STORAGE OF RENEWABLE ELECTRICITY IN METHANOL

Technology development
for CO₂ air capture and
conversion to methanol

Martin Bos

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OPSLAG VAN DUURZAME ELECTRICITEIT IN METHANOL

Technologie ontwikkeling voor CO₂ afvang uit lucht
en omzetting naar methanol.

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Summary

Since the start of the industrial era, the CO_2 concentration in the air has risen from 250ppm to more than 400ppm nowadays. A large part of the increase can be contributed to use of fossil fuels for energy production. To reduce CO_2 emissions, more and more capacity of renewable energy sources such as, wind power, solar PV and hydro-power are installed. However, most of these sources result in intermittent supply of electricity leading to a mismatch in supply and demand. To level supply and demand, storage of electricity is required. In this thesis, the storage of renewable electricity into methanol is studied. The goal of thesis is to develop technology for direct air capture of CO_2 and improve efficiency of – small scale – CO_2 to methanol technology. Technologies for conversion of H_2O into H_2 – required for the synthesis of methanol – are outside the scope of this project.

In **Chapter 1** it is shown that for long term and large scale storage (i.e. seasonal storage), storage in chemicals is required. Methanol is liquid at ambient conditions and therefore an excellent storage medium, as it is easy to store and transport. Moreover, it can be produced from the abundant available chemicals CO_2 and H_2O . Furthermore, methanol is a very flexible product as it can be converted back to electricity, used as a gasoline substituent, converted to a diesel replacement and used as feedstock in the chemical industry.

To produce the CO_2 required for the production of methanol, the transport phenomena for CO_2 adsorption in solid amine sorbents are studied in **Chapter 2**. The adsorption kinetics are determined to be able to optimize CO_2 air capture systems. For this, a new experimental method is developed to exclude heat and mass transfer limitations during kinetic adsorption experiments. Hereto, a novel contactor was designed and good process control, working with pure CO_2 and small particle diameters enabled the measurement of intrinsic kinetics. A mathematical model describing convection, diffusion and reaction rate inside a particle confirmed the absence of mass and heat transfer limitations in the experiments. During normal adsorption conditions however, the uptake rate of CO_2 will be strongly inhibited by diffusional resistances inside the particle.

Linear driving force and Toth-isotherm reaction rate equations are evaluated for the CO_2 adsorption process studied. The results show that the experimental particle loading with time could not be described by the linear driving force models. On

the other hand, the Toth reaction rate equation, consistent with the Toth isotherm to describe the adsorption equilibrium, showed a very good fit to the experimental data. This shows that a rate based isotherm equation is necessary for consistent prediction of both, adsorption rate and equilibrium loading.

In Chapter 3 and 4 the desorption of CO₂ from the adsorbent is studied. While Chapter 3 focuses on the regeneration of sorbents, Chapter 4 focuses on the production of high purity CO₂ from air. In **Chapter 3** the regeneration conditions of a solid amine sorbent are evaluated by experiments and equilibrium modelling. It was found that when using an inert purge flow the desorption rate is strongly influenced by equilibrium between the gas and adsorbed phase. Because of the strong dependency of the isotherm on temperature, heat transfer is found to be an important design parameter. With elevated temperature (>80°C) both the working capacity and the productivity increase significantly. Therefore, most important design considerations are heat transfer and the trade-off between sorbent working capacity and energy consumption for sorbent heating.

The effects of water co-adsorption and steam purge on the CO₂ working capacity and energy requirement for CO₂ desorption are reported in **Chapter 4**. Working capacities are studied by fixed bed operation for changing temperature, pressure and amount of steam purge. Results show that for pressure-temperature swing adsorption a temperature above 100°C and a pressure below 200 mbar as desorption conditions are required to maximize CO₂ working capacity and reduce energy requirement for desorption. Co-adsorption of water reduces energy requirement due to an increased CO₂ working capacity. Application of a steam purge increases the CO₂ working capacity and hence reduces sorbent inventory required. However, the net energy requirement per kilogram CO₂ does not decrease due to the latent heat of water. Concluding, steam purge regeneration for air capture does not reduce OpEx but might reduce CapEx.

A novel reactor concept for the conversion of CO₂ and H₂ to methanol is developed in **Chapter 5**. Conversion limitations because of thermodynamic equilibrium are bypassed via in situ condensation of a water/methanol mixture. Two temperatures zones inside the reactor ensure optimal catalyst temperature, automatic gas circulation by natural convection and full conversion by condensation at a lower temperature in a separate zone. Experimental work confirmed full carbon conversion (>99.5%) and high methanol selectivity (>99.5% on carbon basis). Because of full gas conversion there is no need for an external recycle of unconverted reactants. Moreover, proof of concept for operation under natural convection conditions was shown.

A more detailed analysis of the condensing reactor for conversion of CO₂ to meth-

anol is given in **Chapter 6**. The reactor is characterized under forced convective conditions, both experimentally and by modelling. The goal of the study is to optimize the operation conditions and identify limitations of the reactor concept. Experimental results show that the productivity is limited by reaction equilibrium and mass transport at high temperature ($>250^{\circ}\text{C}$), while reaction kinetics limit productivity at low temperature ($<220^{\circ}\text{C}$).

Further analysis of the LOGIC concept is performed by an adiabatic 1D-reactor model in combination with an equilibrium flash condenser model. To enable autothermal operation without excessive heat exchange area, it was found that a condenser temperature below 70°C is required. Most important design parameter is found to be the conversion per pass over the catalyst bed. Increasing dimensions of the catalyst section will increase the conversion per pass, unless equilibrium is reached. On the other hand, heat exchanger and condenser area are reduced because of a lower recycle ratio. With the model developed, overall reactor performance can be optimized by finding the most optimal combination of reaction and condenser conditions.

In **Chapter 7** a 100MW wind power to methanol process has been evaluated to determine the capital requirement and power to methanol efficiency. Power available for electrolysis determines the amount of hydrogen produced. The stoichiometric amount, for the methanol synthesis, of CO_2 is produced using direct air capture. Capital cost for all process steps is estimated using short-cut equipment sizing and economics. Power to methanol efficiency was determined to be around 50%. The cost of methanol is around 800€ ton^{-1} including wind turbine capital cost. Excluding 300M€ investment cost for 100MW of wind turbines, total plant capital cost is around 200M€. About 45% of the capital cost is reserved for electrolyzers, 50% for the CO_2 air capture installation, and 5% for the methanol synthesis system. The conceptual design and evaluation shows that renewable Methanol from CO_2 from air, water and renewable electricity is becoming a realistic option at reasonable costs of $750\text{--}800\text{ € ton}^{-1}$.

The production of renewable methanol using direct air capture and electrolysis is currently not economical viable. As discussed in Chapter 7 the cost of wind energy, electrolysis, and air capture are expected to go down in the future, improving process economics. As discussed in **Chapter 8**, government legislation might be an important driver for the process. For example, the European Renewable Energy Directive II) requires 14% of renewable energy to be used in transportation by 2030. Moreover, the European Commission proposes a climate-neutral Europe in 2050, thereby renewable methanol could fulfil the role of sustainable carbon source for the chemical industry.

Samenvatting

Sinds het begin van de industriële revolutie is de CO_2 concentratie in de lucht gestegen van 250 ppm tot meer dan 400 ppm. Het grootste deel van deze stijging kan worden toegekend aan het gebruik van fossiele brandstoffen. Om de uitstoot van CO_2 te verminderen wordt er steeds meer gebruik gemaakt van duurzame energiebronnen zoals zonne-energie, windenergie en waterkrachtenergie. De stroomproductie door deze duurzame bronnen kent echter pieken en dalen, waardoor het moeilijk is om vraag en aanbod op elkaar af te stemmen. Opslag van elektriciteit is daarom essentieel om deze wisselingen op te vangen. Voor opslag van elektriciteit op langere termijn, bijvoorbeeld seizoensopslag, is de opslag in chemicaliën zeer geschikt. In dit proefschrift wordt de opslag van duurzame elektriciteit in methanol onderzocht. Het doel van dit proefschrift is om technologie te ontwikkelen voor de afvang van CO_2 uit lucht en om de omzetting van CO_2 naar methanol efficiënter te maken op kleinere schaal. De technologie om water om te zetten in waterstof, dat nodig is voor de synthese van methanol, wordt niet onderzocht in dit proefschrift.

In **Hoofdstuk 1** wordt aangetoond dat opslag van elektriciteit in chemicaliën nodig is voor elektriciteitsopslag op lange termijn. Omdat methanol vloeibaar is bij standaarddruk en -temperatuur is deze stof hiervoor zeer geschikt. Vloeistoffen zijn namelijk makkelijk op te slaan en te transporteren. Daarnaast is methanol een zeer veelzijdig product: het kan worden gebruikt voor elektriciteitsproductie, als vervanger van benzine, het kan worden opgewaardeerd tot diesel en gebruikt worden als grondstof in de chemische industrie.

Om methanol te produceren is CO_2 nodig. In dit proefschrift wordt CO_2 afgevangen uit de lucht. De transportverschijnselen tijdens de afvang van CO_2 worden besproken in **Hoofdstuk 2**. De kinetiek van de adsorptiereactie wordt bepaald om CO_2 afvangsystemen te kunnen optimaliseren. Om kinetiek te kunnen bepalen is een nieuwe experimentele methode ontwikkeld om warmte- en massatransportlimiteringen uit te kunnen sluiten tijdens meten van adsorptiekinetiek. Intrinsieke kinetiek kan worden gemeten door de ontwikkeling van een nieuwe reactor, een goede procescontrole en het gebruik van puur CO_2 en kleine sorbentdeeltjesdiameters. Daarnaast is een wiskundig model ontwikkeld dat convectie, diffusie en reactiesnelheid beschrijft. Met behulp van dit model kon worden aangetoond dat

er geen warmte- en massatransportlimiteringen aanwezig waren tijdens de experimenten en dat intrinsieke reactiekinetiek daadwerkelijk is gemeten. De opnamesnelheid van CO_2 uit lucht, tijdens normale operatie condities, wordt echter sterk gelimiteerd door diffusietransport in het sorbentdeeltje.

Het 'linear driving force' model en de Toth-isothermreactiesnelheidsvergelijking zijn bestudeerd om de CO_2 adsorptie te beschrijven. De experimentele deeltjesbelading in de tijd kan niet worden beschreven met het 'linear driving force' model. De reactiesnelheidsvergelijking gebaseerd op de Toth-isotherm is daarentegen goed in staat om de experimentele deeltjesbelading in de tijd te beschrijven. Daaruit kan geconcludeerd worden dat voor een consequente beschrijving van de reactiesnelheid en het beladingsevenwicht een reactiesnelheidsvergelijking nodig is die gebaseerd is op een isotherm.

De desorptie van CO_2 van het sorbentdeeltje wordt geanalyseerd in de hoofdstukken 3 en 4. De focus van hoofdstuk 3 ligt op het regenereren van het sorbentdeeltje, terwijl hoofdstuk 4 focust op de productie van pure CO_2 . In **Hoofdstuk 3** worden de condities om een sorbentdeeltje te regenereren bestudeerd door het uitvoeren van experimenten en het modeleren van adsorptie evenwichten. Eén van de uitkomsten was dat de desorptie van CO_2 tijdens het gebruik van een spoelgas sterk gelimiteerd wordt door het evenwicht tussen de vaste fase en de gasfase. Omdat de isotherm sterk afhankelijk is van de temperatuur, is de warmteoverdracht een belangrijke ontwerpparameter. Daarnaast werd aangetoond dat boven de 80°C de werkapaciteit en de productiviteit sterk toenamen. Daarom zijn de belangrijkste overwegingen tijdens het ontwerp de warmteoverdracht en de afweging tussen de werkapaciteit en de benodigde hoeveelheid energie voor het opwarmen van het sorbent.

De effecten op de werkapaciteit van co-adsorptie van water en het spoelen met stoom zijn onderzocht in **Hoofdstuk 4**. De invloed van druk, temperatuur en de hoeveelheid stoom tijdens desorptie zijn experimenteel onderzocht in een vastbedopstelling. De resultaten laten zien dat een druk lager dan 200 mbar en een temperatuur hoger dan 100°C nodig zijn om de werkapaciteit te maximaliseren en het energieverbruik te minimaliseren. Ondanks de co-adsorptie van water neemt de hoeveelheid energie die nodig is voor desorptie niet toe, omdat de CO_2 werkapaciteit toeneemt. Het gebruik van stoom als spoelgas vergroot ook de CO_2 werkapaciteit en verlaagt daarmee de hoeveelheid sorbent die nodig is. Door de verdampingswarmte van water neemt de totale energie die nodig is voor desorptie echter niet af. Daarom kan geconcludeerd worden dat het gebruik van stoom als spoelgas de investeringskosten verlaagt, maar de operatiekosten niet.

