], the value of \( n \) was found to be in the range of 0.38 to 0.53. More recently, it has also been used to describe the deactivation of SAPO-34 during the methanol-to-olefins process [248].

\[
C_c = b \cdot t_c^n
\]  

(5-1)

The correlations of activity with contact time and coke content provide the most accurate description of the deactivation of a catalyst. However, measuring the coke content in some cases is impractical, if possible at all, especially under the conditions of a differential recycle reactor. In the present investigation, the quantification of the coke content of the samples was indeed impractical for two reasons. First, the amount sample used during experiments was relatively low; and second, the catalyst was diluted with SiC to contribute with heat dissipation and isothermal operation during catalytic tests. Separation of the spent catalyst from SiC was not possible because they were used in the same size fraction to avoid segregation of these materials during preparation of the catalytic beds. Finally, the determination of the coke content vs. time on stream would have required too many experimental runs and the advantage of the fast sampling equipment would have been lost.

In consequence, our approach was to make use of an empirical description of the catalyst deactivation that only considered the time on stream of the individual sample. The equation was developed by Mahoney [253], and it is shown in equation (5-2). It relates a variable at time \( t \), with the variable at \( t=0 \) and exponential decay function that depends on one empirical parameter and \( t^{0.5} \).

\[
x(t) = x(0) \exp(-\gamma \cdot t^{0.5})
\]  

(5-2)

This model was originally used in the description of n-heptane reforming [253], and it applicability was later extended to cumene disproportionation [254].

![Figure 5-9](image)  

**Figure 5-9.** (A) Data extrapolation; (B) Residuals from data analysis. Experimental conditions: WHSV = 125 h\(^{-1}\), yDME in feed = 0.1, and T = 325 °C.

Considering the wide applicability of equation (5-2), we adopted the equation to extrapolate data to time on stream zero (0). Two results are shown for the conditions of lowest and highest oxygenates conversion, Figure 5-9 and Figure 5-10, respectively. The oxygenates conversions were converted into rates, as explained later in Chapter 6.

For the case of low conversion, Figure 5-9 (A) shows the data (circles) and the model (solid line) show good correspondence. Data seems to be normally distributed around the model, and this is supported by the residual plot shown in Figure 5-9 (B). The regression model did not perform equally well for rate data obtained at high temperature and low space velocities, which is shown in Figure 5-10 (A). Here, we can observe that rate data and model do not share the same behavior, and the difference is even clearer in the residual plot analysis, Figure 5-10 (B). In this plot we can observe that residuals are not normally distributed which one would expect from random experimental error [153].
Extrapolation with a model that does not resemble the trend in the experimental data should be avoided. Unable to find a suitable description of the activation, we tested polynomial equations, that were fitted for each individual data set. It was then decided to utilize a general quadratic empirical fit ($y = ax^2 + bx + c$). This type of fit proved to describe the data much better. In all cases it was possible to accurately describe the observed experimental behavior, and data and models showed similar behavior. A comparison plot, for a number of experiments is shown in Figure 5-11.

**Figure 5-10**. (A) data extrapolation; (B) Residuals from data analysis. Experimental conditions: WHSV = 25 h$^{-1}$, $\gamma_{\text{DME}}$ in feed = 1.0, and $T = 375$ °C.

*Initial interpretation of extrapolated data*

Rates and compositions at $t = 0$ depend also on the kinetic scheme that is evaluated since the number of lumps and the compounds that constitute the different groups vary with each reaction scheme. In this section, we present a short summary of the results obtained for six species/lumps after data extrapolation to $t = 0$. These species have been selected because they will be used in Chapter 6 to perform the kinetic analysis.
First, on graph (A) we can observe that for a given WHSV, the mass fraction of oxygenates decreases with an increase in reaction temperature. The behavior is expected, since higher temperature renders higher reaction rates, thus the mass fraction of the feed should decrease. We can also observe that for the lowest WHSV value, there is little difference in the oxygenates mass fraction measured at 362 °C and 375 °C. This is in accordance with observations made in the previous sections. In addition, if data gained at one particular temperature are considered only, the oxygenates mass fraction increases with increasing WHSV owing to the shorter contact time.

For the graphs that describe products mass fractions, (A2) to (C2), we can observe an increase of the mass fractions with increasing temperature. At the lowest space velocity (see circle markers) propylene and ethylene show the characteristic behavior of an intermediate species passing through a maximum as the reaction proceeds. The overall behavior is characteristic of consecutive reactions.

As will be shown in detail in Chapter 6, the composition of reactants and products can be easily transformed to reaction rates of consumption or production on the basis of their mass fractions on water-free basis and the space time set in the experiments. Then, Arrhenius plots can be used to further evaluate the data. In the current section, the data analysis focuses on the oxygenates conversion rate. It was shown before (Figure 5-1) that oxygenates conversion decreased slightly when the conversion exceeded 90 %, and in Figure 5-12 (A) we observe just a minor change in oxygenates mass fraction when the temperature changes from 362 °C to 375 °C.

The Arrhenius plot for the rates for oxygenates conversion are shown Figure 5-13. The three plots correspond to different molar fractions of DME in feed, i.e. (A) $y_{DME,0} = 0.1$, (B) $y_{DME,0} = 0.5$; and (C) $y_{DME,0} = 1$. In addition, the weight hourly space velocities were varied from 25 h⁻¹ to 125 h⁻¹, and temperatures from 325 °C to 350 °C.

In the three graphs, we observe linear behavior of the oxygenates reaction rate versus the inverse of absolute temperature at the two highest space velocities (shorter contact times). The data taken at the shortest space velocity (25 h⁻¹) deviate from this behavior, and we can observe how the slope changes as temperature increases. This behavior is characteristic for a reaction rate that is limited by mass transfer limitations [189]. This behavior is observed in graphs (A), (B) and (C), meaning that it is independent of the value of $y_{DME,0}$ in the range studied in this investigation.

---

**Figure 5-12.** Lump mass fraction extrapolated to $t = 0$. (A1) Oxygenates; (A2) Ethylene; (B1) Propylene; (B2) Butenes; (C1) Propane and butanes; (C2) C₅⁺ fraction.
Chapter 5

Figure 5-13. Arrhenius plots for the rate of oxygenates conversion extrapolated to time \( t=0 \). Data measured at different WHSV in the range of 25 h\(^{-1}\) to 125 h\(^{-1}\). Graphs (A), (B), and (C) represent experiments at molar fraction of DME in the feed of 0.1, 0.5 and 1.

In the following chapter a broader discussion is provided with reference to the consumption and formation rate of the different lumps and a kinetic model is developed based on these measurements.

5.4 Conclusions

Based on the results shown in this chapter we conclude that the zeolite catalyst suffers from deactivation under all experimental conditions. The deactivation process is enhanced at high temperatures and low space velocities. This behavior was consistently observed through the range of experimental conditions considered, except for data where the oxygenates conversion was above 90 \%.

When the conversion of oxygenates was highest, the mass fraction of the olefin lump passed through a maximum, which is characteristic of intermediate species. This behavior could not be observed at lower conversions.

When mass fractions of products were plotted against oxygenates conversions, it was shown that all the data (independently of experimental conditions) followed one curve. This means that should be possible to describe the product distribution on the basis of only one parameter, the oxygenates conversion.

In reference to the description of the catalyst deactivation and the extrapolation of data to time zero (0), it was shown that the Mahoney correlation worked well at low conversion. On the contrary, its performance was poor when the conversion of oxygenates was high.

Second order polynomials proved to fit the data well and allowed a more accurate extrapolation of lump composition to time zero on stream.

We can also conclude that data obtained at WHSV = 25 h\(^{-1}\) and temperatures of 375 °C were affected by mass transport limitations. Evidence for this was provided by means of an Arrhenius plot of the oxygenates conversion data. Defining the conditions where mass transport was absent is crucial for the correct selection of experimental settings applied for the kinetic analysis in Chapter 6, which will focus on the development of the Dth kinetic model.
“How odd it is that anyone should not see that all observation must be for or against some view if it is to be of any service!”

Charles Darwin (1809 - 1882)
6.1 Introduction

Conversion of methanol and dimethyl ether (DME) to hydrocarbons provides a chemical route to convert carbon-based materials into highly valuable chemicals such as olefins ($C_2^-C_4^+$) and liquid fuels. The methanol to hydrocarbon (MTH) technology was developed by Mobil in the late 1970's, and it was first commercialized in New Zealand in the 1980's [255]. The overall reaction path was initially described by Chang and Silvestri [73], and this is depicted in equation (6-1). It consists in consecutive reactions where methanol is dehydrated to form an equilibrium mixture with dimethyl ether (DME) and water, followed by the formation of small olefins which react further to produce higher hydrocarbons. In addition, the overall reaction is exothermic, with a reaction enthalpy ($\Delta H_r$) estimated to values between 45 kJ∙mol$^{-1}$ and 54 kJ∙mol$^{-1}$ [73, 256] which depend on the degree of conversion and selectivity.

$$2CH_3OH \rightarrow CH_3OCH_3 \rightarrow C_2^-C_5 olefins \rightarrow Paraffins + Aromatics$$  \hspace{1cm} (6-1)

In the same period (late 1970’s – early 1980’s), research focused on the study of the mechanism of the reaction [257, 258] and on understanding the formation of the first carbon-carbon (C-C) bond. In reference to the latter, researchers [33, 37, 49] have recently identified surface acetates as initial intermediates containing C-C bonds. Under typical conditions of oxygenates to hydrocarbon conversion, the formation of this bond is slow [33]. However, the investigators [33] have indicated that this is enough to form traces of acetyl species (C-C bonds) and initiate the formation of a hydrocarbon pool [33], originally proposed by Dahl and Kolboe [50, 51, 52, 53, 54]. As reported by Perez et al [55], it is currently known that formation of hydrocarbons from these oxygenates (methanol and dimethyl ether) proceed in the hydrocarbon pool, via the dual cycle mechanism.

Available kinetic models [125, 240, 241, 256, 259, 260, 261] for the methanol-to-gasoline (MTG) conversion were developed before the dual cycle mechanism was known, therefore they provide little information on the main reaction steps actually taking place and on the product distribution observed.

In this work, we present a kinetic study on the conversion of DME to hydrocarbons. DME is used as feed instead of methanol because of the recent interest in this intermediate, since DME provides advantages in the valorization of feed streams with low H$_2$/CO ratio, which are formed from feedstocks such as biomass, pet-coke and coal [55, 262]. We found that kinetic models developed for the MTG reaction are little suited to describe the conversion of DME-to-hydrocarbons (DtH). Consequently, a new kinetic model has been developed to describe the conversion of DME to hydrocarbons.

6.2 Experimental summary

**Material and methods**

A detailed description of the materials and methods discussed in this chapter was provided in Chapter 2. Therefore, only a short explanation is provided below.

The catalyst used in this chapter was a commercial ZSM-5 sample with a SiO$_2$/Al$_2$O$_3$ of 58. The physicochemical properties of the catalyst were evaluated by different techniques, including argon physisorption, helium pycnometry, XRD, SEM and temperature program analysis. The results are explained in section 3.3.1. Kinetic measurements were performed in a semi-automated gradientless recycle reactor. Process variables such as temperature, pressure, flow rate of reactants, flow rate of auxiliary gases and pump speed were monitored and controlled via proportional-integral-derivative (PID) controllers and LabVIEW, from National Instruments Corporation. A schematic representation of the experimental set-up is shown in Figure 4-1. A P&ID and details of the equipment are provided in Chapter 2.

Five different temperature and WHSV values were varied in order to obtain the necessary kinetic data and understand the effect of process variables on conversion, reaction rates, and selectivity. The details of the experimental program were shown in Chapter 2.

**Definition of basic equations**

During the conversion of DME, hydrocarbons and water are formed. The overall reaction is shown in equation (6-2). The water formed can with DME and produce methanol. This is shown in equation (6-3).

$$nCH_3OCH_3 \rightarrow 2n[CH_2] + nH_2O$$  \hspace{1cm} (6-2)

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH$$  \hspace{1cm} (6-3)

It is clear that the reaction is not equimolar. There is an intrinsic change in the volume of the reacting gas as the reaction proceeds and this must be considered in the calculation
of conversion. Thus, the conversion of oxygenates (methanol + DME) is based on equivalent DME present in the feed and outlet streams and calculated according to equation (6-4). The mixture of methanol and DME is treated as a single species in accordance to \[241, 242, 256, 259\].

\[
\frac{\text{total DME equivalent IN}}{\text{total DME equivalent IN}} = \frac{\text{total DME equivalent OUT}}{\text{total DME equivalent OUT}}
\]

(6-4)

Reaction rates are calculated from mass balances in the recycle reactor, see Sedran et al [241] for details. For a component \(i\), the material balance is given by equation (6-5). There is no accumulation of species in the system (\(\text{Accumulation} = 0\)), and the “±” sign depends on whether species \(i\) is produced or consumed in the process.

\[
m_{\text{in},i} - m_{\text{out},i} \pm \tau_i \cdot W_{\text{cat}} = \text{Accumulation}
\]

(6-5)

Solution of equation (6-5) allows determination of reaction rate of oxygenates \(r_{\text{oxy}}\), see equation (6-6), and reaction rate for any product “p” \(r_p\), see equation (6-7), as function of the mass fractions of oxygenates \(X_{\text{oxy}}\) and products “p” \(X_p\), in water-free basis. The water-free based analysis is adopted to simplify the calculation procedure \[220\]. In this case, \(X_{\text{oxy}}\) and \(X_p\) represent values at time zero \((t = 0)\), and \(\tau\) represent the space-time in hours.

\[
r_{\text{oxy}} = \frac{1 - X_{\text{oxy}}}{\tau}
\]

(6-6)

\[
r_p = \frac{X_p}{\tau}
\]

(6-7)

Extrapolation of data to \(t = 0\) is necessary to conclude about the performance of the fresh catalyst in the absence of deactivation. In each experimental test, the composition of the different species was monitored over time. Regression of data and extrapolation to \(t = 0\) were performed using a standard quadratic model \(y = ax^2 + bx + c\), which was fitted for the individual species in each run. Data taken from \(t = 15\) min and onwards were used for extrapolation purposes, in a similar way as reported by \[244, 245\]. Data taken at 5 min and 10 min of reaction were discarded. In this period, the reaction system was still under a transient condition that falsified the rate data taken. This transient behavior was caused by the displacement of the \(N_2\) atmosphere in which filled the reactor before the reaction was started.

Testing criteria: exclusion of heat and transport limitations

Potential heat and mass transport limitations inside and outside the catalyst particles were evaluated by means of the Weisz-Prater \[150\], Mears \[146\], and Anderson \[151\] criteria. Equations are summarized in section 3.2 \[146, 147, 148, 149\]. A detailed description of the calculations has been included in Appendix A.

Kinetic analysis

After the experimental measurements, the collected data were consolidated and pre-processed in MATLAB. Then, the estimation of kinetic parameters was carried out in Athena Visual Studio®, version 14.2. Athena is a commercial software used for modeling, parameter estimation and optimization problems, supplied by Athena Visual Studio, Inc.

For a kinetic model with \(n\) measurable lumps or species, the system of equations consisted of \(n - 1\) differential equations, and 1 algebraic equation with the overall mass balance. Estimation of kinetic parameters was performed with the software Athena Visual Studio. This software uses Bayesian Estimation with multiple responses to perform the calculation. The rate coefficients \(k_i\) were reparametrized to facilitate convergence during the minimization process \[154, 155\].

Finally, estimated parameters were evaluated against physicochemical constraints to evaluate the performance of the kinetic models tested and determined if parameters are physically meaningful. These constraints included:

- Pre-exponential factors > 0
- Activation energies \(E_{a,i}\) > 0

6.3 Results and Discussions

6.3.1 Catalyst characterization

The MFI structure of the catalyst was confirmed via XRD. The total surface area measured by Ar physisorption was 452 m²·g⁻¹. The pore size distribution analysis (from the physisorption test) confirmed the microporous structure, while mercury intrusion porosimetry results confirmed macroporous. The acidity of the zeolite was characterized by temperature programmed desorption of ammonia (NH₃-TPD). The experimental acidity was estimated to be 25.1·10⁻⁵ mol NH₃ / g ZSM-5, which is in good agreement with
the theoretical value of 27.9 mol NH₃ / g ZSM-5, calculated as explained by Al-Dughaither et al. [170]. Finally, an average crystal size of 300 nm was determined from SEM images. Detail analysis of results is provided in section 3.3.1.

6.3.2 Testing criteria: exclusion of heat and transport limitations

The results from testing criteria to evaluate the presence of heat and mass transport effects are shown in Table 6-1. The criteria were evaluated at conditions where the oxygenates reaction rate was fastest, thus rendering the most stringent conditions for the calculation. These conditions were 325 °C, WHSV = 125 h⁻¹. The results show that all criteria were satisfied. Therefore, it is concluded that experimental data was obtained in the kinetic regime, in the absence of heat and mass transport effects.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Result from this investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weisz-Prater [150]</td>
<td>( N_{wp} = 0.04 \leq 0.3 )</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>( \omega = 0.09 \leq 0.15 )</td>
</tr>
<tr>
<td>Anderson [151]</td>
<td>( \psi = 0.21 &lt; 0.75 )</td>
</tr>
<tr>
<td>Mears [146]</td>
<td>( \chi = 0.04 &lt; 0.15 )</td>
</tr>
</tbody>
</table>

6.3.3 Kinetic analysis

Several kinetic models from literature were tested [125, 241, 256, 259]. It is shown that some of them provided good correlation with the experimental data but in many cases the estimated parameters were negative or not significantly different from zero. This opposed the validity of the models. Moreover, the models from literature are over simplified (most of them developed in the 1980’s) and have little relation to the accepted hydrocarbon pool mechanism.

Probably one of the major sources of deviation from our study with respect to reported kinetic models is the reactant used. It is customary that authors use MeOH as feed [125, 241, 256, 259], which is quickly dehydrated to DME and water. In the conversion of oxygenates to hydrocarbons, the use of DME as feed was given some attention in the 1990’s [70, 226, 231] and it is currently gaining momentum since DME provides advantages in the valorization of feed stream with low H₂/CO ratio, which are formed from feedstocks such as biomass, pet-coke and coal [55, 262]. Just recently kinetic studies have appeared in literature to describe the conversion of DME to olefins [55, 219]. When DME is used as feed, it is transformed into hydrocarbons and water, and it also reacts with water to form MeOH. From these findings the following conclusions can be drawn:

i. According to data presented by [73], it is estimated that when DME is used as feed the heat released is approximately 20 % less as compared to the conventional use of MeOH. This is caused by a reduction of MeOH dehydration reaction and the conversion of DME to MeOH, which is an endothermic reaction.

ii. The amount of water formed during the reaction is half the water released during the reaction starting from MeOH. This in fact could be detrimental for the reaction, since it has been reported that water competes for adsorption sites with oligomers (reaction intermediates), and this competition retards the formation of coke on acid sites [243]. Nonetheless, the use of DME instead of methanol (as starting material) has gained more attention for the valorization of biomass and other feedstocks as described above.

It is important to note that these simplified models grasp the general concept of oxygenates conversion to hydrocarbons but contain little information on the mechanism. Therefore, there is a gap between the chemistry of the system and the mathematical description of the kinetics. To close this gap, a more detailed model was developed, which considered reaction steps of the hydrocarbon pool to describe the formation of species.

Literature models

Several models available in literature [125, 256, 259] consider three lumps to describe the reaction path of the MTG conversion. This is schematically shown in equation (6-8).

\[
\text{Oxygenates} \rightarrow \text{Light Olefins} \rightarrow \text{Products} \tag{6-8}
\]

The kinetic analysis consists in a model description, shown in scheme (6-9) for the kinetic model proposed by Chen and Regan [256]. In this kinetic model, \( A, B, \) and \( C \) denote the mass fractions on water-free basis of oxygenates (MeOH + DME), olefins in the range of C₂-C₄, and remaining products (aromatics + paraffins), respectively.

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
A + B & \xrightarrow{k_2} B \\
B & \xrightarrow{k_3} C
\end{align*}
\tag{6-9}
\]
Since there are three (3) measurable lumps (A, B and C) the system of equations is given by 1 algebraic equation and \( n - 1 \) differential equations, where \( n \) is given by the number of measurable lumps. These are equations (6-10)-(6-12), provided below.

\[
\frac{dA}{dt} = -k_1A - k_2AB \tag{6-10}
\]

\[
\frac{dB}{dt} = k_1A - k_3B \tag{6-11}
\]

\[
C = 1 - A - B \tag{6-12}
\]

The same analysis was applied to the kinetic models developed by Chang [259], and Schipper & Krambeck [125]. Estimation of parameters was done with Athena Visual Studio, as explained above. The performance of the models was evaluated via Akaike’s information criterion [162], which allows to make a relative rank among rival models. This is presented in Table 6-2 together with results of the objective function (OF) and the sum of squares of residuals for the three models from literature that were tested. In addition, the estimated kinetic parameters are provided in Table 6-3.