Een nieuw reactorconcept voor de omzetting van CO_2 en H_2 wordt geïntroduceerd

in **Hoofdstuk 5**. Door het toepassen van *in-situ* condensatie van de reactieproducten zijn reactie-evenwichtslimiteringen verwijderd. Met het gebruik van twee temperatuurzones in de reactor is het mogelijk de katalysatorzone optimaal te gebruiken terwijl volledige conversie mogelijk is door productcondensatie in de tweede zone die opereert op een lagere temperatuur. Daarnaast vindt automatische gascirculatie plaats door natuurlijke convectie. Experimenteel werk laat een hoge conversie (>99.5%) en hoge selectiviteit naar methanol (>99.5% op koolstofbasis) zien. Door de hoge conversie is een externe recycle van niet geconverteerde gasen onnodig. Daarnaast is het principe van operatie onder natuurlijke convectie aangetoond met experimenten.

In **Hoofdstuk 6** is het nieuwe reactorconcept verder onderzocht. Met behulp van experimenten en modellen is het gedrag van de reactor onder geforceerde convectie bepaald. Het doel van dit hoofdstuk is om de operatie condities te optimaliseren en de limiteringen van het nieuwe concept te identificeren. De experimentele resultaten laten zien dat de productiviteit van de reactor bij hoge temperatuur (>250°C) gelimiteerd wordt door de evenwichtsbependingen, terwijl de reactiekinetiek de productiviteit limiteert bij lage temperatuur (<220°C).

Het reactorconcept is verder geanalyseerd met behulp van een adiabatisch 1D-reactormodel gecombineerd met een condensormodel op fasenevenwicht. Om de reactor autotherm te kunnen bedrijven zonder een extreem groot warmte uitwisselend oppervlak, is een condensortemperatuur lager dan 70 °C nodig. Daarnaast werd geconstateerd dat de conversie per katalysatorbed passage de belangrijkste ontwerpparameter is. Een toename van het katalysatorvolume zal de conversie doen toenemen totdat de evenwichtsconversie is bereikt. Aan de andere kant zal het warmte-uitwisselendoppervlak in de warmtewisselaar en condensor afnemen door de lagere recycle ratio. Met het ontwikkelde model kan de meest optimale combinatie van reactie- en condensorcondities worden bepaald.

Een proces om 100 MW windenergie om te zetten in methanol is geëvalueerd op investeringskosten en efficiëntie in **Hoofdstuk 7**. De hoeveelheid vermogen beschikbaar voor elektrolyse bepaalt de hoeveelheid waterstof die geproduceerd wordt. Een stoichiometrische hoeveelheid CO₂ voor de synthese van methanol wordt afgevangen uit lucht. De investeringskosten voor alle proces stappen zijn afgeschat door middel van vereenvoudigd apparaatontwerp. De efficiëntie van elektriciteit naar methanol is bepaald rond de 50%. De berekende kosten voor methanol zijn rond de 800€ ton⁻¹ inclusief de aanschafkosten voor windturbines. De totale investeringskosten voor de methanolfabriek zijn 200 miljoen euro, exclusief 300 miljoen euro investeringskosten voor de windturbines. Ongeveer 45% van de investeringskosten is nodig voor de elektrolyse apparatuur, 50% voor het afvangen van CO₂ uit

lucht en 5% voor de methanol synthese. Het conceptuele design en de evaluatie in Hoofdstuk 7 laten zien dat duurzame methanol, geproduceerd met CO₂ uit lucht, water en duurzame elektriciteit, een realistische oplossing wordt met kosten tussen de 750 en 800 € ton⁻¹.

De productie van duurzame methanol gebaseerd op CO₂ uit lucht en elektrolyse is, op dit moment, nog niet economisch haalbaar. De kosten voor windenergie, elektrolyse en CO₂ afvang uit lucht zullen, zoals bediscussieerd in Hoofdstuk 7, naar verwachting echter afnemen in de toekomst. In **Hoofdstuk 8** is aangegeven dat toekomstige wetgeving een belangrijk impuls kan zijn voor dit proces. De nieuwe Europese 'Renewable Energy Directive II' verplicht bijvoorbeeld dat 14% van de transportbrandstoffen van duurzame bronnen afkomstig moet zijn. Daarnaast is het doel van de Europese Commissie om een volledige klimaatneutraal Europa te hebben in 2050. Duurzame methanol kan dan een excellente koolstofbron voor de chemische industrie zijn.

1

Storage of renewable electricity in methanol

Abstract

The reader is shortly introduced into technologies for storage of electricity and more specifically into the storage of electricity in methanol. The process route from CO₂ and H₂O into methanol is discussed. A general introduction into conventional technologies for CO₂ capture and methanol synthesis is given. The general introduction is followed by a literature overview on developments into solid sorbents for CO₂ capture, CO₂ air capture and advanced methods for methanol production. Finally, the scope and outline of this thesis are presented.

1

The CO₂ concentration in the atmosphere increased from 250ppm in the pre-industrial era to more than 400ppm nowadays [1]. A large part of the increase can be contributed to use of fossil fuels. A decrease in CO₂ emission by a reduction in fuel use is not expected since it is predicted that the world energy use will only increase in the years to come [2]. Nowadays, it is widely accepted that increased CO₂ concentrations in the atmosphere lead to changes in the world's climate. Therefore, energy production with low CO₂ emissions is gaining interest. The installed power of renewable energy sources such as, wind power, solar PV and hydro-power are increasing yearly.

1.1. Storage of renewable electricity

However, the generation of most renewable electricity is dependent on weather conditions and results in intermittent available resources. Therefore, a mismatch between supply and demand will exist from time to time. For this reason, storage of renewable electricity becomes more and more important with increasing production share of renewable electricity. Several technologies to store electricity exist or are currently under development. In literature, review articles [3–9] are presented on energy storage technologies. Also institutions such as International Electrotechnical Commission [10] and the European Commission [11] present their analysis of storage of electricity for an energy grid with high penetration of renewable electricity.

A summary of technologies is shown in Figure 1.1 by characterizing technologies on their typical capacity and time scale of storage [12]. Depending on the time scale of storage in combination with the required capacity of storage a technology can be selected. In the section below a short overview of technologies will be given.

1.1.1. Mechanical energy storage

In mechanical storage methods electrical energy is translated into potential energy. The most mature technology is pumped hydro storage where water is pumped uphill into a reservoir using excess electricity [8]. During peaks of electricity demand, the water is released downhill driving generators and producing electricity. This method of storage is already widely applied in mountainous countries. Depending on the size of the reservoir this technology can be applied at large scale. Pumped hydro storage has a Round Trip Efficiency (RTE) – that is the efficiency from electricity to electricity – between 70-85% [8].

A similar way of storing electricity is Compressed Air Electricity Storage (CAES). Using compressors, air is compressed and stored in an underground cavern when

Figure 1.1 | Typical capacities and time scales of energy storage technologies [12].

high storage capacity is required. At smaller scale (1-10MW), the compressed air might be stored into pressure vessels [5]. When required, the compressed air is converted into electricity by the use of expanders driving a generator. The round trip efficiency of CAES is 70-80% [5].

Transforming electricity into kinetic energy is another method of mechanical storage. Flywheels are an example of storing electricity into kinetic energy. The operation principle of flywheels is a motor rotating a cylinder during periods of excess electricity. Because of the conservation of inertia the cylinder will drive a generator during shortage of electricity. Although flywheels have a high RTE (90-95%), due to high self-discharge they cannot store electricity for a longer times [5]. Because of the ability to store large amount of energy in a short period flywheels are used to filter sudden peaks of demand and supply of electricity [3].

Capacitors provide another technology used to filter short peaks in supply and demand of electricity. In capacitors electricity is transformed into electrical potential. In conventional capacitors the potential is generated by two plates separated by a non-conducting layer. Capacitors with higher capacities (super-capacitors) make use of a electrolyte solution to built up potential [3]. The high charging and discharging rate is an advantage of capacitors but low energy density is a disadvantage. On the other hand the RTE for capacitors is high (85-97%) making it a good technology for short term electricity storage [7].

1

1.1.2. Chemical energy storage

Batteries have been a mobile source of electricity for more than 100 years. Nowadays, batteries are also considered a storage medium for electricity, considering the high RTE of >95% [7]. Lead-acid batteries are the most mature battery technology. A Lead-acid battery consist of lead anode with a lead oxide cathode immersed in dilute sulphuric acid [5]. Because the battery is cheap and widely available it is popular. Disadvantages are the low energy density, high weight and health hazards associated with lead and sulphuric acid [4].

Na-S batteries use a high temperature reaction between a liquid sodium negative electrode and a liquid sulphur positive electrode which are separated by a solid beta-alumina ceramic electrolyte [8]. The batteries are ideal to manage power quality and perform peak shaving because of their ability to handle power pulses (up to 30s) of six times their continuous power rating. The high daily self-discharge, high operating temperature and high cost are significant disadvantages [4].

Li-ion batteries are commonly used in electronics such as mobile phones and laptops. Moreover, electric vehicles are normally powered by Li-ion batteries. The Li-ion battery exist of a negative electrode made of graphite and a lithiated positive electrode such as Lithium Cobalt(III) oxide, Lithium Manganese Oxide or Litium Nickel Oxide [3]. The electrolyte consist of a lithium salt such as LiPF_6 dissolved in organic carbonates. For a battery, Li-ion batteries have a high energy density and low self-discharge loss [5]. Major drawback of Li-ion is their fragility with temperature increases. Special circuits preventing overcharging are necessary.

Redox flow batteries make use of circulating liquid electrolytes. During the charging phase one of the electrolytes is oxidized while the other is reduced. The reactions are reversed in the discharging phase. The delivery power of redox flow batteries depends on the size and number of electrodes installed. The storage capacity is dependent on the volume of electrolytes used [7]. Round trip efficiency depends on the electrolytes used: Vanadium based systems have a RTE of 85%, while Zinc-Bromide and Polysulfide-Bromide stick around 75% [7].

1.1.3. Energy storage in chemicals

For the large scale storage and for storage over a longer time scale electricity storage in chemicals is, apart from hydro power, the only storage method available. Hydrogen is often discussed to be the chemical with the highest potential. Hydrogen can be produced by electrolysis in a renewable way and easily converted to electricity by fuel cells [3]. Disadvantages of hydrogen are relative low energy density and the need for storage under high pressure. Hydrogen can be further con-

verted to chemicals such as methane and methanol to increase the energy density and transportability. Although still being gaseous, methane has the advantage of direct injection in the natural gas grid. Methanol is a liquid at ambient conditions and therefore much easier to store and transport.

1.2. Methanol economy

Producing a chemical from water and carbon dioxide requires energy. In this thesis the point of departure is the availability of renewable electricity. For the renewable character of the produced methanol it is important that during the production of this electricity no additional carbon dioxide is generated. Any preferred chemical used to store electricity should have several requirements as itemized below [13]:

- Liquid at ambient conditions so that is easy to store and transport.
- Selective production to minimize side products and waste.
- The number of hydrogen atoms per carbon atom should be maximized while the removal of oxygen is minimized. More hydrogen atoms increase energy density while extra oxygen removal cost extra energy.

Based on the first criterium the selection is limited to parafins/olefins, aldehydes, acids and alcohols. However, because of the limited selectivity of the Fischer-Tropsch production route for parafins/olefins they are not preferred. The hydrogen content per carbon atom is higher for alcohols compared to aldehydes and acids. Moreover, alcohols are less toxic and corrosive. Therefore an alcohol is the preferred product. Because methanol can be produced with high selectivity and the ratio hydrogen/carbon/oxygen is optimal, methanol is selected as the preferred chemical for storage of renewable electricity.

Methanol as storage medium for electricity and as base chemical has been advocated by two books in literature: *Methanol - Chemie und Energierohstoff* [14] by Friedrich Asinger and *Beyond oil and gas: the methanol economy* [15] by Nobel-laureate George Olah. They both promote methanol as the number one base chemical for a fossil fuel free world. While Asinger envisioned the use of nuclear electricity combined with C_1 chemistry, Olah combines methanol production with a variety of renewable electricity sources such as solar and wind.