<table>
<thead>
<tr>
<th>Model</th>
<th>Objective Function [OF]</th>
<th>Sum of squares of residuals</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen &amp; Reagan</td>
<td>-3.6\cdot10^{2}</td>
<td>5.97\cdot10^{-2}</td>
<td>-139</td>
</tr>
<tr>
<td>Chang</td>
<td>-3.5\cdot10^{2}</td>
<td>6.73\cdot10^{-2}</td>
<td>-136</td>
</tr>
<tr>
<td>Schipper &amp; Krambeck</td>
<td>-3.7\cdot10^{2}</td>
<td>3.94\cdot10^{-2}</td>
<td>-149</td>
</tr>
</tbody>
</table>

These models showed similar overall performance. The models showed similar values of OF and sum of squares of residuals. Considering the AIC, it is clear that the model of Schipper & Krambeck [125] performs the best followed by the model of Chen & Reagan [256] and the model of Chang [259]. It is worth noting that: (i) the model Schipper & Krambeck was used by Mobil in pilot plant data simulation; and (ii) that the trend observed (when comparing the models) agrees with the observations made by Gayubo et al. [242] for the for the conversion of methanol to hydrocarbons. However, after inspection of the kinetic parameters, shown in Table 6-3, it was observed that some of them are negative, or have confidence intervals that include zero (0). This means that such parameters are not significantly different from zero, therefore they lack statistical significance and in the case of negative values, they lack physical meaning.

The model of Chen and Reagan shows a negative activation energy for the third step, which corresponds to the formation of paraffins and aromatics from olefins, as shown in scheme (6-9). In the original publication, Chen and Reagan [256] performed their experiments at only one temperature (370 °C) and did not provide information on the activation energy. Also, they indicated that the model performed well when conversion of oxygenates was below 50 %. This could be a reason why the model fails to provide a meaningful value of activation energy for this step. The results obtained for the model proposed by Chang [259] shows positive values of activation energy and rate constants. However, closer inspection of the estimations indicates that some values are not significantly different from zero (0), since the 95 % confidence intervals (95 % CI) for some parameters cross the zero (0) value. The results obtained for the model of Schipper and Krambeck [125] show the poorest performance in regard to kinetic parameters. Four (4) out of eight (8) estimated parameters are negative, thus they lack physical meaning. These results contrast to the work of Gayubo et al. [242], where they evaluated several kinetic models for the methanol to hydrocarbon conversion. In the work of Gayubo et al. methanol was used as feed material, in contrast to the feed used in this investigation, DME, and that might be the main factor that causes the models to fail.

Three additional models developed by Sedran et al. [241] were also evaluated. The second model developed by these authors considered five (5) lumps and showed the best performance, also in accordance with results reported by Gayubo et al. [242]. However, one of the estimated activation energies showed a confidence interval that included zero (0) which indicated lack of statistical significance.

It is important to note that we have evaluated models from literature that seem to be outdated. These include the models from Chen and Reagan [256] (1979), Chang [259] (1980), Schipper and Krambeck [125] (1986), and Sedran [241] (1990). However, these models are the cornerstone of kinetic models for the conversion of methanol into hydrocarbons, since much recent work is based on them. See for example the work of Gayubo et al. [242] (1996), Zaidi and Pant [232] (2010), and Soltanali et al. [263] (2016).
Chapter 6. Kinetics of DME to Hydrocarbons

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter*</th>
<th>Value</th>
<th>95% CI</th>
<th>Chen and Reagan</th>
<th>Value</th>
<th>95% CI</th>
<th>Chang</th>
<th>Value</th>
<th>95% CI</th>
<th>Schipper and Krambeck</th>
<th>Value</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{o,1}$</td>
<td>14.49</td>
<td>± 0.92</td>
<td>16.94</td>
<td>± 1.31</td>
<td>26.86</td>
<td>± 1.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{o,2}$</td>
<td>131.04</td>
<td>± 17.66</td>
<td>0.31</td>
<td>± 0.31</td>
<td>3215.29</td>
<td>± 869.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{o,3}$</td>
<td>15.25</td>
<td>± 4.06</td>
<td>0.48</td>
<td>± -</td>
<td>16.46</td>
<td>± 12.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{o,4}$</td>
<td>n/a</td>
<td>n/a</td>
<td>7.47</td>
<td>± 6.67</td>
<td>-130.85</td>
<td>± 35.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{a,1}$ (kJ·mol$^{-1}$)</td>
<td>136.4</td>
<td>± 11.1</td>
<td>181.4</td>
<td>± 11.2</td>
<td>187.5</td>
<td>± 10.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{a,2}$ (kJ·mol$^{-1}$)</td>
<td>174.5</td>
<td>± 22.3</td>
<td>2.3</td>
<td>± 134.8</td>
<td>-62.9</td>
<td>± 45.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{a,3}$ (kJ·mol$^{-1}$)</td>
<td>-5.4</td>
<td>± 46.2</td>
<td>27.3</td>
<td>± -</td>
<td>-62.2</td>
<td>± 102.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{a,4}$ (kJ·mol$^{-1}$)</td>
<td>n/a</td>
<td>n/a</td>
<td>88.1</td>
<td>± 1219</td>
<td>-143.0</td>
<td>± 54.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Units of $k_0$ vary depending on the kinetic model. For the model of Chen and Reagan, $k_{o,2}$ has units of $k_0$ (mol·L$^{-1}$·h$^{-1}$). For the model of Schipper and Krambeck, $k_{o,2}$, $k_{o,3}$ and $k_{o,4}$ also have units of $k_0$ (mol·L$^{-1}$·h$^{-1}$); the rest of the kinetic constant has units of $h^{-1}$.

As described in the introduction, the conversion DME to hydrocarbons over ZSM-5 occurs via the dual cycle mechanism [51], which consists in two cycles running in parallel [57,62], namely the aromatics carbon pool cycle and the olefin carbon pool cycle (Figure 6-1). The development of the kinetic model steady state conditions were assumed. Therefore it is considered that a hydrocarbon pool has developed, poly methylbenzenes in the cages of the zeolite, and hydrocarbons are formed via the dual cycle mechanism [51]. In reference to the aromatic cycle (see Figure 6-1), it is assumed that ethylene and propylene are the only products from cyclohexane (MCH + DME), as shown in Figure 6-1. (Adapted from [56, 57, 266]).

In the development of the kinetic model, steady state conditions were assumed. Moreover, under the assumption of steady state conditions, the conversion of dimethyl ether into methanol, was not considered.

There is plenty of work in the conversion of oxygenates to olefins with several kinetic models developed in the last year (see for example [56]). However, these models were not considered for the reaction that favors olefins, which means that the reaction of the cycle is suppressed. Therefore, it is considered that a hydrocarbon pool has developed, poly methylbenzenes in the cages of the zeolite, and hydrocarbons are formed via the dual cycle mechanism [51]. In reference to the aromatic cycle (see Figure 6-1), it is assumed that ethylene and propylene are the only products from cyclohexane (MCH + DME), as shown in Figure 6-1. (Adapted from [56, 57, 266]).

In the development of the kinetic model steady state conditions were assumed. Moreover, under the assumption of steady state conditions, the conversion of dimethyl ether into methanol, was not considered.

Other kinetic models were considered but not included in this work. One of them is the model proposed by Gayubo et al. in 2004 [264]. This model used 8 kinetic constants to describe the methanol to gasoline conversion. However, after inspection of the mechanism studies, it is shown that ethylene can be practically considered as a final product, and it was realized that the model included steps that are inconsistent with the dual cycle mechanism (see next section). For example, it is claimed that two (2) molecules of a lump C could produce gasoline, (C is a lump of ethylene and propylene). However, from the mechanistic studies, it is shown that ethylene can be practically considered as a final product, and it was realized that the model included steps that are inconsistent with the dual cycle mechanism (see next section).
In addition, according to the dual cycle mechanism, polymethylbenzenes dealkylate to form ethylene and propylene. This is represented by steps 2 and 3 of the reaction scheme 6-13. It was assumed that ethylene is produced and does not react further. In this respect, Ilias and Bhan [57] have shown that ethylene does not participate (at least to a significant extend) in the olefin-based cycles. This assumption is also supported by the investigation of Hill et al. [58, 59, 60], who studied the methylation of C2-C4 olefins over different zeolites using DME as methylating agent and showed that the reactivity of ethylene is at least two orders of magnitude lower than that of propylene. The authors attribute this behavior to more stable intermediates resulting from more substituted olefins. Therefore, it is possible to assume that the amount of ethylene that is methylated to propylene is small compare to the propylene that is methylated to produce C4 olefins, and in consequence the methylation of ethylene was neglected.

On the other hand, propylene initiates the olefin cycle where molecules grow via methylation. Successive methylations occur to produce butenes and C5's. This is shown on the right side of Figure 6-1, and considered in the reaction scheme (6-13), in steps 4 and 5.

The formation of the C2-C4 saturated fraction is considered to depend only on the olefin fraction of the same carbon number. Some propylene and butenes are hydrogenated, either from small amounts of H2 in the medium or by hydrogen transfer, to form the respective saturated compounds. E is the lump of propane and butane. A minor amount of ethane is also detected (< 0.1 %) but it was neglected. The reaction scheme presented in (6-13) also includes the formation of these compounds, they are included in steps 6 and 7.

The formation of hydrocarbons with 6 or more carbon atoms is considered to occur from additional reactions between molecules of propylene and butenes (dimerization reactions). This is accounted for in the last three steps of the reaction scheme presented in equation (6-13).

The resulting kinetic scheme is provided below, see equation (6-13). It considers seven (7) kinetic species (or lumps), and the lumps have been selected to avoid modifications of the main characteristics of the mechanism [267], shown in Figure 6-1. The lumps are: oxygenates (A), polymethylbenzenes (I), ethylene (B), propylene (C), butenes (D), a lump of saturated C2-C4 (E), and the C5+ liquid fraction (G).

\[
\begin{align*}
\text{Step 1:} & \quad A \xrightarrow{k_1} I \\
\text{Step 2:} & \quad I \xrightarrow{k_2} B \\
\text{Step 3:} & \quad I \xrightarrow{k_3} C \\
\text{Step 4:} & \quad A + C \xrightarrow{k_4} D \\
\text{Step 5:} & \quad A + D \xrightarrow{k_5} G \\
\text{Step 6:} & \quad C \xrightarrow{k_6} E \\
\text{Step 7:} & \quad D \xrightarrow{k_7} E \\
\text{Step 8:} & \quad C + C \xrightarrow{k_8} G \\
\text{Step 9:} & \quad C + D \xrightarrow{k_9} G \\
\text{Step 10:} & \quad D + D \xrightarrow{k_{10}} G
\end{align*}
\]
Equations (6-14) to (6-19) represent the system of algebraic and ordinary differential equations that was solved to estimate the kinetic parameters. In addition, the concentration of polymethylbenzenes is described by equations (6-20) and (6-21).

\[
\frac{dA}{dt} = -k_1A - k_4AC - k_6AD 
\]

(6-14)

\[
\frac{dB}{dt} = \frac{k_1k_2A}{k_2 + k_3}
\]

(6-15)

\[
\frac{dC}{dt} = \frac{k_1k_3A}{k_2 + k_3} - k_4AC - k_5C - k_6C^2 - k_6CD
\]

(6-16)

\[
\frac{dD}{dt} = k_4AC - k_5D - k_4AD - k_6CD - k_6D^2
\]

(6-17)

\[
\frac{dE}{dt} = k_5C + k_2D
\]

(6-18)

\[
G = 1 - A - B - C - D - E
\]

(6-19)

\[
\frac{dI}{dt} = k_1A - k_2I - k_3I = 0
\]

(6-20)

\[
I = \frac{k_1A}{k_2 + k_3}
\]

(6-21)

At this point, we evaluated the reaction rate data based on Arrhenius plots for the different kinetic species. This allowed us to identify experimental conditions where mass transport process might be dominant (limiting step). The results are shown in Figure 6-2.

Inspection of Figure 6-2 indicates that the rate values follow a straight line at space velocities of 50 and higher, with the exception of data for oxygenates, ethylene and propylene at the highest temperature (375 °C), where a clear deviation from the straight line is observed. In addition, for ethylene, propylene and butenes, the data at the lowest space velocity (25 h⁻¹) and temperatures above 350 °C seem to be mass transport limited, thus, they were not utilized for the determination of the kinetic expression. Further analysis of the raw data shows that the highest conversion was observed in these particular experiments (WHSV = 25 h⁻¹ & T > 350 °C), exceeding in all cases 90 %. This is an interesting result and defines the upper limits of conversion to obtain kinetic data free from mass transfer limitations for the determination of the kinetic parameters.

Figure 6-2. Arrhenius plots. Logarithmic rate versus inverse temperature, for six lumps: Oxygenates, Ethylene, Propylene, Butenes, Saturated C2-C4 and C₅⁺ liquid fraction.
After estimation of the parameters, parity plots of predicted versus observed mass fraction of the different species are used to evaluate the quality of the model. These plots are included in Figure 6-3 and the estimated kinetic parameters are shown in Table 6-4.

The parity plots presented in Figure 6-3 show the good performance of the model. It is possible to observe a good agreement between experimental data and predicted values of the model with data randomly distributed around the line y=x, where predicted and observed values are the same. Most of the data lay within the ± 15 % bands (red dotted lines in the plots shown in Figure 6-3).

We can observe that the correlation between model description of oxygenates, ethylene, C_2-C_4 saturates and the C_5+ mass fraction is rather accurate, while main deviations are observed in the propylene and butenes fraction.

In reference to the ethylene and propylene fractions, Wang et al. [61] indicated that these olefins are formed with almost the same probability in the aromatic cycle, and propylene is favored in the olefin cycle. In appearance this could lead to the conclusion that higher propylene yield is expected in the reaction, which contrasts with our experimental results. However, one must consider that Wang et al. [61] performed their calculations under theoretical conditions that favored the formation of olefins. In our case, we favor the formation of the C_5+ fraction, which are formed in the olefin cycle. It means that ethylene and propylene are considered intermediates. As explained above, previous authors have shown that the reactivity of ethylene is at least two orders of magnitude lower than that of propylene [58, 59, 60]. In fact, Ilias and Bhan [57] showed that ethylene does not participate (at least to a significant extend) in the olefin-based cycles. It means ethylene could be treated as a final product while propylene is an intermediate that reacts further to produce C_4 and C_5+ species. Therefore, its concentration decreases compared to the “final” ethylene product.

In the case of propylene, the discrepancy can be related to simplification in the model. For example, it is claimed that cracking of higher hydrocarbons can take place to yield propylene [57]. However, this reaction has been neglected considering that the DTH reaction takes place at relative mild conditions (T ≤ 375 °C) when compared to catalytic cracking reactions (T > 530 °C) [175]. Ilias and Bhan [62] have explained that the relative rate of olefins methylation to olefins cracking influences the product selectivity on the methanol to hydrocarbon reaction. When the methylation rate is faster, then the product distribution is reach on the C_5+ fraction, which is the case presented in this research. On the contrary, when the product stream is rich in olefins, it indicates that cracking is predominant [62]. The work of Sardesai et al [70] exemplifies this analysis. In their work,
the authors showed a dramatic increase in the small olefins yield (presumably formed from cracking) when the reaction temperature was increased from 400 to 640 °C.

In the case of the butenes lump, the main source of deviation is likely caused by the definition of the lump itself [267]. In this lump, three compounds are grouped together (1-butene, cis-2-butene and trans-2-butene). Their behavior is shown in Figure 6-4.

![Figure 6-4](image)

**Figure 6-4.** Mass fraction of C4 olefins and C4 lump in water-free basis. Data for WHSV = 25 h⁻¹ and temperature in the range of 325 °C to 375 °C.

It is possible to observe that the C4 olefins’ lump and 1-butene have analogous behavior, i.e. a steady increasing concentration in the product with increasing reaction temperature. On the contrary, the cis- and trans- isomers show a plateau over 350 °C. It is likely that C4 olefins isomerize to yield the product distribution shown in Figure 6-4. In spite of this different behavior, we decided to lump all the C4 olefins and neglect the isomerization reactions between these isomers to maintain a degree of simplicity in the process.

In reference to the C5+ liquid fraction lump, small deviations are observed. At very low conversions, the model slightly underestimates the formation of this lump. Nonetheless, the overall performance is good confirming the adequacy of the model [153, 267].

The performance of the experimental data can also be evaluated by comparing the experimental and predicted mass fractions of the different species/lumps versus the space time (τ). This is shown in Figure 6-5 for experiments carried out between 325 and 362 °C.

We can observe the adequacy of the model, given the good correlation between experimental data and predicted values. We can also observe that the experimental data and model follow the expected behavior in reference to composition of the different species. For example, an increase in the space time leads to a decrease in the concentration of oxygenates (reactant), the concentration of products increases. Also, it can be observed that higher temperatures favor the formation of the C5⁺ species with a drastic increase from ~ 10% at 325 °C and τ = 0.04 h in graph A, to ~40% at 361 °C and τ = 0.04 h in graph D.

![Figure 6-5](image)

**Figure 6-5.** Mass fraction of the different lumps in water-free basis versus space time. Symbols represent experimental values and lines represent model prediction. The graphs correspond to different temperatures (A) 325 °C; (B) 337 °C; (C) 350 °C; and (D) 362 °C.

Inspection of the kinetic parameters that resulted from this model, which are shown in Table 6-4, demonstrates that all of them are positive, thus they are physically significant. Methylation of aromatic rings to produce polymethylenylbenzene intermediates had an estimated energy barrier of 173.1 kJ·mol⁻¹, which agrees well with previously reported results [268, 269] obtained via DFT calculation in the range of 162 kJ·mol⁻¹ - 195 kJ·mol⁻¹, [268, 270, 271]. In reference to the methylation of propylene and butenes, the estimated
energy barriers are 126.6 kJ \cdot mol^{-1} and 97.2 kJ \cdot mol^{-1}, respectively. The value for methylation of butenes is lower than that of propylene as had been reported by other authors [59, 60], and this trend is related to better stabilization of the C_4 intermediates. In addition, they are in good agreement with previously reported results of corrected activation energy [68, 69].

Furthermore, dealkylation of polymethylbenzenes to produce ethylene had an estimated activation energy of 43.1 kJ \cdot mol^{-1}, which contrasts with the DFT estimated value of 132 kJ \cdot mol^{-1}, reported [61]. The reason for this large deviation is assumed to be related to the reaction scheme selected. In our scheme ethylene is considered to be formed only from dealkylation of aromatics and cracking of higher alkenes has been neglected. In contrast, there is good agreement between the estimated activation barrier of dealkylation of polymethylbenzenes to produce propylene (73.1 kJ \cdot mol^{-1}) and theoretical results, showing values of approximately 82 kJ \cdot mol^{-1} for this step [61].

### Table 6-4. Estimated kinetic parameters for the in-house developed model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>95 % CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{0,1} (h^{-1})</td>
<td>19.25</td>
<td>± 0.60</td>
</tr>
<tr>
<td>k_{0,2} (h^{-1})</td>
<td>0.69</td>
<td>± 0.03</td>
</tr>
<tr>
<td>k_{0,3} (h^{-1})</td>
<td>1.85</td>
<td>± 0.06</td>
</tr>
<tr>
<td>k_{0,4} (kg_{tot \cdot \text{org}} \cdot kg_{\text{lump}}^{-1} \cdot h^{-1})</td>
<td>139.83</td>
<td>± 12.62</td>
</tr>
<tr>
<td>k_{0,5} (h^{-1})</td>
<td>27.70</td>
<td>± 2.44</td>
</tr>
<tr>
<td>k_{0,6} (kg_{tot \cdot \text{org}} \cdot kg_{\text{lump}}^{-1} \cdot h^{-1})</td>
<td>141.99</td>
<td>± 20.04</td>
</tr>
<tr>
<td>E_{a,1} (kJ \cdot mol^{-1})</td>
<td>173.1</td>
<td>± 6.3</td>
</tr>
<tr>
<td>E_{a,2} (kJ \cdot mol^{-1})</td>
<td>43.1</td>
<td>± 6.7</td>
</tr>
<tr>
<td>E_{a,3} (kJ \cdot mol^{-1})</td>
<td>73.1</td>
<td>± 8.5</td>
</tr>
<tr>
<td>E_{a,4} (kJ \cdot mol^{-1})</td>
<td>126.6</td>
<td>± 17.6</td>
</tr>
<tr>
<td>E_{a,5} (kJ \cdot mol^{-1})</td>
<td>109.4</td>
<td>± 16.4</td>
</tr>
<tr>
<td>E_{a,6} (kJ \cdot mol^{-1})</td>
<td>97.2</td>
<td>± 26.2</td>
</tr>
</tbody>
</table>

6.4 Conclusions

Experiments were carried out in a gradientless fixed bed external-recycle reactor, in a wide range of operating conditions. High flow rates in the recycle loop and low conversions per pass allowed gradientless-operation. Thus, meaningful kinetic data could be obtained. Kinetic parameters were estimated with a commercial software, Athena Visual Studio. Then, the parameters were evaluated against physicochemical constraints to assess their physical significance.

Experimental data were taken in a wide range of operating conditions to perform the kinetic analysis. Evaluation of testing criteria showed that the data were obtained in the absence of internal and external heat & and mass transport effects.

Models available in literature for methanol conversion to hydrocarbon showed a fair performance but they have little resemblance to the accepted mechanism and usually showed parameters that were negative or not significantly different from zero (0), thus lacking physical and statistical meaning. It is concluded that simplified kinetic models established for the MTG conversion have limited applicability when dimethyl ether is used as feedstock. Although they provide information regarding trends in lump composition, the parameters obtained are usually not physically meaningful.

Finally, a new kinetic model was developed that has better resemblance to the accepted mechanism of the reaction. This in-house developed model proved to perform well and provided parameters which are physically meaningful and, in most cases, showed good agreement with DFT values reported in literature. It was clear that the propylene and butene lumps showed the highest deviations, which were probably caused by simplifications in the model. In the case of propylene, cracking reactions of higher alkenes were neglected because of the relative mild conditions of the DtG reaction. In the case of butenes, isomerization reactions were neglected in a trade-off between simplicity and over fitting of parameters. Therefore, it was possible to describe how the reaction proceeds and have a good prediction of the product distribution of the different lumps.
Conclusions and Outlook

This is not the end. This is just the beginning of a new journey in life. In the four years that lead to this PhD thesis, I have cultivated hard work and friendship. Today I move on filled with wonderful memories and grateful to those who made this possible.