A big advantage of methanol is its versatility as a product. Using a direct methanol fuel cell it can be converted back to electricity. Furthermore, it can be directly used as a substitute for gasoline and, if upgraded to dimethyl ether (DME), as a diesel substitute. Using the Methanol to Gasoline (MTG) process methanol can be

1

converted to regular gasoline. Moreover, methanol is used in transesterification of bio-oils to FAME for the production of biodiesel. Production of all kinds of plastic can be done by the production of ethylene and propylene using the Methanol to Olefins (MTO) process. Furthermore, methanol can be easily converted to syn gas by which basically any chemical is within reach [16].

Making methanol the feedstock for fuels and chemicals and an energy storage medium one can surely speak of a *methanol economy*. The methanol economy and the technologies required are discussed in review articles by Olah et al. [17], Jadhav et al. [18], Goepfert et al. [19] and Martens et al. [20].

In the section below, first an overview about capture of CO_2 will be reported, followed by a literature review about methanol synthesis. Finally, the most optimal synthesis route from H_2O and CO_2 will be discussed.

1.3. Capture of CO_2

CO_2 is abundantly available in the atmosphere and from industrial flue gases. Before it can be used for methanol synthesis, CO_2 needs to be purified and concentrated. Diluted CO_2 can be obtained from two main types of sources. First, it can be captured from flue gases emitted by power plants and the chemical industry. Typically these flue gases have a CO_2 concentration between 5-15% for power plants and 15-30% for the cement and steel industry [1].

However, since the proposed process is a storage method for renewable electricity it is unlikely that flue gas emitting sources and excess electricity are available at the same physical location. Normally, in the vicinity of power plants and chemical industries electricity demand is high and chances of excess electricity thereby lower. Therefore, it is proposed to capture the CO_2 from the second main source: the atmosphere. Capturing CO_2 from air makes it a location independent source. Thereby the CO_2 can be provided at the location of excess electricity. However, downside is that the concentration of CO_2 is significantly lower in air, around 0.04% (400ppm) of CO_2 in air.

1.3.1. Direct air capture of CO_2

Despite having a CO_2 concentration about 300 times lower in air compared to flue gas, a thermodynamic analysis by Lackner [21] showed a more positive picture. Because the outlet concentration is less strict for air capture compared to flue gas capture the ratio in thermodynamic minimal energy for separation is less worryingly. For separation of CO_2 from air (400ppm to 200ppm at 300K) 21kJ mol^{-1} is

required while CO₂ separation from flue gas (13kPa to 1kPa at 300K) costs about 11kJ mol⁻¹ [21]. Therefore, thermodynamics show no principle limitations for air capture. However, besides thermodynamics a major challenge for CO₂ air capture is the amount of air to be processed to capture one kilogram of CO₂. At 100% capture efficiency 1400m³ of air have to be processed to capture 1 kg of CO₂. This fact raises challenges for reactor design and process engineering.

Apart from the fact that air capture can provide a location independent source of CO₂ it also is a technology enabling negative CO₂ emissions. The latest IPCC reports [22, 23] showed that reducing CO₂ concentrations in the atmosphere is necessary to stay within the 1.5°C temperature increase limits [24]. Therefore, technologies for negative carbon emissions have to be identified and implemented to limit the increase in worldwide temperature.

Recently, Sanz-Perez et al. [25] published a review comparing different methods for air capture. However, selecting the best technology needs more research which is addressed in this thesis. Several technologies exist for direct air capture (DAC) of CO₂. The group of Lackner at Arizona State University works on so-called moisture swing adsorption of CO₂ from air. The CO₂ is adsorbed in dry conditions and desorbed by increasing the humidity of the gas. One of their system uses an amine-based anion exchange resin [26, 27].

The Jones research group at Georgia Tech focus on development of amine-based sorbents. The work includes amine impregnated [28, 29] and grafted [30, 31] on silica and metal organic frameworks [32]. The company Global Thermostat is affiliated with the group of Jones and uses an amine bonded to monolith structure to perform DAC [33].

Analogue to the idea presented by Zeman [34] the group of Keith at the Harvard University develops an alkaline hydroxide process. CO₂ is captured by a reaction with liquid NaOH or KOH to form a carbonate solution [35]. The carbonate solution reacts with calcium hydroxide to form calcium carbonate (CaCO₃). At the same time the alkaline hydroxide is regenerated and can be reused in the absorber. The calcium carbonate is regenerated in a calcination loop at high temperature, a disadvantage of this process. Carbon Engineering develops the alkaline hydroxide/calcium calcination technology on commercial basis. A 1Mt-CO₂/year plant is designed in their latest paper [36]. The levelized cost per ton of CO₂ ranged from 94 to 232 dollar.

Steinfeld's group at ETH Zurich also investigated a carbonation loop for DAC. They directly contacted CO₂ with CaO to form CaCO₃ [37]. In later work, the group started working on solid amine sorbents. The process is based on a temperature-vacuum

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swing adsorption to produce CO_2 from air [38]. The process is able to produce high purity CO_2 from air [39]. The company Climeworks is started by alumni of Steinfeld's group and is using granulated material with amines to capture CO_2 by a temperature vacuum swing adsorption. Earliest estimation of the cost of air capture are about 600 dollar per ton of CO_2 [40].

1.3.2. Conventional technology for CO_2 capture

Flue gas capture of CO_2 is commonly done by using aqueous amine solvents, of which MEA is the current benchmark amine [41]. Amine technology for CO_2 is already developed in 1930's for removal of unwanted CO_2 from gas streams. The process is operated by contacting a MEA-water solution in a column (absorber) with flue gas. CO_2 is absorbed by MEA in the solution while the other gases are passed through. By heating the CO_2 containing MEA solution to temperatures around 120°C in a second column (desorber) the CO_2 is released at high purity. The MEA solution can now be reused in the absorber column to capture CO_2 . The energy use for MEA-based systems is 3 - 4 MJ/kg CO_2 while more advantage systems can go as low as 2.7 MJ/kg CO_2 [42].

The first commercial application of aqueous amine CO_2 capture systems for carbon capture and storage (CCS) has been shown by Statoil in the Sleipner area in Norway. In the Sleipner project 1 million ton of CO_2 is removed from natural gas and stored underground yearly since 1996 [43]. CO_2 capture from flue gas is already shown in 1978. North American Chemical built a CO_2 capture plant (800t/day) for a coal-fired boiler. The produced CO_2 could be sold to the nearby Searles Valley Mineral plant which required significant amounts of CO_2 for their production. The first large scale CCS application in the power sector was shown at the Boundary Dam Power Station operated by SaskPower in Canada in 2014. Although, most of the captured CO_2 is sold for enhanced oil recovery, the unsold CO_2 is stored in a nearby saline formation. Another project using amine technology at a coal power plant is the Petro Nova project outside Houston in the USA [43].

Other (smaller scale) projects included several CO_2 capture plants for enhanced oil recovery, where CO_2 is injected in the oil well to increase production. However, for most of these project the CO_2 is produced from natural gas processing, fertilizer production, or coal gasification facilities where CO_2 capture is required for their process. Therefore, the cost of CO_2 capture is already included in the production cost. The extra cost for storage and transportation is covered by the oil companies because of enhanced production [43].

1.3.3. CO₂ capture by solid amine sorbents

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Advancements in CO₂ capture using amine compounds have been shown by the development of more advantageous solvents [44]. Another path of research is CO₂ capture by solid amine sorbents. Compared to aqueous amines, the solid amines have the advantages of lower heat capacity, higher CO₂ capacity, lower energy requirement for CO₂ amine contacting and high selectivity for CO₂.

Choi et al. [45] published an overview of the properties of multiple solid sorbents for CO₂ capture. It was shown that solid amine sorbents are excellent CO₂ capture compounds because of high capacities at low partial pressure of CO₂ and low regeneration temperature (<100°C) [45]. The advantages of solid amine sorbents versus liquid amine solvents for CO₂ capture are given by Shakerian [46]. Ünveren et al. [47] reviewed the mechanism and capacity of CO₂ adsorption on different solid amine sorbents. The application of amine sorbent for gas separation in the iron and steel industry is reviewed by Ramirez-Santos et al. [48].

Adsorption of CO₂ from air using solid amine sorbents has been described in literature [38, 49–54]. Large scale application of DAC using solid sorbent was not demonstrated nor piloted at the beginning of this thesis work. The CO₂ air capture part of this thesis will therefore not focus on the development of new sorbents but on engineering challenges related to air capture using a solid amine sorbent.

Lewatit VP OC 1065

Since this thesis aims to develop larger scale DAC equipment a commercial state of the art sorbent used. The sorbent Lewatit VP OC 1065 [55] is produced by Lanxess and easily available at kilogram scale making it suitable for piloting. Lewatit VP OC 1065 has a benzylamine functional group supported on a polystyrene backbone crosslinked with divinylbenzene. The sorbent is shipped as spherical particles with a number average diameter of 520 µm. The surface area, pore volume and pore diameter are 50 m² g⁻¹, 0.27 cm³ g⁻¹ and 25 nm respectively [55].

In our research group Lewatit VP OC 1065 has already been used for flue gas capture in the PhD-thesis by Rens Veneman [56]. Veneman developed a trickle-bed reactor to capture CO₂ from flue gases of coal and natural gas power plants. The solid sorbent trickle-bed outperforms aqueous MEA-based systems in productivity by a factor two and has the potential to reduce utility cost with 26%. Other research in the group involved upgrading of biogas by removal of CO₂ [57]. Parallel to the work in this thesis, Lewatit VP OC 1065 is used for deep removal of sour gases from natural gas [58] in the PhD project of Rick Driessen.

Also parallel to this thesis was the PhD work of Qian Yu [59] at direct air capture

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of CO₂ using Lewatit. The work of Yu focused on adsorber reactor development [60] and stability of the sorbent [61]. Conventional fixed bed reactors have too high pressure drop leading to excessive cost for air sorbent contacting. Therefore, Yu et al. developed a shallow radial flow fixed bed adsorption reactor combined with a moving bed desorber reactor for large scale Direct Air Capture (DAC). For smaller scale application of DAC it is expected that the adsorption/desorption cycle is performed in the same vessel for operation simplicity. This later concept is currently being further optimized in the PhD work by Michel Schellevis.

In literature, outside the University of Twente, Lewatit VP OC 1065 is studied for biogas upgrading [62] and flue gas capture [63–66]. Furthermore, fundamental studies into the reaction mechanism [67, 68] are performed.

1.3.4. Reaction Mechanism of amine and CO₂

For adsorption of CO₂ in aqueous amine systems two reaction mechanisms are commonly assumed. That is, the zwitterion mechanism (see equations 1.1 and 1.2) initially proposed by Caplow [69] and the termolecular mechanism (see equation 1.3) initially proposed by Crooks and Donnellan [70]. In the termolecular mechanism it is assumed that the amine bonding to CO₂ and the proton transfer from the amine to an additional base is simultaneously. Whereas, in the zwitterion mechanism this process is assumed to be a two step process with the zwitterion as an intermediate. In aqueous systems the additional base can either be a H₂O molecule or an amine group.

In Lewatit VP OC 1065 the functional group for CO₂ capture is a benzylamine group. The reaction mechanisms of benzylamine in aqueous solutions can be found in publications of Mukherjee et al. [71] and Richner et al. [72]. Mukherjee et al. [71] concluded that the termolecular mechanism is more likely than the zwitterion mechanism based on interpretation of experimental results of CO₂ absorption in aqueous benzylamine.

Zwitterion mechanism

Termolecular mechanism

In absence of H₂O during CO₂ adsorption on solid amine sorbent the only available base for the proposed carbamate forming reaction is another amine group. There-

fore two amine groups should be in close proximity to adsorb one molecule of CO₂. Molecular modelling of Lewatit VP OC 1065 by Buijs and de Flart [67] showed that the amine groups alternate in position and are in close vicinity of each other. This shows that two amine groups could react with each other despite being fixated on the surface. DFT calculations by Buijs and de Flart indicated that either the H₂O catalysed (in humid conditions) or the amine catalysed (in dry conditions) formation of a carbamic acid is the most likely reaction mechanism.

Membrane et al. [73] showed the importance of diffusive intermediates in the CO₂ adsorption in PEI on silica. Hypothesised was the mobility of zwitterions, however DFT calculations questioned the stability of zwitterions in dry conditions. For the adsorption of CO₂ on amines on SBA-15 Hahn et al. [74] showed the formation of carbamate using in-situ FTIR. In the presence of H₂O the carbamate was found to be more stable. Yu et al. [75] found the formation of carbamate for primary amines while carbamic acid was formed for secondary amines. Again H₂O was found to stabilize the products. Bacsik et al. [76] showed formation of both carbamate and carbamic acid using in-situ FTIR for propylamines on silica. Literature seems to have reached consensus that carbamate is formed with primary amines on solid sorbent. The exact reaction mechanism however remains unclear. DFT calculations question the formation of zwitterions and therefore the formation by a termolecular mechanism seems more likely.

1.3.5. Effect of humidity on CO₂ capture

Because water vapour is a major component in air it is important to study the effect of humidity on solid amine sorbents. In literature there is no evidence that supported amine sorbents degrade under the presence of humid vapours during adsorption. On the contrary, the CO₂ capacity increases in many cases in the presence of H₂O [31, 77–81]. The increase in CO₂ is usually attributed to the interaction of H₂O with the reaction mechanism. As discussed in the section above, H₂O can act as the second base for the adsorption reaction. As a result, the reaction product is bicarbonate – see equation (1.4) – instead of carbamate formation in dry conditions [80]. This results in a shift of reaction stoichiometry, while in dry conditions two amine groups are needed to bound one CO₂ molecule, in humid conditions one amine group in combination with a H₂O molecule is theoretically sufficient.

During regeneration conditions the presence of water vapour seems to increase sorbent stability. The stability is increased because the formation of urea – see equation (1.5) – is prevented in the presence of H₂O [80, 82–84]. Even at low relative humidity (0.4%RH) the formation of urea is significantly reduced [80].

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Bicarbonate formation

Urea formation

The effect of humidity on Lewatit VP OC 1065 has been studied by Veneman [85]. The adsorption of H_2O shows the characteristics of multilayer physical adsorption. The highest capacity for H_2O on Lewatit VP OC 1065 was found to be 12.5 mol kg^{-1} (at 95%RH) which is significantly higher than the maximum CO_2 capacity measured of 2.8 mol kg^{-1} (at 303K, $P_{\text{CO}_2}=81 \text{ kPa}$). Moreover, also for Lewatit VP OC 1065 an increase in CO_2 capacity was seen with increasing relative humidity of the adsorption gas.

The co-adsorption of H_2O might have implications for the air capture process. The H_2O content in air is significantly higher than the CO_2 concentration. Therefore, it is expected that more H_2O will adsorb compared to CO_2 . This might become a serious penalty in energy requirement for desorption of CO_2 and regeneration of the sorbent. For example, at a H_2O working capacity of 4 mol kg^{-1} and a CO_2 working capacity of 1 mol kg^{-1} the energy penalty for the adsorption heat of H_2O is $3.6 \text{ MJ/kg}_{\text{CO}_2}$. That is about twice the reaction heat for CO_2 desorption.

1.4. Regeneration of solid sorbents

For large scale CO_2 capture, the ease of regeneration and the stability of the sorbent are important parameters in determining the efficiency, the cost and the feasibility of a process [86]. Desorption of CO_2 from the sorbent can be categorized into three main methods. Desorption by (1) increase in temperature (Temperature Swing Adsorption – TSA) or (2) lowering the (partial) pressure of CO_2 by (2A) reducing the total pressure (Pressure Swing Adsorption – PSA) or by (2B) introducing purge gas (Purge Gas Adsorption - PGA) and (3) the combination of temperature and pressure swing adsorption (Pressure Temperature Swing Adsorption – PTSA).

The three methods of desorption are illustrated by the isotherm lines in Figure 1.2. The lines show the loading of CO_2 as a function of the CO_2 partial pressure for two temperatures. After adsorption a certain (equilibrium) adsorption capacity is reached (q_{ads}). Applying a pure pressure swing the isotherm line is followed to determine the desorption capacity, since the temperature is constant. It is important to note that at air capture conditions ($P_{\text{CO}_2} = 40 \text{ Pa}$) the total pressure should be reduced below 40 Pa to produce pure CO_2 using pure PSA. At increased temperature,

Figure 1.2 | Illustrative isotherm lines: CO₂ loading as function of CO₂ partial pressure. The effect of PSA, PTSA and TSA on the loading is shown.

pure CO₂ can be produced at atmospheric pressure as long as the temperature is high enough. This is demonstrated in Figure 1.2 by the second isotherm line at increased temperature (T_2). Following this line to reduced pressures – a pressure and temperature swing – the working capacity can be increased. The working capacity is defined as the difference between the adsorption and desorption capacity.

An overview of regeneration studies of solid amine sorbent has been given by Bollini et al. [87]. Regeneration studies using a purge medium resulting in low purity CO₂ have been shown in literature [30, 88, 89]. Regeneration of solid amine sorbent by PGA under almost isothermal conditions was shown to be energy efficient for a TEPA-based sorbent in simulations by Pirngruber et al. [90]. In general, PSA is mainly superior to TSA due to its lower thermal and mechanical energy demand [91]. Other studies indicate that Temperature Vacuum Swing Adsorption (TVSA), might be the most attractive option [92–94]. Increasing the temperature during the desorption step permits utilization of a weaker vacuum for removal of CO₂ and thus reduced the energy requirements for desorption [95]. More advantage desorption methods can be quick heating by the Joule effect [88, 96]. By this method electricity can be directly used for the desorption of CO₂. However, this method cannot be (directly) applied for polystyrene supported sorbents because a conductive support is required.

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Production of high purity CO_2 can be done by applying a temperature or pressure swing adsorption without purge flow [90, 97]. Moreover, CO_2 recovery can be increased by use of a steam purge [79, 98–100]. Additionally, Sandhu et al. [98] showed increased desorption kinetics with the use of steam. Wurzbacher et al. [39] and Stuckert & Yang [101] demonstrated the production of high purity CO_2 from air. The energy required for regeneration for CO_2 capture from air is discussed by Elfving et al. [102] using isotherm based working capacities. Elfving concluded that a PTSA is necessary to reach a reasonable working capacity for air capture.

1.4.1. Amine Sorbent Stability

The application window of regeneration conditions might be limited by the sorbent stability. Therefore, it is important to have more knowledge about sorbent stability. Especially at the regeneration conditions which are more challenging with respect to stability. For example, urea formation was observed in the presence of CO_2 at high temperature [82, 86, 103, 104].

Several studies found that amine sorbents degrade in an oxidizing environment [84]. Primary amine were found to be more stable than secondary/tertiary amines [105–107]. The degradation rate was found to be dependent on the temperature. Below 75°C the degradation rate (6% in 30h) was significantly lower than at 120°C (100% in 30h) [84].

NO_2 was shown to adsorb irreversible on PEI impregnated sorbents resulting in loss of CO_2 capacity [108]. In another study [109] nitrite and nitroamine derivatives were found as degradation products. However, NO_2 adsorption on supported amine sorbents seems limited [110] which might limit loss of CO_2 capacity. Also SO_2 seems to adsorb competitively with CO_2 on amine sorbents. Significant loss of CO_2 capacity was seen in literature [108, 111].

The stability of amine sorbents during steam regeneration has also been questioned in literature. Sakwa-Novak et al. [29] showed leaching of PEI from the sorbent. Also Hammache et al. [112] found reduction of capacity of PEI based sorbents because of steam regeneration. Chaikittisilp et al. [28] concluded that PEI-alumina based sorbents are suitable for steam regeneration in contrast to PEI-silica based sorbents. Isenberg and Chuang [113] showed that copper ions from the steam boiler degraded a TEPA based amine sorbent. Li et al. [114] discussed degradation because of structural changes of the sorbent due to steam regeneration.

Stability of Lewatit VP OC 1065

The stability of Lewatit VP OC was analyzed in work by Qian Yu at the University of Twente parallel to this thesis work. The sorbent is shown to be stable in N_2 up

to 150°C [61]. In the presence of oxygen significant reduction in capacity is shown above 80°C because of oxidative degeneration. Below 70°C no significant oxidative degradation is seen. Above 120°C some degradation is reported in a pure CO₂ environment, probably because of urea formation. In the presence of water vapour the stability was increased in pure CO₂. Moreover, 48 hour exposure to steam at 100°C showed no degradation issues. The influence of O₂ and SO₂ is studied by Hallenbeck and Kitchin [64]. It was shown that oxygen had no influence (at low temperature) on the sorbent capacity. However, SO₂ showed quick degradation of the sorbent. Regeneration was partially possible using NaOH.

The above limits with respect to sorbent stability should be taken into account. Especially, while studying regeneration it is important to keep track of the temperature limits. Concentrations of SO₂ (around 75ppb [115]) and NO₂ (around 15ppb [116]) in air are significantly lower compared to CO₂ concentrations and therefore not expected to significantly degrade the sorbent.

1.5. Methanol synthesis

Historically, methanol was produced by distillation of wood into so-called *wood alcohol*. The first production of organic compounds, including methanol, from CO + H₂ (syn gas) was shown by employees of BASF. The compounds were produced using the iron oxide catalyst developed for the catalytic synthesis of ammonia [117]. The first industrial process of syn gas to methanol was shown by BASF in 1923. A sulphur and chlorine resistant zinc oxide - chromium catalyst was used with severe process conditions of 320-450°C and 250-350bar. Although the more active Cu-based catalyst was already known, it was not stable enough. Activity was quickly lost because of sulphur and chlorine compounds present in syn gas these days [118].

For more than 40 years the high pressure process was the leading industrial methanol production method, until the introduction of the low pressure (50-100bar and 200-300°C) methanol process by ICI. In the early 1960s ICI identified a process route with the production of higher purity syn gas (less sulphur and chlorine) suited to be used with the copper based catalyst. Today, the copper-based low pressure methanol production is the most important industrial methanol process [117, 118]. Worldwide the production of methanol increased from 32 to 70 million tonnes per year from 2004 to 2015 [119].

The reactions involved in methanol synthesis are shown in equations 1.6–1.8. Both methanol formation reactions are exothermic and the number of moles reduces during the reaction. Therefore, methanol formation is favoured by low tempera-

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ture and high pressure. Each of the reactions are reversible and thus limited by thermodynamic equilibrium.

In industry, methanol is normally produced from syn gas. Syn gas is a mixture of CO, CO₂ and H₂, usually richer in CO content than in CO₂. The Stoichiometric Number (or Syn gas Number), as defined in equation 1.9, ideally is 2.0 for methanol. However, in industry a small excess of H₂ – SN=2.05 to SN=2.08 is used to improve catalytic performance [120].

$$\text{SN} = \frac{\text{mol H}_2 - \text{mol CO}_2}{\text{mol CO} + \text{mol CO}_2} \quad (1.9)$$

Syn gas for methanol production is commonly produced from natural gas or coal. Globally, natural gas is the most common resource for the production of syn gas. However, in China about 75% of the 40 million tonnes of methanol in 2009 originated from coal [120].

Well proven technologies for natural gas to syn gas conversion include, steam reforming, autothermal reforming, combined reforming and non-catalytic partial-oxidation. The most used technology is steam reforming because it does not need pure oxygen and is available at low capital cost. When pure oxygen is available autothermal reforming can be applied at all sizes. If oxygen is unavailable, autothermal reforming is only (cost) efficient for large (>6,000 tpd) methanol plants. Combined reforming is applied when feedstock prices are higher because of higher efficiency. Again either pure oxygen needs to be available or the plant needs to be large. Non-catalytic partial-oxidation is only applied for special feedstock and/or in combination with oxo-alcohol or acetic acids plants [120].

1.5.1. Conventional methanol synthesis

The principle of methanol synthesis is the feeding syn gas to a heterogeneous catalyst containing reactor. Because of the exothermicity of the reactions and equilibrium constraints heat has to be removed from the reactor. Two main types of reactor concepts can be distinguished: the isothermal and the adiabatic reactor.

In an isothermal reactor normally a shell and tube heat exchanger design is combined with the catalyst for the reaction. The catalyst can be placed on the tube side

Figure 1.3 | Process scheme for Lurgi MegaMethanol synthesis process. A) Feed gas compressor; B) Gas cooled reactor; C) Water cooled reactor; D) Methanol separator; E) Recycle compressor; F) Expansion vessel; G) Light ends column; H) Pure methanol column; I) Atmospheric methanol column. [121]

(Lurgi) or in the shell side (Linde, ICI). Medium pressure steam is produced as a result of cooling [120].