Carlos Ortega
In this work, we have discussed the use of dimethyl ether (DME) as a building block for the production of liquid fuels. The analysis focused on the effect of process variables on conversion and selectivity and a kinetic description of the DME to hydrocarbon reaction was provided. The main conclusions are summarized below.

In Chapter 2, we presented a description of the experimental set-up and the testing protocols that were used in this research. We showed that our experimental system could test fast deactivating catalysts under homogeneous conditions. The system was designed to operate as a continuous stirred tank reactor (CSTR), and its fluid dynamic behavior was confirmed by measurements of residence time distribution using the pulse-tracer technique. The limitation of a slow analytical systems was compensated with the addition of gas sampling loops that worked coordinated with the reaction, taking samples while the catalyst deactivated and performing the GC analysis in off-line mode. This allowed close monitoring of the product stream in the initial instants of the reaction.

In this chapter we also show the good performance capabilities of a microstructure reactor (MSR) for the conversion of methanol to DME. The MSR had high heat transfer capacities which makes it suitable to perform exothermic reactions under isothermal conditions. It was also shown that the methanol dehydration reaction could be carried out with a ZSM-5 catalyst, which showed stable performance under the operating conditions.

The methanol to DME dehydration reaction was further evaluated in Chapter 3. The study focused on the kinetic analysis of this reaction on a commercial ZSM-5 zeolite. Initial physicochemical characterization confirmed the MFI structure of the material and allowed the determination of properties such as surface area, acidity and average crystal size. It was shown that the ZSM-5 zeolite is an effective and stable catalyst to convert MeOH to DME. The reaction was highly selective when operated at temperatures below 190 °C. Moreover, heat and mass transfer effects (inside and outside the catalyst particle) were evaluated and it was concluded that experimental tests were performed in the kinetic regime.

The best kinetic description was provided by a modification of the model of Klusáček & Schneider, which showed kinetic parameters with physical and statistical significance and in good agreement with independent data of adsorption on ZSM-5 and DFT studies. The final model discrimination was done based on adsorption entropies determined from the regression analysis. The selection of this kinetic model supports a reaction mechanism with dissociative adsorption of methanol and a surface reaction as rate determining step.

In Chapter 4, we focused the analysis on the effect of process variables on the conversion of DME to hydrocarbons over ZSM-5 catalysts. We showed that catalysts tested under quasi-adiabatic conditions are greatly affected by the temperature profiles that developed in the catalytic bed (heat effects). A dramatic impact was observed on catalyst stability and selectivity and the magnitude of these effect varied among catalysts based on their acidic properties, where more acidic catalysts deactivated faster. We conclude that assessment of the effects of process parameters on highly exothermic reactions and fast deactivating catalysts cannot be done with simple tests in an integral reactor without biased results. A catalyst tested under these conditions will be subject to different simultaneous processes, that make it cumbersome to discern the real effect of individual process parameters. Therefore, our approach was to test the catalyst under isothermal conditions, in a differential reactor and extrapolate the measured values to time on stream equal zero (t=0), when deactivation effects are negligible.

After the experimental analysis, we concluded that faster deactivation of the catalysts is observed with higher reaction temperature, lower space velocities and high partial pressure of reactant in the feed. In addition, the operational mode of the reactor also influenced the deactivation behavior. The catalyst decayed faster when the reactor operated in single pass mode and under adiabatic or quasiadiabatic conditions. In addition, our observation allowed us to conclude that the formation of C5+ was favored at high reaction temperature, high concentration of reactants in the feed, and low space velocities. These observations agreed with expected results for a set of reactions that occur in series, and when the desired product is not an intermediate but the final product of the reaction sequence.

In Chapter 5, we analyzed the catalyst deactivation phenomena during the DME to hydrocarbon conversion, with the aim of obtaining information on the behavior of the fresh catalyst. We conclude that the zeolite catalyst suffers from deactivation under all experimental conditions, and that the deactivation process is enhanced at high temperatures and low space velocities. Moreover, it was shown that the product distribution data (independently of experimental conditions) followed one trend that could be described on the basis of on only one parameter, the oxygenates conversion.

In reference to the description of the catalyst deactivation and the extrapolation of data to time zero (0), it was shown that the Mahoney correlation worked well at low conversion. On the contrary, its performance was poor when the conversion of oxygenates was high.
Second order polynomials proved to fit the data well and allowed a more accurate extrapolation of lump composition to time zero on stream. It was also shown that data obtained at WHSV = 25 h⁻¹ and temperatures of 375 °C was limited by mass transport. Evidence for this was provided by means of an Arrhenius plot of the oxygenates conversion data.

Finally, in Chapter 6 we centered the discussion of the kinetic analysis of the DME to hydrocarbons reactions. The experimental data were taken in a wide range of operating conditions to perform the kinetic analysis. The evaluation of testing criteria showed that the data were obtained in the absence of internal and external heat & and mass transport effects. After evaluation of kinetic models available in literature for methanol conversion to hydrocarbon, we showed that some of them provide a fair performance although they have little resemblance to the accepted mechanism and usually showed parameters that lacked physical and/or statistical meaning. It was concluded that simplified kinetic models established for the MTG conversion have limited applicability when dimethyl ether is used as feedstock. Although they provide information regarding trends in lump composition, the parameters obtained are usually not physically meaningful.

In order to provide a better description of the kinetic behavior of the DME to hydrocarbon reaction, we developed a new kinetic model with resemblance to the accepted mechanism of the reaction. This in-house developed model proved to perform well and provided parameters which were physically meaningful and, in most cases, showed good agreement with DFT values reported in literature. It was clear that the propylene and butene lumps showed the highest deviations, which were probably caused by simplifications in the model. In the case of propylene, cracking reactions of higher alkenes were neglected because of the relative mild conditions of the DtG reaction. In the case of butenes, isomerization reactions were neglected to limit the complexity of the final model. The final kinetic model provided a good description of the progress of the reaction and allowed for a good prediction of the product distribution of the different lumps.

It would be tempting to apply the kinetic models developed in this research on other catalysts. However, the application is not direct, meaning that the use of the kinetic scheme we developed in this investigation is valid but the kinetic parameters we obtained cannot be used. The kinetic parameters need to be re-estimated for a new catalyst whenever its physicochemical properties are different to the ZSM-5 catalyst we use in our investigation.

When determining kinetic expressions, differences appear owing to intrinsic characteristics of the material under investigation. In the case of ZSM-5 catalysts their acidity plays a key role. To avoid ambiguity, we want to clarify that acidity has two determining factors, namely the number of acid sites and the strength of the acid sites themselves. Two opposing situations could be considered. On one side, we could have a material with only a few acid sites but with significant strength. On the other side, we could have a material with plenty of acid sites, but relatively weak. If we now consider the accepted reaction mechanism for the oxygenates conversion to hydrocarbons, it has been shown that weaker acid sites enhance the contribution of the olefin/alkene cycle and are unfavorable for the aromatic cycle [61]. Thus, differences in acidity (strength and quantity) will enhance specific reactions (e.g. reactions in the aromatic cycle vs reactions in the olefin cycle) and in consequence these changes or shifts in mechanism will be reflected in the estimated kinetic parameters for a certain catalyst.

Other catalytic properties such as shape or porosity, and difference in experimental conditions, do not account for the kinetic expressions which were determined. This means that the catalytic behavior could be masked or hindered from one test to the other, even when using the same catalytic material. This is one of the reasons why we have used an external recycle reactor to overcome heat and mass transfer limitations and to be able to determine a kinetic expression in absence of such effects. Our work yielded a kinetic model that has wider application and closer resemblance to the reaction mechanism than other models available in literature, though it is still limited to the catalyst under investigation.
Notation

\begin{align*}
A_i & \text{ Chemical species } i \\
AIC & \text{ Akaike's information criterion (dimensionless)} \\
C_{i,b} & \text{ Concentration of species } i \text{ in the bulk phase (mol} \cdot \text{m}^{-3} \text{)} \\
C_p & \text{ Heat capacity at constant pressure (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{)} \\
C_s & \text{ Concentration of species } i \text{ on the surface of the catalyst (mol} \cdot \text{m}^{-3} \text{)} \\
d_p & \text{ Particle diameter (m)} \\
d_{\text{pore}} & \text{ Pore diameter (nm)} \\
D_p & \text{ Bulk diffusivity (m}^2 \cdot \text{s}^{-1} \text{)} \\
D_T & \text{ Gas diffusivity (m}^2 \cdot \text{s}^{-1} \text{)} \\
D_K & \text{ Knudsen diffusivity (m}^2 \cdot \text{s}^{-1} \text{)} \\
Da_H & \text{ Second Damköhler number (dimensionless)} \\
Da_{IV} & \text{ Forth Damköhler number (dimensionless)} \\
E_{\text{app}} & \text{ Apparent activation energy (J} \cdot \text{mol}^{-1} \text{)} \\
E_{\text{t,act}} & \text{ Activation energy for diffusion of species } i \text{ (J} \cdot \text{mol}^{-1} \text{)} \\
E_{\text{true}} & \text{ True activation energy (J} \cdot \text{mol}^{-1} \text{)} \\
F_i & \text{ Outlet molar flow rate of species } i \text{ (mol} \cdot \text{s}^{-1} \text{)} \\
F_{i,0} & \text{ Inlet molar flow rate of species } i \text{ (mol} \cdot \text{s}^{-1} \text{)} \\
G & \text{ Superficial mass velocity (kg} \cdot \text{m}^{-2} \cdot \text{K}^{-1} \text{)} \\
G_T & \text{ Standard Gibbs energy of formation of the compound } i \text{ (J} \cdot \text{mol}^{-1} \text{)} \\
\Delta G^\circ & \text{ Standard Gibbs energy change of the reaction (J} \cdot \text{mol}^{-1} \text{)} \\
h_p & \text{ Gas phase to particle heat transfer coefficient (W} \cdot \text{m}^{-2} \cdot \text{K}^{-1} \text{)} \\
\Delta H^\circ & \text{ Standard enthalpy change of the reaction (J} \cdot \text{mol}^{-1} \text{)} \\
\Delta H^\circ_{\text{ads},i} & \text{ Standard enthalpy of adsorption of species } i \text{ (J} \cdot \text{mol}^{-1} \text{)} \\
\Delta H_R & \text{ Reaction enthalpy (J} \cdot \text{mol}^{-1} \text{)} \\
J_B & \text{ Colburn factor for mass transfer} \\
J_H & \text{ Colburn factor for heat transfer} \\
k & \text{ Kinetic factor (mol} \cdot \text{kg}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \text{)} \\
k_{i} & \text{ Kinetic factor for reaction } i \text{. For units see Table 6-4} \\
k_B & \text{ Boltzmann constant (1.38048 x 10}^{-23} \text{ J} \cdot \text{K}^{-1} \text{)} \\
k_C & \text{ Mass transfer coefficient (m} \cdot \text{s}^{-1} \text{)} \\
k_{T_0} & \text{ Kinetic factor at the reference temperature } T_0 \text{ (mol} \cdot \text{kg}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \text{)} \\
K_{\text{eq}} & \text{ Equilibrium constant of the reaction (dimensionless)} \\
K_{i} & \text{ Adsorption constant of species } i \text{ (bar}^{-1} \text{)} \\
m_i & \text{ Mass of the molecular species } i \\
M_i & \text{ Molecular weight of species } i \text{ (g} \cdot \text{mol}^{-1} \text{)} \\
n_i & \text{ Order of reaction of species } i \text{ (dimensionless)} \\
N & \text{ Number of experimental measurements (dimensionless)} \\
N_A & \text{ Avogadro's number (6.02283 x 10}^{23} \text{ mol}^{-1} \text{)} \\
N_{\text{WP}} & \text{ Weisz-Prater number (dimensionless)} \\
OF & \text{ Objective function} \\
P & \text{ Total pressure. In bar for kinetic analysis. In Pa for } N_{\text{WP}} \text{ estimations} \\
P_0 & \text{ Standard state pressure (1 bar)} \\
p_i & \text{ Partial pressure of } i \text{. In bar for kinetic analysis. In Pa for } N_{\text{WP}} \text{ estimations} \\
Pr & \text{ Prandtl number } Pr = C_p \cdot \mu / \lambda_T \text{ (dimensionless)} \\
r^* & \text{ Forward rate of reaction (mol} \cdot \text{m}^{-1} \cdot \text{cat}^{-1} \cdot \text{s}^{-1} \text{)} \\
r_i & \text{ Reaction rate of species } i \text{ (kg} \cdot \text{kg}^{-1} \cdot \text{cat}^{-1} \cdot \text{s}^{-1} \text{)} \\
r_{\text{obs}} & \text{ Observed reaction rate (mol} \cdot \text{m}^{-1} \cdot \text{cat}^{-1} \cdot \text{s}^{-1} \text{)} \\
r_{\text{obs,v}} & \text{ Observed reaction rate (mol} \cdot \text{m}^{-1} \cdot \text{cat}^{-1} \cdot \text{s}^{-1} \text{)} \\
r_p & \text{ Catalyst particle radius (m)} \\
R & \text{ Ideal gas constant (8.314 J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{)} \\
\mathcal{R} & \text{ Recycle ratio (dimensionless)} \\
Re_p & \text{ Particle's Reynolds number } Re_p = \rho \cdot d_p \cdot u / \mu \text{ (dimensionless)} \\
S_{G,i}^\circ & \text{ Standard ideal gas entropy of species } i \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{)} \\
\Delta S_{G,i}^\circ & \text{ Standard entropy of adsorption of species } i \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{)} \\
\Delta S^\circ & \text{ Standard entropy change of the reaction (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{)} \text{, defined at } T=298.15 \text{ K} \\
Sc & \text{ Schmidt number (dimensionless)} \\
T & \text{ Temperature (K)} \\
T_0 & \text{ Reference temperature (K)} \\
T_{\text{ads}} & \text{ Temperature at which adsorption takes place, during TPD analysis (°C)} \\
u & \text{ Superficial gas velocity (m} \cdot \text{s}^{-1} \text{)} \\
\text{WHSV} & \text{ Weight hourly space velocity (h}^{-1} \text{)} \\
X_e & \text{ Equilibrium conversion} \\
X_{\text{oxy}} & \text{ Oxygenates conversion} \\
X_i & \text{ Mass fraction in water-free basis for species } i \\
y_i & \text{ Molar fraction of species } i \\
y_{i,0} & \text{ Molar fraction of species } i \text{ in the feed}
Greek symbols

\( \varepsilon_p \)  Pellet porosity (or volume void fraction)
\( \kappa \)  Number of parameters (dimensionless)
\( \lambda_f \)  Thermal conductivity of the fluid phase (W m\(^{-1}\) K\(^{-1}\))
\( \lambda_i \)  Mean free path of molecules of species \( i \) (m)
\( \lambda_{p,eff} \)  Effective thermal conductivity of the particle (W m\(^{-1}\) K\(^{-1}\))
\( \lambda_s \)  Thermal conductivity of the solid (W m\(^{-1}\) K\(^{-1}\))
\( \lambda_{XRD} \)  Wave length used during diffraction tests (nm)
\( \mu \)  Viscosity of the fluid (Pa s)
\( \rho \)  Density of the fluid (kg m\(^{-3}\))
\( \rho_B \)  Diluted catalyst bed density (kg m\(^{-3}\))
\( \rho_{UB} \)  Undiluted catalyst bed density (kg m\(^{-3}\))
\( \sigma_c \)  Constriction factor
\( \sigma_{r,i} \)  Molecular radius of molecule \( i \) (m)
\( \tilde{\tau} \)  Tortuosity
\( \tilde{\tau}_f \)  Tortuosity factor (\( \tilde{\tau}_f = \tau / \sigma_c \))
\( \tilde{v} \)  Mean velocity of gas molecules (m s\(^{-1}\))
\( \nu_i \)  Stoichiometric coefficient of species \( i \)
\( \tau \)  Space time (h)
\( \chi \)  Mears’ criterion - external heat transfer limitations (dimensionless)
\( \psi \)  Anderson’s criterion - internal heat transfer limitations (dimensionless)
\( \omega \)  Mears’ criterion - external mass transfer limitations (dimensionless)
“An expert is a person who has made all the mistakes that can be made in a very narrow field”

Niels Bohr (1885 - 1962)
A. Testing criteria – exemplary calculation

A.1. Internal mass transfer limitations

The effect of internal mass transfer limitations can be evaluated by the Weisz-Prater criterion [150], according to eq. (A1) for a second order reaction (worst case scenario).

\[ N_{WP} = \frac{r_p^2 \cdot r_{obs,v}}{D_e \cdot C_s} \leq 0.3 \]  

(A1)

Where \( N_{WP} \) is the Weisz-Prater number, \( r_p \) is the catalyst particle diameter (m), \( r_{obs,v} \) is the observed reaction rate per volume of solid catalyst (mol m\(^{-3}\) s\(^{-1}\)), \( D_e \) is the effective diffusion coefficient (m\(^2\) s\(^{-1}\)) and \( C_s \) is the concentration of the limiting reactant (mol m\(^{-3}\)) at the outside catalyst surface. For reaction rates with order from 0 to 2, the specific criteria are [131, 176]:

- \( N_{WP} = D a_b \leq 6 \) for zero-order reaction
- \( N_{WP} = D a_b \leq 0.6 \) for first-order reaction
- \( N_{WP} = D a_b \leq 0.3 \) for second-order reaction

\( N_{WP} \) can be evaluated at two levels: (i) at the level of catalyst particle size in which the characteristic length (\( L \)) is the radius of a catalyst particle (125-10\(^{-6}\) m) and the molecules travel through transport pores with diameter 55-10\(^{-9}\) m; and (ii) at the level of catalyst’s crystal size in which the characteristic length is approximately 300-10\(^{-9}\) m (from SEM images) and molecules travel through the crystals with pore diameter of 5-10\(^{-9}\) m (pores in MFI structure).

The observed rate \( r_{obs,v} \) was fixed to the maximum value observed during the experimental tests. The value of rate and the experimental conditions are reported in Table A1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Partial pressure of MeOH ( [P_{MeOH}] ) (bar)</th>
<th>Water and N(_2) content in feed</th>
<th>WHSV (h(^{-1}))</th>
<th>Rate of methanol conversion ( [r_{obs,v}] ) (mol m(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.931</td>
<td>0.0</td>
<td>100</td>
<td>89.9</td>
</tr>
</tbody>
</table>

Table A1. Experimental conditions at which maximum rate was observed

Estimation of \( D_e \) and \( C_s \) was done according to Vannice [176]:

- Calculation of \( C_s \)
- Determination of \( D_e \)

First approximation is to use the ideal gas law equation to determine the concentration of methanol at reaction temperature (T). Rearranging, equation (A2) is obtained.

\[ C_s = \frac{P_{MeOH}}{R \cdot T} \]  

(A2)

Exemplary calculation is given below for \( T = 463.15 \) K (190 °C):

\[ C_s = \frac{93.1 \cdot 10^3 \text{Pa}}{8.314 \text{ J/(mol} \cdot \text{K}) \cdot 463.15 \text{ K}} = 24.2 \text{ mol/m}^2 \]

The effective diffusivity \( D_e \) can be calculated from bulk diffusivity \( (D_b) \) and the Knudsen diffusivity \( (D_K) \) values. The latter two depend on the mean velocity (\( \bar{v}_i \)) and mean free path (\( \lambda_i \)) of molecules, for species \( i \).

The mean velocity of molecules of species \( i \) (\( \bar{v}_i \) (m s\(^{-1}\))) is given by eq. (A3) [176, 272, 273]. Where, \( k_B \) is the Boltzmann constant (1.38048 \times 10\(^{-23}\) J K\(^{-1}\)), \( m_i \) is the mass of the molecular species \( i \) (m\(_i\) = \( M_i / N_A \)), \( N_A \) is Avogadro’s number (6.02283 \times 10\(^{23}\) mol\(^{-1}\)), and \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). All constants were taken from [192].

\[ \bar{v}_i = \left( \frac{8 \cdot k_B \cdot T}{\pi \cdot m_i} \right)^{\frac{1}{2}} = \left( \frac{8 \cdot R \cdot T}{\pi \cdot M_i} \right)^{\frac{1}{2}} \]  

(A3)

The mean free path (\( \lambda_i \)) (m) is given by eq. (A4) [176, 273]. Where \( \sigma_{ri} \) is the molecular radius of molecule \( i \) (for methanol \( \sigma_r = 3.626 \cdot 10^{-10} \) m [274]), \( N_i / V \) is density of molecules \( i \), expressed as molecules m\(^{-3}\) (N = \( n \cdot N_A \)) and \( P \) is the total pressure.

\[ \lambda_i = \frac{1}{\sqrt{2} \cdot \pi \cdot \sigma_{ri}^2 \cdot (N_i / V)} = \frac{k_B \cdot T}{\sqrt{2} \cdot \pi \cdot \sigma_{ri}^2 \cdot P} \]  

(A4)