The adiabatic reactor is cooled by adding cold feed gas along the reactor length. A sawtooth temperature profile is created along the reactor. The adiabatic reactor can also be used with interstage heat exchangers instead of feeding cold gas. Combination of an adiabatic reactor with a water cooled reactor is used to quickly preheat the gas to the boiling water part. This ensures efficient use of the relative expensive water cooled reactor since it is only used for heat removal and not for heating the feed gas [120, 121].

After the gas is (partially) converted in the reactor, the product gas is cooled by heat exchanger and the methanol is condensed and separated. Unreacted feed gas is (partially) recycled to the reactor. Typical recycle ratios are 7-9 which can be reduced to 3-4 by the use of a water cooled reactor due to the higher heat removal rate [120].

In Figure 1.3 a typical process layout for the Lurgi MegaMethanol plant can be seen. In this reactor concept the syn gas is preheated in the shell side of the gas cooled reactor (B) and fed to the tube side of the water cooled reactor (C). The water cooled reactor prevents overheating of the catalyst by good heat removal. Next, the gas

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is fed to the tube side of the gas cooled reactor where the conversion is optimized by reduced operating temperature along the reactor. The process is operated at a pressure of 50-100bar and with a temperature of 260°C in the water cooled reactor and 260°C (inlet) to 220°C (outlet) of the gas cooled reactor. With such a combined reactor system the recycle ratio is reduced to 2 [120].

1.5.2. Advanced methanol synthesis

The major challenges of methanol synthesis are reaction heat removal and thermodynamic equilibrium limitations. Where heat removal is more important for syn gas (CO-feed) system [121], the equilibrium limitations are more significant for pure CO₂ feedstocks because of reduced equilibrium yields [122, 123]. In Chapter 5 this will be discussed in more details. Below advanced methods to deal with the above issues are discussed.

Liquid phase methanol synthesis

A liquid phase methanol production process was developed by Air Products offering superior temperature control and higher conversions compared to the conventional gas phase process [120]. A mineral oil / powdered catalyst slurry is used as heat removal and reaction medium. The process is operated as a slurry bubble column. Advantages are the isothermal operation and ability to handle feed with excess of CO because of excellent heat removal. Disadvantage is the inferior life time of the catalyst compared to conventional gas phase process [121].

Membrane reactors

Several methods for shifting the equilibrium – and thereby reducing the amount of unreacted material in the recycle – have been proposed in literature. For example, the equilibrium can be shifted by the use of membranes as studied by van der Ham et al. [124]. The work by Struis et al. [125] showed the use of a Nafion membrane. However, because of material properties maximum conditions of 200°C and 5 bar could be used. Thereby, limiting the conversion due to reaction kinetics and thermodynamics. Gallucci et al. [126] showed increase in conversion and selectivity to methanol by the use of a zeolite membrane. However, still relatively low pressures of 20 bar were used. Rahimpour et al. [127] showed 4.7% increase in the per pass methanol yield by the use of palladium-silver membrane tube walls.

Solvents and sorbents

Another solution to surpass the equilibrium conversion is to use a solvent to adsorb reaction products. Hagihara et al. [128] showed a methanol yield of 95% by the use of n-dodecane as extraction solvent. Westerterp et al. [129] showed almost full

single pass conversion by absorption of products by TEGDME. Also Krishnan et al. [130] showed improved conversion up to 80% by the use of TEGDME as solvent although conversion rates were 2-3 times lower due to diffusion limitations. More recently, Xu et al. [131] showed improved conversion by the use of alcohol as a solvent. Adsorption of product vapors by silica-alumina powder with conversion up to 100% was shown by Westerterp et al. [132, 133].

Condensing methanol

When the operation pressure is increased to sufficient high pressure the methanol (and water) product will condensate at the operating conditions. By condensation, the reaction products are removed from the reaction phase and equilibrium limitations are removed. Condensation at high pressure was shown by van Bennekom et al. [134] at 200 bar and by Tidona et al. [135] at pressures up to 360 bar. On the other hand, condensation can be initiated at lower pressures by a reduction in the (local) temperature. Haut et al. [136] showed increased conversion by a radial temperature gradient over the catalyst bed. At the outer radius the temperature is decreased below the dew point to initiate in situ condensation. Perko et al. [137] used a temperature gradient by a parallel hot and cold plate. The catalyst is placed at the hot plate while the products are condensed at the cold plate.

However, most of the proposed methods introduce extra process steps, process equipment or increased capital cost due to high pressure equipment. Additionally, both designs using a temperature gradient do not achieve full reactant conversion in a single reactor pass and still require an external recycle of reactant gases. Moreover, the proposed condensation concepts all allow for liquid condensate being formed at the catalyst particles. Liquid formation at the catalyst might reduce reaction rates due to extra mass transport limitations. Moreover, the condensate is corrosive and causes significant catalyst deactivation [138]. Furthermore, the above temperature gradient designs have been verified with CO-rich syn gas feeds only. In chapter 5 a novel reactor for full conversion of a CO₂ feedstock to methanol will be presented.

During the time frame of this thesis theoretical studies were published by Iyer et al. [139] and Stangeland et al. [140] which confirmed the possibilities of increased methanol yield by condensation of product vapours. Furthermore, increased CO₂ conversion at high pressure operation was shown experimentally by Gaikwad et al. [141] and by Raymond et al. [142] at very high pressure (>450 bar).

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1.5.3. Thermodynamics and kinetics of methanol synthesis

The three reactions occurring during methanol synthesis are presented in equations 1.6 to 1.8. Chemical equilibria during methanol synthesis have been determined by Graaf et al. [143] back in 1988. However recently, Graaf and Winkelman published a reassessment [144] of chemical equilibria during methanol synthesis using over 300 experimental data points. The equilibrium constants are determined for equation (1.6) and (1.8). By combination of these two the equilibrium constant of equation (1.7) can be found.

The carbon source of methanol have been discussed in literature for a long time. Historically, CO was considered to be the main source for methanol while CO₂ was seen as a stable component [145, 146]. In later work, consensus changed to CO₂ as the main source of methanol [147–149]. However, others [143, 150, 151] considered both CO and CO₂ as source for methanol production. C₁₃-isotope experiments by Studt et al. [152] showed that under industrial conditions the CO₂ hydrogenation is much faster than the CO hydrogenation.

Choi et al. [153] showed that CO₂ activity increased on reduced catalyst surfaces while CO hydrogenation is more active on oxidized surfaces. This proves that CO and CO₂ hydrogenation take place at different catalyst sites. The change of catalyst morphology with changing gas feed composition (e.g. CO₂ / CO feed ratio) is discussed in literature [154–157]. Deuterium isotope experiments by Kunkes et al. [158] in the kinetic regime of CO₂ hydrogenation showed an inverse kinetic isotope effect that is stronger for methanol formation than for CO formation. This suggests that the CO₂ hydrogenation and CO-formation pathways do not share a common intermediate. In contrast to CO₂ hydrogenation, the hydrogenation of CO does not show a strong kinetic isotope effect. This indicates that methanol formation from CO₂ does not proceed via the reverse water gas shift. Differences in product inhibition by water between the methanol synthesis from CO₂ and the reverse water gas shift show that these reaction proceed on different catalyst sites.

Kinetic models for methanol synthesis have been widely studied in literature [143, 147, 149, 151, 159–162]. Recently, Bozzano and Manenti [157] gave an overview of kinetics models in literature. The most widely used models in literature are the kinetic rate equations of Graaf et al. [143, 159] and Bussche and Froment [149].

1.6. Process route

When producing methanol from CO₂ and H₂O, oxygen has to be removed because the oxygen content in methanol is lower than the sum of the oxygen content in

Figure 1.4 | Overview of process routes of methanol production from CO_2 and H_2O .

H_2O and CO_2 . Methanol can be produced from either syn gas ($\text{CO} + \text{H}_2$) or by the direct hydrogenation of CO_2 . Syn gas can be produced in three ways: by CO_2 deoxygenation, by H_2O deoxygenation or by deoxygenation of both. Therefore, in total four process routes to methanol can be identified. In Figure 1.4 the four process routes are shown: syn gas production via CO_2 deoxygenation in combination with the water gas shift (Route A), syn gas production via H_2O deoxygenation in combination with the reverse water gas shift (Route B), direct catalytic conversion of CO_2 with H_2 (Route C) and deoxygenation of both CO_2 and H_2O in order to produce syn gas (Route D). In the section below the separate steps are discussed in more detail.

The thermodynamic amount of energy required is approximately equal for the two possible deoxygenation routes, see equation 1.10 and 1.11 [163]. The dissociation of water is technologically much more developed and researched compared to the dissociation of carbon dioxide. Because of the advanced state of water splitting, the efficiency is higher for water than for carbon dioxide splitting [13]. The maximum energy efficiency of CO_2 dissociation with the current techniques is 50% [163, 164], while the dissociation of water can reach efficiencies up to 80% [13, 163, 165, 166]. Also separation of products from unreacted reactants is easier for $\text{H}_2\text{O}/\text{H}_2$ because water could easily be condensed, while CO/CO_2 is gas phase based separation. [163].

Table 1.1 | Thermodynamic energy comparison of routes. E1 = Energy required to deoxidised one mole or reactant (kJ mol^{-1}). E2 = Energy required to produced one mole of methanol (kJ mol^{-1}). [13, 163–166]

	Route	Efficiency	E1	E2	Notes
A	$\text{CO}_2 \rightarrow \text{CO}$	50%	566	1525	3 moles CO, WGS, syn gas reaction
B	$\text{H}_2\text{O} \rightarrow \text{H}_2$	75%	381	1095	3 moles H_2 , RWGS, syn gas reaction
C	$\text{H}_2\text{O} \rightarrow \text{H}_2$	75%	381	1095	3 moles H_2 , direct reaction
D	$\text{CO}_2 \rightarrow \text{CO}$	50%	566	1238	1 mole CO
	$\text{H}_2\text{O} \rightarrow \text{H}_2$	75%	381		2 moles H_2 , syn gas reaction

Another way of CO_2 dissociation is the reverse water gas shift (RWGS) reaction – see reaction 1.8 – where hydrogen and CO_2 are combined. A disadvantage of the RWGS is the need for high temperatures ($>850^\circ\text{C}$) to shift the equilibrium to the CO side. Water shall be removed since this negatively influences the equilibrium reactions in both, the RWGS and methanol reactors. Water can also be deoxygenated by CO to produce hydrogen by the water gas shift reaction (WGS). For the water gas shift (WGS) temperatures of 400°C are needed [166].

For producing methanol two routes have been identified; from syn gas – a mixture of carbon monoxide and hydrogen – or from a mixture of carbon dioxide and hydrogen. As shown in reaction 1.6 and 1.7 the production of methanol from syn gas is much more exothermic than the production of methanol from carbon dioxide [167].

The theoretical energy need for the four routes are analysed in order to find the most energy efficient route. The reaction energy and the state-of-the-art realized efficiency of the deoxygenation step are taken into account. The energy requirement to deoxygenate one mole reactant is given in the fourth column (E1) of Table 1.1 and the energy use for one mole of methanol is given in the fifth column (E2). It can be seen that the energy need is more or less determined by the efficiency of the deoxygenation step. For that reason, the theoretical energy need for route B and C is the lowest. Since, the extra conversion step of the water gas shift is not necessary for route C a slight – theoretical – advantage is gained over route B.

Summarizing, four routes from CO₂ and water to methanol have been identified. Three are based on syn gas based production of methanol and one is based on the direct conversion of CO₂ with hydrogen to methanol. Route A and D require more energy because of the low efficiency of CO₂ deoxygenation with the 2012 state of technology. While route B and C have similar energy requirement, route B needs an extra high temperature process step. Therefore, route C has been selected as the route with the highest potential.

1.7. Scope and outline

In this thesis storage of renewable electricity in methanol is researched. The abundant available reactants CO₂ and H₂O are converted to methanol. This thesis is focused around technology development for CO₂ air capture and CO₂ conversion to methanol. Technology for conversion of H₂O into H₂ is outside the scope of this thesis.

To design a CO₂ capture system it is important to know where limitations in the system are present. For sizing of equipment the uptake rate and reaction kinetics are important. Therefore, in **Chapter 2** the transport phenomena and kinetics of CO₂ adsorption on solid amine sorbents are studied. However, because of fast adsorption kinetics measuring intrinsic kinetics is challenging. The aim of Chapter 2 is therefore to develop a experimental method to measure adsorption kinetics in absence of mass and heat transport limitations. The second aim is to use the developed method to measure the adsorption kinetics of CO₂ on Lewatit VP OC 1065.