Exemplary calculations are given below at \( T = 463.15 \) K (190 °C):

\[ \bar{v}_i = \left( \frac{8 \cdot 8.314 \cdot \frac{1}{\text{mol} \cdot \text{K}} \cdot 463.15 \text{ K}}{\pi \cdot 0.03204 \frac{kg}{mol}} \right)^{\frac{1}{2}} = 553.2 \text{ m/s} \]
Known $\bar{v}_i$ and $\lambda_i$, the bulk ($D_b$) and Knudsen ($D_{Kn}$) diffusivities can be calculated from eq. (A5) and (A6) [176, 189, 273, 275, 276], respectively. A modification of the original $D_{Kn}$ equation was implemented, so that SI units could directly be used.

$$D_b = \frac{\bar{v}_i \cdot \lambda_i}{3} \quad (A5)$$

$$D_{Kn} = 9.7 \cdot r_{pore} \cdot \sqrt{\frac{T}{10 \cdot M}} \quad (A6)$$

Exemplary calculations are shown below at $T = 463.15 \, K$ (190 °C), for the case when the whole catalyst particle is considered, thus pore diameter is 55 nm and the radius ($r_{pore}$) 27.5 nm.

$$D_b = \frac{553.2 \, m^3}{s} \cdot \frac{1.08 \cdot 10^{-7} \, m}{3} = 1.99 \cdot 10^{-5} \, m^2/s$$

$$D_{Kn} = 9.7 \cdot 27.5 \cdot 10^{-9} \, m \cdot \sqrt{\frac{463.15 \, K}{10 \cdot 0.03204 \, \text{kg/mol}}} = 1.01 \cdot 10^{-5} \, m^2/s$$

These values must be corrected to the ‘effective values’ since diffusion inside catalyst particles occurs in pores of irregular shape, of varying cross-section areas, and only part of the cross-section area perpendicular to the direction of the flux is available. To account for these drawbacks an effective diffusivity for bulk and Knudsen diffusion must by calculated according to eq. (A7) [131, 189]. Where $\epsilon_p$ is the pellet porosity (or volume void fraction), $\tau_f$ is the tortuosity factor ($\tau_f = \tau/\sigma_c$), that account for both the tortuosity $[\tau]$ and the constriction factor $[\sigma_c]$.

$$D_{i,e} = \frac{D_i \cdot \epsilon_p}{\tau_f} \quad (A7)$$

$^4$ Tortuosity is defined as the distance a molecule travels between two points divided by the shortest distance between the same two points. The constriction factor account for variation in the area that is normal to the diffusion flux [131, 189].

Values of porosity and tortuosity factors are taken from Satterfield [189]. These correspond to a porosity of 0.40 and a tortuosity of 0.725. Therefore, the effective bulk diffusion and the effective Knudsen diffusion at 463.15 K (exemplary calculations) are:

$$D_{be,e} = \frac{D_b \cdot \epsilon_p}{\tau_f} = \frac{1.99 \cdot 10^{-5} \, m^2/s \cdot 0.40}{0.725} = 1.09 \cdot 10^{-5} \, m^2/s$$

$$D_{Kn,e} = \frac{D_{Kn} \cdot \epsilon_p}{\tau_f} = \frac{1.01 \cdot 10^{-5} \, m^2/s \cdot 0.40}{0.725} = 5.60 \cdot 10^{-6} \, m^2/s$$

Finally, the effective diffusivity is calculated with eq. (A8) [176, 189].

$$D_e = \frac{1}{1/D_{be,e} + 1/D_{Kn,e}} \quad (A8)$$

Exemplary calculation is shown at 463.15 K:

$$D_e = \frac{1}{1/1.09 \cdot 10^{-5} \, m^2/s + 1/5.60 \cdot 10^{-6} \, m^2/s} = 3.71 \cdot 10^{-6} \, m^2/s$$

This value is in the same range as that reported by Ha et al. [19] (1.934·10-6 m2·s-1) for the diffusion coefficient of methanol.

Finally, $N_{W,F}$ can be calculated using eq. (A1). The criterion for second order reaction has been considered, because of a more stringent condition. However, results from this investigation showed that the order of the reaction with respect to MeOH was less than 0.5.

$$N_{W,F,particle} = \frac{(125 \cdot 10^{-6} \, m)^2 \cdot 89.9 \, mol}{3.71 \cdot 10^{-6} \, m^2/s \cdot 24.2 \, mol/m^3} = 0.016 \leq 0.3$$

A.2. External mass transfer limitations

The Mears criterion was used to determine the influence of external mass transfer limitations, see eq. (A9) [123, 131, 146].

$$\omega = \frac{r_{obs} \cdot \rho_b \cdot r_p}{K_c \cdot C_{M,b}} \leq 0.15 \quad (A9)$$
Where, $r_{obs}$ is the observed rate of methanol conversion in mol·kgcat$^{-1}$·s$^{-1}$, $\rho_p$ is the density of catalyst bed in kg·m$^{-3}$, $r_p$ is the particle radius in m, $n$ is the order of the reaction, $k_c$ is the mass transfer coefficient in m·s$^{-1}$, and $C_{M,B}$ is the concentration of methanol in the bulk phase in mol·m$^{-3}$.

Calculation was done at the experimental condition at which the maximum reaction rate was observed. Experimental conditions and data used for calculations are presented in Table A2.

Using ideal gas law, the concentration of methanol in the bulk phase $[C_{M,B}]$ is determined from eq. (A10).

$$C_{M,B} = \frac{p_M}{R \cdot T}$$  \hspace{1cm} (A10)

The only term missing from the criterion is the mass transfer coefficient ($k_c$), which can be determined by solving a Chilton-Colburn correlation [181], see eq. (A11).

$$j_D = k_c \cdot \frac{p}{G} \cdot Sc^{2/3} = k_c \cdot \frac{u}{Sc^{2/3}}$$  \hspace{1cm} (A11)

The Colburn factor, $j_D$, must be determined from a correlation suitable to the particular Reynolds number [Re]. The Re was calculated according to eq. (A12). Where, $\rho$ and $\mu$ are the density (kg·m$^{-3}$) and viscosity (Pa·s) of the fluid.

$$Re_p = \frac{\rho \cdot d_p \cdot u}{\mu}$$  \hspace{1cm} (A12)

**Table A2. Data needed to calculate Mears criterion**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Universal gas constant $[R]$ (J·mol$^{-1}$·K$^{-1}$)</td>
<td>8.314</td>
<td>[192]</td>
</tr>
<tr>
<td>Boltzmann constant $[k_B]$ (J·mol$^{-1}$)</td>
<td>1.38048×10$^{-23}$</td>
<td>[192]</td>
</tr>
<tr>
<td>Methanol molecular mean diameter (Å)</td>
<td>3.626</td>
<td>[274]</td>
</tr>
<tr>
<td>Methanol molecular weight (kg·mol$^{-1}$)</td>
<td>0.0320419</td>
<td>[277]</td>
</tr>
<tr>
<td><strong>Experimental condition and rate observed</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate observed $[r_{obs,v}]$ (mol·m$^{-3}$·s$^{-1}$)</td>
<td>89.9</td>
<td>-</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>190</td>
<td>-</td>
</tr>
<tr>
<td>Total pressure $[P]$ (bar)</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Partial pressure of MeOH $[p_M]$ (bar)</td>
<td>0.931</td>
<td>-</td>
</tr>
<tr>
<td>Weight hourly space velocity [WHSV] (h$^{-1}$)</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst particle diameter $[d_p]$ (m)</td>
<td>250×10$^{-6}$</td>
<td>-</td>
</tr>
<tr>
<td>Superficial gas velocity $[u]$ (m·s$^{-1}$)</td>
<td>2.74</td>
<td>-</td>
</tr>
<tr>
<td><strong>Other data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Undiluted catalyst bed density $[\rho_{und \text{ bed}}]$ (kg·m$^{-3}$)</td>
<td>1300</td>
<td>[189]</td>
</tr>
<tr>
<td>Diluted catalyst bed density $[\rho_p]$ (kg·m$^{-3}$)</td>
<td>118</td>
<td>-</td>
</tr>
<tr>
<td>Reaction order $[n]$</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

Under reaction conditions and working with a recycle flow rate of 5 L·min$^{-1}$, $Re_p$ is 38. At this low value of $Re_p$, the correlation from Petrovic and Thodos [177] is adequate to estimate $j_D$, since it is valid in the range of $3 < Re_p < 2000$. The correlation is given by eq. (A13).
Appendices

\[ \varepsilon_{bl} = \frac{0.357}{Re_{bl}} \] (A13)

A value of \( j_D = 0.2415 \) was obtained. Then solving the corresponding Chilton-Colburn correlation, a mass transfer coefficient of 0.750 \( m/s \) is obtained. Assuming reaction order of 1, the application of the Mears' criterion yields:

\[ \omega = \frac{0.0692 \text{ mol/(kg} \cdot \text{s)} \cdot 118 \text{ kg/m}^3 \cdot 125 \cdot 10^{-6} \text{ m} \cdot 1}{0.750 \text{ m/s} \cdot 24.2 \text{ mol/m}^3} = 5.6 \cdot 10^{-5} \leq 0.15 \]

Please note that the reaction order determined in this investigation yielded less 0.5 with respect to methanol. A value of 1 used in the calculation to consider a more rigorous condition.

A.3. External heat transfer limitations

Mears [146] explained that heat transfer resistances are more likely to occur in a boundary layer, between bulk fluid and particle surface, than within a particle. This is a result of the higher effective thermal conductivity of the catalyst as compared with the conductivity of the gas phase. This author developed a criterion in which deviation of the observed rate deviates less than 5 %, resulting in eq. (A14) [146].

\[ \chi = \left| \frac{\Delta H_r \cdot \tau_{obs} \cdot \rho_p \cdot T_p \cdot E_{app}}{h_p \cdot T^2 \cdot R} \right| < 0.15 \] (A14)

Where, \( \Delta H_r \) is the heat of reaction in \( \text{J} \cdot \text{mol}^{-1} \), \( E_{app} \) is the apparent activation energy of the reaction in \( \text{J} \cdot \text{mol}^{-1} \), and \( h_p \) is the gas to particle heat transfer coefficient in \( \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1} \).