To reuse the sorbent, the adsorbed CO₂ has to be removed from the sorbent. Equally important to the adsorption rate, the desorption rate might determine equipment sizes. The objective of **Chapter 3** is to identify methods to (completely) clean the sorbent and the transport mechanism determining the desorption rate of CO₂. For the production of methanol high purity CO₂ is required. For this reason, the production of high purity CO₂ from air is studied in **Chapter 4**. The first aim of Chapter 4 is to determine the effect of steam purge on the CO₂ working capacity and energy required for desorption. The second goal is to study the consequences of water co-adsorption on the energy required for desorption. The penalty for desorption of co-adsorbed water might be severe, as discussed in section 1.3.5.

Chapter 5 focusses on the challenges when converting CO₂ to methanol. The major challenge of CO₂ to methanol conversion is the decrease in thermodynamic equilibrium conversion when switching CO-rich for CO₂-rich feedstocks. As discussed in section 1.5.2 removal of products from the reactant gas can increase conversion

1

beyond the equilibrium. A novel reactor concept using two temperature zones to initiate product condensation is introduced in Chapter 5. The temperature zones are placed in such a way to benefit from natural convection for gas recirculation. The aim of the chapter is to show proof of concept for both increased CO₂ conversion and gas circulation under natural convection conditions.

Further characterization of the novel reactor concept is shown by modelling in **Chapter 6**. First, the characteristics and limitations of the current reactor are identified. Second, the energy efficiency of the concept will be presented. Finally, improvements to be made in a second generation reactor will be discussed. The main objective of the chapter is to identify the feasibility of the concept for next generations of the reactor.

In the final **Chapter 7** the complete process from CO₂ and H₂O to methanol is evaluated. Because the capture of CO₂ from air is energy intensive it is important to study (energy) integration options within the process. Of course, the viability of the proposed process is strongly correlated with the economics. For this reason, a economic evaluation is made. Finally, the efficiency of electricity storage in methanol is presented.

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1.8. Abbreviations

1

Table 1.2 | List of symbols and abbreviations.

Symbol	Meaning
CAES	Compressed Air Electricity Storage
CCS	Carbon Capture and Storage
CH ₃ OH	Methanol
CO	Carbon monoxide
CO ₂	Carbon dioxide
DAC	Direct Air Capture
H ₂	Hydrogen
H ₂ O	Water
Li-ion	Lithium ion
MEA	Monoethanolamine
NaS	Sodium - Sulphur
Pb	Lead
PEI	Polyethyleneimine
PGA	Pressure Gas Adsorption
PSA	Pressure Swing Adsorption
PTSA	Pressure Temperature Swing Adsorption
RTE	Round Trip Efficiency
RWGS	Reverse Water Gas Shift
TSA	Temperature Swing Adsorption
VSA	Vacuum Swing Adsorption
WGS	Water Gas Shift

CO₂ ADSORPTION

I

2

Transport phenomena and intrinsic kinetics for CO₂ adsorption in solid amine sorbent

Abstract

A study on the intrinsic kinetics of CO₂ adsorption on a solid amine sorbent is performed. For this, a new experimental method is developed to exclude heat and mass transfer limitations during kinetic adsorption experiments. Hereto a novel contactor was designed and good process control, working with pure CO₂ and small particle diameters enabled the measurement of intrinsic kinetics. A mathematical model describing convection, diffusion and reaction rate inside a particle confirmed the absence of mass and heat transfer limitations in the experiments. Linear driving force and Toth-isotherm reaction rate equations are evaluated for the CO₂ adsorption process studied. The results show that the experimental particle loading with time could not be described by the linear driving force models. On the other hand, the Toth reaction rate equation, consistent with the Toth isotherm to describe the adsorption equilibrium, showed a very good fit to the experimental data. This shows that a rate based isotherm equation is necessary for prediction of both adsorption rate and equilibrium loading. It also implies that there is a strong correlation between the kinetic rate parameters found and the adsorption equilibrium parameters used, which was confirmed in this study.

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2.1. Introduction

Analysing kinetics of adsorption is important for reactor sizing and process optimization. Commonly, kinetics of adsorption are determined in fixed bed experiments [168–171] or in a TGA apparatus [172–177]. However, in fixed bed adsorption experiments isothermal plug flow conditions are almost never achieved. Therefore, significant numerical modelling [168] has to be applied to determine kinetics from fixed bed operation, accounting for dispersion and temperature increases. In TGA, supply limitations might be present due to low gas flow rates and isothermal operation is challenging. To determine intrinsic kinetics experiments have to be performed under well-defined conditions. For example, in a spinning basket reactor [178] or a differential fixed bed reactor [179].

This chapter describes a new experimental method to measure intrinsic kinetics of CO₂ adsorption on solid amine sorbents. In this method a flat bed reactor is used in combination with the supply of pure CO₂ to the sorbent. Thereby, external mass transfer and supply limitations are eliminated. Good heat transfer is achieved by direct contact of the monolayer of sorbent with the temperature controlled bottom support plate. Validation of the new experimental method is discussed. Next to the new experimental method, the results for the intrinsic kinetics of Lewatit VP OC 1065 are presented.

2.2. Materials and methods

2.2.1. Materials

The solid amine sorbent studied in this work is Lewatit VP OC 1065 supplied by Lanxess. Lewatit VP OC 1065 has a primary benzylamine group that reacts with CO₂ [63]. The benzylamine group is supported on a polystyrene backbone crosslinked with divinylbenzene. The sorbent is shipped as spherical particles with an average diameter of 520 μm . The surface area, pore volume and pore diameter are 50 $\text{m}^2 \text{g}^{-1}$, 0.27 $\text{cm}^3 \text{g}^{-1}$ and 25 nm respectively [55]. The CO₂ gas used is supplied by Praxair, the Netherlands in 99.9993% purity. More material properties, model symbols and abbreviations can be found in Table 2.S1.

2.2.2. Experimental Setup

About 1.35 gram of sorbent is loaded in a flat bed reactor (see Figure 2.1) of 150 mm diameter and 10 mm height, constructed of stainless steel. A thin layer of sorbent – close to monolayer – is in contact with the thermostated bottom plate of the reactor.

Figure 2.1 | Experimental set-up to measure adsorption kinetics.

The thin layer of sorbent is covered with a 5 μm stainless steel wire mesh topped with 1 mm diameter stainless steel spheres to fixate the layer of sorbent. Initially, the sorbent is cleaned from H_2O and CO_2 by heating to 80°C (Julabo 6-MW) and reducing the absolute pressure to less than 1 mbar in the reactor by a vacuum pump (Edwards E2M2). After cooling (Julabo F12-MW) the reactor to experimental temperature, Grade 5.3 CO_2 (Praxair) is fed from the supply vessel (E-1, Fig. 2.1) to the headspace in the reactor (E-2) through the inlet in the cylindrical wall.

Pressure in the reactor and supply vessel is monitored by high precision pressure sensors (Heise DXD $\pm 0.02\%$ full scale, PI-1: 0-30PSI, PI-2: 0-20PSI). The pressure inside the reactor is controlled by a pressure controller (PCV-1, Fig. 2.1, Brooks 5866 series). Because the response of the pressure control valve is slow compared to adsorption kinetics a bypass solenoid valve (V-2) is installed to instantaneously increase the reactor pressure to the experimental pressure. The opening of the valves and data acquisition is performed using Labview. The bypass valve is opened for a few hundred milliseconds after which it is automatically closed. Flow through V-2 can be restricted by a needle valve. Temperature is monitored using PT-100 temperature sensors. Temperature is monitored in the buffer vessel (TI-1, Fig. 2.1) and two radial positions inside the reactor (TI-2 and TI-3).

2.2.3. Experimental and interpretation methods

An experimental cycle consist of three steps: regeneration, cooling and experiment. The same batch of sorbent is reused for all experiments. Regeneration is performed at 80°C and vacuum pressure ($<1\text{mbar}$) to clean the sorbent from CO_2 . Before the first experiment of a sorbent batch the sorbent is cleaned from water and CO_2 by heating to 80°C and purging nitrogen overnight. After 1.5 hours of regeneration, cooling to the experimental temperature is performed under vacuum pressure. At the start of the experiment, the reactor is at experimental tempera-

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ture and vacuum pressure (<1mbar). The supply vessel has a pressure of approximately 2 bar of pure CO₂ and is at room temperature at the start of the experiment. Next, the pressure control valve and bypass valve are opened in parallel (defined as $t = 0$). From this point on the experiment is performed at isothermal and isobaric (after reaching the experimental pressure) conditions. Experiments have been performed at 50/100/200 mbar and in the temperature range of 5-40°C.

Using the pressure and temperature in the supply vessel and the reactor the number of moles of CO₂ on the sorbent can be calculated using Equation 2.1. In this equation the (small) volume of the pipelines upstream and downstream the valves is clubbed with respectively the value of either the buffer vessel volume or the reactor volume. The compressibility factor of CO₂ is not taken into account because the maximum pressure is 2.5 bara, which means the compressibility factor is higher than 0.99 [180]. Following, the sorbent loading can be calculated from Equation 2.2 where $m_{\text{sorbent,wet}}$ [kg] is the wet sorbent mass as weighted and MC_{sorbent} the moisture content on the stock sorbent, see Table 2.2.

$$n_{\text{CO}_2,\text{ads}}(t) = \left[\frac{P_{\text{reac}}V_{\text{reac}}}{RT_{\text{reac}}} + \frac{P_{\text{buf}}V_{\text{buf}}}{RT_{\text{buf}}} \right]_{t=0} - \left[\frac{P_{\text{reac}}V_{\text{reac}}}{RT_{\text{reac}}} + \frac{P_{\text{buf}}V_{\text{buf}}}{RT_{\text{buf}}} \right]_{t=t} \quad (2.1)$$

$$q(t) = \frac{n_{\text{CO}_2,\text{ads}}(t)}{m_{\text{sorbent,wet}} \cdot (1 - MC_{\text{sorbent}})} \quad (2.2)$$

From the sorbent loading the adsorption kinetic constant (k_{ads}) is found by fitting the integrated rate equation (see section 2.2.4) on the experimental loading versus time curve. The rate equation is integrated either manually for the linear driving rate force equations or numerically using the ode45 function in Matlab for the Toth rate equation. Fitting of the loading curve is performed by the least-square fit function lsqcurvefit in Matlab.

2.2.4. Reaction rate equation

In this study we evaluate the sorption kinetics of CO₂ on a solid amine sorbent, aiming to identify the intrinsic reaction kinetics in absence of mass transfer limitations. In section 1.3.4 of the introduction more details about the reaction mechanism of CO₂ with solid sorbents is given. In the evaluation of the experimental data multiple kinetic rate equations are used. Below, the equations used are shortly summarized:

- **Pseudo-first order** linear driving force model: The most simple and straight forward model and therefore often used in literature. The linear driving force (LDF) definition by Glueckauf [181] is used and not the often used Lagergren

[182] pseudo first order definition. Differences in both interpretations are discussed by Rodrigues and Silva [183].

$$\frac{\partial q}{\partial t} = k_{LDF1} P_{CO_2} (q_e - q) \quad (2.3)$$

In this equation k_{LDF1} is the kinetic constant, P_{CO_2} is the CO_2 (partial) pressure in the reactor, q_e the equilibrium loading at the corresponding CO_2 (partial) pressure and temperature in the reactor and q the loading at time t . q_e is determined by the Toth isotherm, see Table 2.1. The gas concentration is included in the form of the CO_2 pressure, in accordance with the findings by Veneman et al. [184]

- **Pseudo-second order** linear driving force model: Because in dry conditions two amine molecules are needed to capture one CO_2 molecule, the pseudo-second order model seems more correct from a mechanistic point of view.

$$\frac{\partial q}{\partial t} = k_{LDF2} P_{CO_2} (q_e - q)^2 \quad (2.4)$$

Again k_{LDF2} is the kinetic constant, P_{CO_2} is the CO_2 pressure, q_e and q the loading at equilibrium with the reactor conditions and at time t respectively.

- **Toth** rate equation: The Toth isotherm is a Langmuir-based isotherm modified with a surface heterogeneity parameter t_h , see Table 2.1. Consequently, this parameter is found in the rate equation [185].

$$\frac{\partial q}{\partial t} = k_{Toth} \left\{ P_{CO_2} \left[1 - \left(\frac{q}{q_s} \right)^{t_h} \right]^{\frac{1}{t_h}} - \frac{1}{b} \frac{q}{q_s} \right\} \quad (2.5)$$

In this equation k_{Toth} is the kinetic constant, P_{CO_2} is the CO_2 pressure in the reactor, q_s is the maximum loading of CO_2 on the sorbent at any conditions, b is the equilibrium parameter which is also defined as $b = \frac{k_{ads}}{k_{des}}$ and q is the loading at time t . The parameters q_s , t_h and b can be determined by fitting the equilibrium capacities on the isotherm, see section 2.3.1 and Tables 2.1 and 2.3.

To determine the accuracy of fitted rate constants the Sum of Squared Errors of prediction (SSE) was calculated. For the fit of k_{ads} on the loading versus time curve this can be done with equation 2.6.

$$SSE = \sum (q(t)_{exp} - q(t)_{mod})^2 \quad (2.6)$$

Table 2.1 | Toth isotherm equations

Toth Isotherm	
$q_e = \frac{q_s b P_{\text{CO}_2}}{\left(1 + (b P_{\text{CO}_2})^{t_h}\right)^{\frac{1}{t_h}}} \quad (1)$	
$b = b_0 \cdot \exp\left(\frac{\Delta H_0}{RT_0} \left(\frac{T_0}{T} - 1\right)\right) \quad (2)$	
$t_h = t_{h0} + \alpha \left(1 - \frac{T_0}{T}\right) \quad (3)$	
$q_s = q_{s0} \cdot \exp\left(\chi \left(1 - \frac{T}{T_0}\right)\right) \quad (4)$	

In this equations $q(t)_{\text{exp}}$ is the experimental measured loading at time t and $q(t)_{\text{mod}}$ is the loading predicted by the rate equation. To determine the SSE for the Arrhenius plot the $q(t)_{\text{exp}}$ and $q(t)_{\text{mod}}$ are replaced by k_{exp} and $k_{\text{Arrhenius}}$.

2.2.5. Error analysis and reproducibility

Error analysis have been performed on the experimental determined loading. The method of propagation of errors is used [186]. In section 2.6.2 of the Supporting Information more details about the calculations can be found. In Table 2.2 the parameters and their errors are shown. The error of pressure sensors have been checked by calibration using a dead weight tester (Tradinco T2400-1) in the pressure range above atmospheric pressure and a pressure calibrator (Beamax MC-5) in the reduced pressure range. The errors found after calibration are within sensor accuracy. The PT-100 temperature sensors have been checked using a water bath and a analogue mercury temperature indicator.

The buffer vessel and reactor volumes have been determined using a separate calibration vessel (V_{cal}) and equilibration of nitrogen pressure. Using the pressure before and after equilibration the unknown volume can be determined. The volume of the calibration vessel is determined by filling it with water and measure the mass increase. The error shown for the calibration vessel in Table 2.2 is the standard deviation (95% confidence interval) of four measurements. The error shown for the reactor and buffer vessel is either the standard deviation of four measurements (column standard deviation, Table 2.2) or the error by propagation of the error in the pressure and calibration vessel (column Error, Table 2.2). The value of the stan-

Table 2.2 | Error in parameters. The column 'standard deviation' shows the value of two standard deviations (95% confidence intervals) from the experiments. The column 'error' shows either the error by accuracy of the device or the error by propagation of errors for calculated values.

Parameter	Symbol	Value	Standard deviation	Error	Unit
Moisture content sorbent	MC_{sorbent}	0.449	0.016	—	$\frac{kg_{\text{moisture}}}{kg_{\text{sorbent}}}$
Pressure Reactor	P_{reac}	$1.4 \cdot 10^5$		28	Pa
Pressure Buffer vessel	P_{buf}	$2.1 \cdot 10^5$		41	Pa
Temperature	T_i			0.5	K
Volume Buffer vessel	V_{buf}	114.4	1.2	0.7	mL
Volume Reactor	V_{reac}	160.2	1.3	1.1	mL
Volume calibration vessel	V_{cal}	516.6	1.2	—	mL
Wet mass sorbent	$m_{\text{sorbent,wet}}$	1.35		0.01	g

standard deviation has been used in further error propagation calculations.

The moisture content of the sorbent has been determined using TGA apparatus (Netsch STA-449). The average value and standard deviation of four measurements are shown in Table 2.2. The wet sorbent mass added to the reactor has been determined using an analytic balance (Mettler AE100).

The error found in the loading is $\pm 0.19 \text{ mol kg}^{-1}$ which is a significant relative error at low sorbent loading, although the relative error goes down rapidly with increasing sorbent loading. However, the reproducibility of the data seems to be much better than suggested by the $\pm 0.19 \text{ mol kg}^{-1}$ as is shown in Figure 2.2. It is seen that the maximum difference between a duplicate measurement is 0.02 mol kg^{-1} for the fast experiment (30°C & 200 mbar) and 0.03 mol kg^{-1} for a triplet measurement of a slow experiment (5°C & 100 mbar). More duplicate experiments are shown in section 2.4.1.

2.2.6. Particle model

A mathematical model for diffusion and reaction into a spherical particle is constructed to analyse and verify the absence of mass and heat transport limitations in the experimental dataset.

During adsorption of CO_2 on porous solid sorbents three stages of mass transfer can be distinguished as shown in Figure 2.3. First, CO_2 has to be transported from the bulk through the film layer resistance to the interface (1, Fig. 2.3), also ref-

Figure 2.2 | Examples of reproducibility of a slow (5 °C & 100 mbar) and a fast (30 °C & 200 mbar) experiment. Symbols are added to increase distinction between lines.

Figure 2.3 | Schematic overview of transport phenomena during CO₂ adsorption into a particle. $C_{g,b}$ is the gas bulk concentration, $C_{g,i}$ the gas interface concentration on the particle outer surface and C_p the gas concentration inside the particle pores. (1) shows the film layer resistance, (2) the diffusional transport into the pores and (3) reaction with the amine on the solid surface.

erenced to as external mass transfer. Next, CO₂ has to be transported into the pores of the particle (2, Fig. 2.3) as only little CO₂ can adsorb on the outer surface of the particle. This internal mass transfer is normally limited by either molecular or Knudsen diffusion [187]. In case of a total pressure difference inside the pores viscous flow can play a role [187]. Finally, the CO₂ can react with the amine groups on the surface (3, Fig. 2.3). Transport phenomena for heat transfer are analogue, as internal transfer by conduction through the particle plays a role and external transport by convection or conduction into the surrounding gas or the reactor wall.

In equation 2.7 the gas phase balance can be seen. The variables used in the equations below can be found in Table 2.S1. For transport into the pores Knudsen diffusion and viscous flow [187] are included.

$$\varepsilon \frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\varepsilon}{\tau} \left(\frac{4}{3} \frac{r_{\text{pore}}}{2} \sqrt{\frac{8RT}{\pi M}} + \frac{r_{\text{pore}}^2}{8\mu} CRT \right) \frac{\partial C}{\partial r} \right] - \rho_s R_{\text{ad}} \quad (2.7)$$

The solid phase balance is shown in equation 2.8 and R_{ad} is defined by the rate equations shown in equations 2.3-2.5.

$$\frac{\partial q}{\partial t} = R_{\text{ad}} \quad (2.8)$$

The energy balance is shown in equation 2.9 and used to determine temperature profiles inside the particle.

$$\rho_s C_{p,s} \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \lambda_s \frac{\partial T}{\partial r} \right] + \Delta_r H \rho_s R_{\text{ad}} \quad (2.9)$$

2.2.7. Thermal Conductivity

The thermal conductivity of the sorbent particle was found to be an important parameter to predict if significant temperature gradients exist within a particle. As no literature data was found for Lewatit VP OC 1065 or similar polystyrene particles, it was decided to measure the thermal conductivity of the sorbent.

The thermal conductivity of the sorbent is determined by investigating temperature gradients within a fixed bed of particles, heated from the cylindrical wall and bottom area. From these experiments the effective thermal conductivity through the combined sorbent/air bulk can be determined. Using the equation by Zehner and Schlünder [188] the measured effective thermal conductivity can be translated

into the solid thermal conductivity. An average value of $0.43 \text{ W m}^{-1} \text{ K}^{-1}$ was found for the solid thermal conductivity. More details about the experimental methods and calculations can be found in Appendix B

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2.3. Validation of the experimental method

2.3.1. Equilibrium capacity

The equilibrium capacity is an important factor in the rate equations as shown in the section 2.2.4. From literature [57, 58, 62, 85] it is known that the Toth isotherm fits the equilibrium capacity well. However, in the study of Veneman et al. data for a limited temperature range (303-373 K) has been obtained, especially when considering CO₂ capture from ambient air. In order to validate the kinetic rate equation over a larger temperature range new isotherm parameters are fitted. The experimental equilibrium data of Veneman et al. [85] is used. Additionally, equilibrium data from Sutanto et al. [57] is included in the dataset to cover high temperature data. In this study, additional low temperature (278 K & 288 K) equilibrium capacities are measured. To check the experimental method used in this study equilibrium capacities are measured at 313 K and compared to data measured by Veneman et al. The found equilibrium capacities correspond well with capacities by Veneman et al. In Figure 2.4 an overview of the data points and model fits is given.

The data have been fitted using least square minimization by the Globalsearch function in Matlab. The Normalized Standard Deviation (NSD) has been calculated with equation 2.10. In this equation q_{exp} is the experimental measured equilibrium capacity and $q_{isotherm}$ the loading predicted by the isotherm. N is the number of experimental points.

$$NSD(\%) = \sqrt{\frac{\sum [(q_{exp} - q_{isotherm}) / q_{exp}]^2}{N - 1}} \times 100 \quad (2.10)$$

The parameters found are shown in Table 2.3 and compared with the Veneman parameters. It should be noted that the maximum capacity q_{s0} is fixed to 3.4 mol kg^{-1} for two reasons. First, the nitrogen loading in the sorbent is 6.8 mol kg^{-1} [61] and two amine molecules are needed to capture one CO₂ molecule in dry conditions. Second, it was seen that the fixation of q_{s0} significantly reduced the NSD. Next to fitting the data to the Toth isotherm it was tried to fit the Langmuir isotherm in order to reduce fitting parameters on both the isotherm and rate equation. However, opposite to results by Sonnleitner et al. [62] no accurate fit could be found.

Figure 2.4 | Experimental equilibrium capacity (symbols) determined by Veneman [85] (squares), Sutanto [57] (triangles) and this work (rounds). The lines represent the Toth isotherm fitted in this work (lines) and by Veneman (stripes) as comparison. The lines plotted range from 273 K to 413 K with 20 K intervals.

Table 2.3 | Isotherm parameters.

Symbol	Veneman et al. [85]	This work	Unit
	Parameter set A	Parameter set B	
q_{s0}	3.40	3.40	mol kg ⁻¹
χ	0	0	—
T_0	353.15	353.15	bar ⁻¹
b_0	408.84	93.0	bar ⁻¹
ΔH_0	86.7	95.3	kJ mol ⁻¹
t_{h0}	0.30	0.37	—
α	0.14	0.33	—
<i>NSD</i>	15.4	7.7	%

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As is shown in Table 2.3 the NSD on the data set presented in Figure 2.4 for the Veneman isotherm is significantly larger than for the fit in this work. In the parity plots in Figure 2.S1 can be seen that the Veneman isotherm significantly deviates outside the original temperature range. That is, at lower (<30°C) and higher (>100°C) temperatures. This means that the average accuracy of the isotherm reduces from $\pm 0.09 \text{ mol kg}^{-1}$ originally to $\pm 0.15 \text{ mol kg}^{-1}$ on the dataset presented here.

Furthermore, it is seen that both isotherms are under predicting the capacity at temperatures below 20°C. This might be an effect of change in mechanism as the absolute maximum (3.4 mol kg^{-1}) of one CO₂ molecules reacting with two amine groups is approached. Additionally, it is shown in the parity plot in Figure 2.S2 that the isotherm presented in this chapter is accurate in range from 20-140°C resulting in an average accuracy of $\pm 0.12 \text{ mol kg}^{-1}$ over the whole temperature range.

2.3.2. Effect of bypass valve V-2

During initial screening experiments it was found that the adsorption rate is fast. As a result, the initial pressure increase from vacuum to the experimental pressure was found to be relatively slow. As shown in Figure 2.6 the pressure increase takes about 5 seconds to reach the experimental pressure for the 100 mbar experiment. This might have two consequences.

First, the reactor pressure is not constant in the initial phase of the adsorption process. However, this is the most optimal phase to determine adsorption kinetics since the influence of equilibrium is minimal. As seen in Figure 2.5 the sorbent loading is already as high as 0.5 mol kg^{-1} after 5 seconds which is around 20% of the equilibrium capacity.