The gas to particle heat transfer coefficient \( (h_p) \) was calculated from eq. (A15), known as Chilton-Colburn equation [181].

\[ j_H = \frac{h_p \cdot C_p}{G} Pr^{2/3} \] (A15)

\[ j_H = \frac{h_p \cdot C_p}{G} Pr^{2/3} \] (A15)

Where, \( j_H \) is determined from eq. (A16), which is a correlation derived for fixed and fluidized bed systems with \( Re > 20 \) [182].

\[ j_H = 1.076 \cdot j_D \] (A16)

Then, to determine \( h_p \), the Prandtl number must be determined. It is defined by eq. (A17).

\[ Pr = \frac{C_p \cdot \mu}{\lambda_f} \] (A17)

Correlations were used to determine the heat capacity at constant pressure \( [C_p] \) and the thermal conductivity of the fluid phase \( \lambda_f \) at reaction conditions. The heat capacity at constant pressure \( [C_p] (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \) is given by eq. (A18) [192].

\[ C_p = C_1 + C_2 \left( \frac{C_4 / T}{\sinh(C_3 / T)} \right)^2 + C_4 \left( \frac{C_5 / T}{\cosh(C_3 / T)} \right)^2 \] (A18)

Thermal conductivity of the fluid phase \( \lambda_f (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}) \) is determined by eq. (A19) [192].

\[ \lambda_f = \frac{C_4 \cdot T^4}{1 + C_3 / T + C_5 / T^2} \] (A19)

In both cases temperature is in \( \text{K} \). The constants \( C_i \) are included in Table A3.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Heat capacity ([C_p])</th>
<th>Thermal conductivity ([\lambda_f])</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>0.39252 ( \times 10^5 )</td>
<td>5.7992 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>0.879 ( \times 10^5 )</td>
<td>1.7862</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>1.9165 ( \times 10^2 )</td>
<td>0</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>0.53654 ( \times 10^5 )</td>
<td>0</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>896.7</td>
<td>-</td>
</tr>
</tbody>
</table>

At reaction conditions, it was found that \( Pr \) and \( j_H \) are 0.801 and 0.260, respectively. Then, the particle heat transfer coefficient \( (h_p) \) is 1.23 \( \text{kw} \cdot \text{m}^{-2} \cdot \text{K}^{-1} \). The application of the Mears' criterion for heat transfer between the particle and the bulk phase yields:

\[ \chi = \left| \frac{-21.56 \cdot 10^3 \text{J} / \text{mol} \cdot 0.0692 \text{ mol/(kg} \cdot \text{s}) \cdot 118 \text{ kg/m}^3 \cdot 125 \cdot 10^{-6} \text{ m} \cdot 102 \cdot 10^{-3} \text{ J} / \text{mol}}{1.23 \cdot 10^4 \text{ W/(m}^2 \cdot \text{K}) \cdot (463.15 \text{K})^2 \cdot 8.314 \text{J/(mol} \cdot \text{K})} \right| < 0.15 \]

\[ \chi = 1.0 \cdot 10^{-3} < 0.15 \]
Appendices

A.4. Internal heat transfer limitations

Internal heat transfer limitations were evaluated via the Anderson’s criterion [151], shown in eq. (A20).

\[
Da_N = \frac{\Delta H_r \cdot r_{obs} \cdot r_0^2}{\lambda_{p,eff} \cdot T} < 0.75 \left( \frac{R \cdot T}{E_a} \right)
\]  
(A20)

Rearranging, equation (A21) is obtained and used as criterion.

\[
\left( \frac{E_a}{R \cdot T} \right) \frac{\Delta H_r \cdot r_{obs} \cdot r_0^2}{\lambda_{p,eff} \cdot T} < 0.75
\]  
(A21)

All parameters have been defined above, except \( r_{obs} \), observed rate of methanol conversion per unit volume (mol·m\(^{-3}\)·s\(^{-1}\)), and \( \lambda_{p,eff} \), the effective thermal conductivity of the particle (J·m\(^{-1}\)·s\(^{-1}\)·K\(^{-1}\)).

For non-metallic substances, Satterfield [189] has indicated that \( \lambda_{p,eff} \) values fall within in a narrow distribution, in spite of differences in pore-size and void fraction. According to Hill [276], most \( \lambda_{p,eff} \) values fall in the range of 0.16 W·m\(^{-1}\)·K\(^{-1}\) to 0.64 W·m\(^{-1}\)·K\(^{-1}\). In the case of calcined ZSM-5, it has been shown [178, 179] that thermal conductivity values are in the range of 1 W·m\(^{-1}\)·K\(^{-1}\).

According to Woodside [180], the effective thermal conductivity (\( \lambda_{p,eff} \)) can be estimated from the thermal conductivity of the fluid (\( \lambda_f \)), thermal conductivity of the solid (\( \lambda_s \)), and the porosity of the pellet (\( \varepsilon_p \)) using eq. (A22).

\[
\lambda_{p,eff} = \lambda_f \cdot \varepsilon_p^{1/2} \cdot \lambda_s^{1/2}
\]  
(A22)

From this equation, and \( \varepsilon_{pellet} = 0.4 \), one obtains \( \lambda_{p,eff} = 0.257 \) W·m\(^{-1}\)·K\(^{-1}\). Then the internal heat transfer criterion becomes:

\[
\left( \frac{102 \cdot 10^3 \text{ J mol}^{-1}}{8.314 \text{ mol} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot \text{mol} \cdot \text{K} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \cdot \frac{10^{-3} \text{ J mol}^{-1}}{9.19 \text{ mol}^{-3} \cdot \text{m}^{-3} \cdot \text{s}^{-1}} \cdot \frac{1}{125 \cdot 10^{-6} \text{ m}^2} \right) \cdot \frac{21.56 \cdot 10^3 \text{ J mol}^{-1}}{0.257 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \cdot 463.15 \text{ K}} < 0.75
\]

\[
6.7 \cdot 10^{-3} < 0.75
\]

B. Accuracy and traceability of the measurement

In the kinetic analysis, the temperature represents a critical parameter. Therefore, a certified thermocouple was used to verify the response of the K-type thermocouples used to control the oven temperature and to monitor the temperature inside the reactor. The results are shown in Figure B1.

![Figure B1. Confirmation of temperature response](image)

On graph (A), the temperature of oven during the calibration check is shown. The temperature was manually adjusted to the temperatures 200 °C, 300 °C, 350 °C, 400 °C, and 550 °C using the calibrated thermocouple. The temperature was then stabilized for a period of 30 min and the output of the thermocouples from the oven and reactor bed was monitor. The resulting temperature are shown in graph (B). Only a small deviation (ca. 2 °C) was observed at the 550 °C level. At lower temperatures, deviations from the calibrated thermocouple were below 0.5 °C.
C. Software

In this section, we provide a brief description on the software used give some notes and tips on data processing.

Two main software were used in the data processing and analysis step.

- Matlab, version R2016b, was used for data processing and kinetic analysis of MDP reaction.
- Athena visual studio, version 14.2, was used to perform the kinetic analysis of the DTH reaction.

D. Definition of basic equations

D.1. Reaction rates – derivation of equation

The experimental reaction rate can be estimated from equation (D 1) [130], where $W_{\text{cat}}$ represents the weight of catalyst in kg, $R$ is the recycle ratio, and the other variables as defined above.

$$\frac{W_{\text{cat}}}{F_{\text{MeOH},0}} = (R + 1) \int_{\frac{x}{RT}x_{\text{MeOH}}}^{x_{\text{MeOH}}} \frac{d{x_{\text{MeOH}}}}{x_{\text{MeOH}} - R_{\text{MeOH}}} \quad (D \ 1)$$

If $R$ is high enough the recycle reactor behaves as a well-mixed continuous stirred tank reactor (CSTR) [130]. In our case, this approach is also supported by the results of the fluid dynamics analysis, which are explained in section 2.5.1. We have used equation (D 2), solved for $R_{\text{MeOH}}$ to determine the experimental values of the reaction rate used in the model fitting and discrimination steps.

$$\frac{W_{\text{cat}}}{F_{\text{MeOH},0}} = \frac{x_{\text{MeOH}}}{x_{\text{MeOH}} - R_{\text{MeOH}}} \quad (D \ 2)$$

References


References


References

[60] I. M. Hill, Y. S. Ng, A. Bhan, ACS Catalysis 2012, 2, 1742–1748.
References


References


References


References


List of publications

Scientific journal publications


Conference contributions

Oral presentations


Poster presentations

- C. Ortega, Q. Wang, G. Kolb, V. Hessel. Kinetic analysis of the methanol to gasoline reaction in a gradientless recycle reactor. 12th International Conference on Renewable Resources and Biorefineries, 30-31 May & 1 June 2016, Ghent, Belgium.
Acknowledgements

I come to the end of this journey with happy memories and grateful for the technical and moral support I received in this period. I am not a person of too many words, so here it goes...

I would like to thank my wife for her continuous support and encouragement. Sometimes a PhD is not an easy ride and she was always there for me. Also, I would like to thank my friends and family. Specially my mother, my dad, my siblings and my parents in law. They’ve always believed in me and have encourage me to grow and pursue my dreams.

Coming to The Netherlands was only possible thanks to Dr. Kolb, Volker and Qi. After two rounds of interviews they took their chances with a Venezuelan student (me). Thank you for this opportunity. Specially, I would like to thank Dr. Kolb for all his support and guidance. Thank you for the technical discussions and the interesting questions you always made.

What is theory without experimentation? I do not plan to answer here, but my experimental work was only possible thanks to Marlies, Erik, Carlo, Peter, Paul and Jan. The construction of the MTG set-up and its move in my fourth years (yes, I had to move my set up to another lab, it did happen), was successfully achieved with Marlies and Peter experience with analytics, Carlos expertise on safety and Erik’s knowhow on equipment selection and construction. Also, Paul and Jan provided all the technical knowledge to automatize the equipment and having running is short time. I really appreciate all your support and the nice discussions we had before, during and after the construction of the experimental unit.

José and Denise, what would be the life of a PhD without your support? PhD life is already kind of chaos, so I cannot imagine going through this process without you. Thank you for all the insight on procedures and the TU/e life.

I would also like to thank all my PhD/Post-doc colleagues. Specially to my office mates and to the catalysis group, thanks for the interesting talks and discussions.

I would like to thank my committee members for their time and questions in the review process. To the personnel of University of Warwick for the ZMS-5 sample prepared and that we partially tested in this research, and to Fraunhofer ICT-IMM for the construction and preparation of essential equipment and microstructure reactors used in this project.

About the author

Carlos Ortega was born on August 14th 1984 in Maracaibo, Venezuela. He obtained his BSc in Chemical Engineering at the University of Zulia (Maracaibo, Venezuela) in July 2007. In his graduation project, he developed a control system for a pilot scale propylene polymerization unit.

He continued his education at the University of Zulia (Maracaibo, Venezuela). In July 2007, he enrolled in the MSc Program in Chemical Engineering. He completed his master’s thesis at the Surface and Catalysis Institute (INSUC) of the University, focusing on the development of a regeneration strategy for spent hydrogenation catalysts used in steam cracker units. He obtained the MSc degree in Chemical Engineering in December 2013. From February 2008 till February 2014 he also worked as a Project Leader at INDESCA, the R&D center of the Venezuelan Petrochemical Company.

In February 2014, he joined Eindhoven University of Technology as a PhD candidate, under the supervision of Prof. G. Kolb. Since 2016, he also worked as a co-lecturer in the Mater’s course Micro Flow Chemistry and Process Technology, led by Prof. Hessel, at TU/Eindhoven. His doctoral research project focused on the conversion of oxygenates to hydrocarbons. The results of his PhD project are explained in this dissertation.

In April 2018, he joined Avantium and he currently works as a Project Leader in the Services Catalysis Business Unit.