Second, because of the slow increase in pressure the initial adsorption rate might be limited by the supply of CO₂ and thereby no truly intrinsic kinetics are measured. Because tuning of the PI control settings of the pressure control valve did not speed up the pressure increase sufficiently a bypass valve (V-2, Figure 2.1) is installed. The pressure control valve (PCV-1, Figure 2.1) and the bypass are opened in parallel. The bypass valve is closed after several hundreds of milliseconds depending on the desired reactor pressure. As shown in Figure 2.6 the reactor pressure is significantly faster increased when V-2 is used. Thereby, CO₂ supply limitations are eliminated.

2.3.3. CO₂ concentration

External mass transfer limitations can be removed by using pure CO₂ as this will remove the film layer resistance. The effect of the CO₂ concentration is clearly seen

Figure 2.5 | Effect of the bypass valve V-2 on the initial reaction rate at 20°C and 100mbar of pure CO₂ for particles with a diameter between 150-250 µm.

Figure 2.6 | Typical initial pressure profile during a at 20°C and 100mbar of pure CO₂ experiment

in Figure 2.7. The difference between 25% and 50% of CO₂ is a result of the increase in driving force for mass transfer with increasing concentration. Internally, mass transfer limitations by molecular diffusion will be eliminated by using pure CO₂. However, internal mass transfer limitations by Knudsen diffusion and viscous flow [187] might still influence the adsorption rate.

2.3.4. Particle size

The diameter of adsorbent particles will influence both, the internal and external heat and mass transfer properties. Where internal transfer is directly influenced by the diameter of the particle because of the penetration depth, external transfer is indirectly influenced since external heat and mass transfer coefficients are dependent on the diameter of the particle [189]. The diameter of the particles has been varied to see if heat and mass transfer limitations are minimized. In Figure 2.8 is shown that largest fraction (355-500 μm) has a significant lower adsorption rate than the other two fractions. The adsorption rate for the 150-250 μm and 250-355 μm fractions are almost equal. The results found are in line with results published by Goeppert et al. [190] which showed that adsorption kinetics increase with smaller particle diameters. Additionally, Goeppert et al. showed that below 250 μm influence of particle diameter on adsorption rate is minimized. It should be noted that Goeppert et al. used a PEI-based sorbent.

The results in Figure 2.8 show that by reducing the particle diameter the influence of mass and heat transfer is minimized. As the influence of external mass transfer is already excluded by using pure CO₂, heat transfer is most probably the reason that (355-500 μm) fraction has a lower adsorption rate. When the heat removal rate is insufficient the particle temperature might increase and the equilibrium capacity might be influenced and with this the uptake rate is influenced. Next to that, to be able to determine the temperature dependency of kinetic parameters, isothermal conditions are desirable. The influence of heat transfer and mass transfer inside the particles on the adsorption rate will be further discussed in section 2.4.4 in relation to the particle model.

2.3.5. Summary

In the section above the influence of heat and mass transfer on the adsorption rate has been evaluated. Supply rate limitations of CO₂ have been eliminated by the use of a bypass valve. By using pure CO₂ limitations by external mass transfer and molecular diffusion into the sorbent pores have been removed. Analysis of the particle diameter showed that influence of heat transfer and internal mass trans-

Figure 2.7 | Influence of the CO₂ concentration on reaction rate at 20°C, 100mbar of CO₂ pressure and particle diameter between 150-250 μm . Dilution of the CO₂ is performed by filling the reactor with nitrogen pressure (0/100/300 mbar N₂) before the start of the experiment. Symbols are added to increase distinction between lines.

Figure 2.8 | Reaction rate as a function of sorbent particle size at 40°C and 100mbar of pure CO₂. Symbols are added to increase distinction between lines.

fer is minimized. All experiments discussed in section 2.4 are performed with the particle diameter fraction between 150-250 μm .

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2.4. Results and discussion

2.4.1. Effect of temperature and CO₂ pressure

The effect of temperature and pressure is shown in Figures 2.9 and 2.10. It is clear that a higher pressure will lead to a higher adsorption rate as shown in Figure 2.10. The exact order of the reaction in the gas phase is discussed in the section 2.4.2 below. A higher temperature will also increase the reaction rate as can be seen in Figure 2.9. The temperature dependency of the reaction rate will be described using the Arrhenius equation and is further discussed in section 2.4.3.

In Figure 2.9 is seen that loading for the 40°C experiment levels off because it reaches the equilibrium capacity. The 40°C experiment reaches the equilibrium capacity faster than the lower temperatures because of two reasons. First, the equilibrium capacity decreases with temperature, see Figure 2.4. Second, because of the increased reaction rate the equilibrium capacity is reached quicker. Similarly to literature [168, 169, 171] it is seen that the initial adsorption rate is high since it takes about 200 seconds to reach 80% of the equilibrium capacity. However, the last 20% takes over 1000 seconds at 40°C. At 5°C the situation is even worse; in the first 200 seconds about 50% of the equilibrium capacity is reached. However, reaching equilibrium at these low temperatures takes over an hour. This effect of temperature is of importance for air capture applications as the air capture system may behave totally different on a cold winter day compared to a hot summer day. Therefore, it is important to include temperature effects during design of the capture equipment.

2.4.2. Gas phase reaction order

In literature [184] it is shown that the reaction rate of CO₂ is first order in the gas phase concentration. This statement is verified by plotting the logarithm of the $\partial q/\partial t$ versus the CO₂ pressure in Figure 2.11. The slope of the line is equal to power of the CO₂ pressure and thus the reaction order in the gas phase. $\partial q/\partial t$ is determined by fitting a rational polynomial – both first order in the nominator and denominator – to the loading versus time curve. Next, the derivative of the continuous polynomial can be determined. The reaction order in CO₂ partial pressure has been evaluated with experiments performed at 5°C. Due to the slow reaction rate at 5°C the reaction order can be evaluated at low loading and thereby the influ-

Figure 2.9 | Effect of temperature at 100mbar of CO₂ on the reaction rate for particle diameter between 150-250 μm . Lines show an experiment and symbols show a duplicate experiment.

Figure 2.10 | Effect of pressure at 20°C on the reaction rate for particle diameter between 150-250 μm . Lines show an experiment and symbols show a duplicate experiment.

Figure 2.11 | Log-Log Plot to determine the reaction order in the gas phase. Experiments at 5°C are used to fit at a low loading to minimize the influence of the equilibrium. Symbols represent the experimental point and lines show the linear fit.

ence of equilibrium is minimized. In Figure 2.11 can be seen that the apparent gas phase reaction order is an function of the loading. However, since the fits of 0.8 and 1.2 mol kg⁻¹ are more accurate and the found reaction order is close to one it is seems justified to conclude that the reaction rate dependency on the gas phase concentration can be described as first order.

2.4.3. Reaction rate equation

The reaction rate equations presented in section 2.2.4 are fitted to the experimental data to find the corresponding kinetic rate constant. Experiments have been performed in the temperature range of 5-40°C, at 50, 100 and 200mbar of CO₂ pressure and using the particle diameter fraction between 150-250µm. The fitting of k_{ads} is performed on the time range from 5-90s. The starting point of 5s is chosen to be sure that the pressure and temperature inside the reactor are constant in the fitting range. The end point of 90s is chosen to reach a maximum of 90% of the equilibrium capacity. For every reaction rate equation the fit for a 100mbar and 20°C experiment is shown as an example. Moreover, the Arrhenius plot is given to see the temperature effect on the reaction rate parameters.

Linear driving force

First, the pseudo-first order linear driving force (PFO-LDF) and pseudo-second order linear driving force (PSO-LDF) rate equations are analysed. In Figures 2.12 and 2.13 the results for the PFO-LDF rate equation are shown and in Figures 2.14 and 2.15 the results of the PSO-LDF rate equation are shown. In Figure 2.12 it is seen that the pseudo-first order is not able to describe the shape of the experimental curve. In Table 2.S2 of the Supporting information the kinetic rate constant and SSE of all experiments fitted are reported. It is seen that the SSE is increasing with temperature and pressure. This shows that the steeper the loading curve versus time is, the worse the fit becomes. It can be concluded that the PFO-LDF is no suitable equation to describe the adsorption reaction.

From the SSE in Figure 2.14 can be seen that the PSO-LDF describes the shape of the experimental curve significantly better as the SSE is only one-third of the SSE of the PFO-LDF. The pseudo-second order fits better due to the second order in the number of free adsorption site. This is in accordance with the mechanism of adsorption in which two amine groups are needed to react with one CO₂ molecule in absence of H₂O. For the PSO-LDF no effects of temperature and pressure on the goodness-of-fit parameters were observed, see Table 2.S2 of the Supporting information. From Figures 2.13 and 2.15 can be seen that the Arrhenius equation describes the temperature dependency well for the LDF equations. However, the influence of pressure is not accounted for correctly by the LDF models.

Toth rate equation

Second, the Toth reaction rate equation is evaluated with both parameters set A and B from Table 2.3. The results are given in Figures 2.16 to 2.19. Overall it is seen in (Figure 2.16 and 2.18) that the fit of both Toth reaction rate equations are much better than the LDF equations. Evaluating the SSE of all experiments as shown in Table 2.S3 of the Supporting Information shows that SSE for the Veneman et al. parameters (set A) is slightly higher than for the parameters presented in this work (set B). On the other hand, looking at the SSE of the Arrhenius plot in Figures 2.17 and 2.19 shows the opposite. The Arrhenius fit has a lower SSE with the Veneman et al. parameters compared to the parameters from this work. Also remarkable is the difference in pre-exponential factor by a factor 1000. This might be an effect of the change in activation energy which is discussed in more detail below.

Activation Energy

Looking at the activation energy for the Veneman Toth fit $E_{act} = 28.8 \text{ kJ mol}^{-1}$ it is seen that this is very close to the values found by Mukherjee et al. [71] for aqueous benzylamine reaction with CO₂ of 26 kJ mol^{-1} . Additionally, Wang et al. [178]

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Figure 2.12 | Fit results at 100mbar and 20°C for pseudo-first order linear driving force (PFO-LDF) equation. The equilibrium capacity is determined by the isotherm from this work (set B).

Figure 2.13 | Arrhenius plot for pseudo-first order linear driving force (PFO-LDF) equation. The equilibrium capacity is determined by the isotherm from this work (set B).

Figure 2.14 | Fit results at 100mbar and 20°C for pseudo-second order linear driving force (PSO-LDF) equation. The equilibrium capacity is determined by the isotherm from this work (set B).

Figure 2.15 | Arrhenius plot for pseudo-second order linear driving force (PSO-LDF) equation. The equilibrium capacity is determined by the isotherm from this work (set B).

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Figure 2.16 | Fit result at 100mbar and 20°C for Toth reaction rate equation using isotherm set B, this work.

Figure 2.17 | Arrhenius plot for Toth reaction rate equation using isotherm set B, this work.

Figure 2.18 | Fit results at 100mbar and 20°C for Toth reaction rate equation using isotherm set A, Veneman et al. [85].

Figure 2.19 | Arrhenius plot for Toth reaction rate equation using isotherm set A, Veneman et al. [85].

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found an activation energy in the same range of 31.7 kJ mol⁻¹ for quaternary ammonium based resin of PES. On the other hand the activation energy of the PSO-LDF of 38.1 kJ mol⁻¹ is similar to values reported by Richner et al. [72] (38 kJ mol⁻¹) and Penny and Ritter [191] (39.5 kJ mol⁻¹) for aqueous benzylamine systems.

The activation energy (15.2 kJ mol⁻¹) of the Toth equation with the isotherm parameters from this work seems to be on the low side for a chemisorption system. Although, similar low values are reported in literature for other solid amine systems. Monazam et al. [192] reported a value of 13 kJ mol⁻¹ for a amine/bentonite sorbent and Raja Shahrom et al. [193] found a value of 7.23 kJ mol⁻¹ for a poly[VBTMA][Arg] sorbent.

The difference in activation energy for both the Toth rate equation fits might be explained by the equilibrium parameter b . The equilibrium parameter b is an Arrhenius type of equation with the isosteric heat of adsorption ΔH as parameter, see Table 2.1. The value of the isosteric heat of adsorption will influence the temperature effect on the reverse reaction, see equation 2.5. As the degree of sorbent saturation in the fitting range (12-80%) is such that the reverse reaction can not be neglected, it might have an effect on the apparent temperature dependency of the forward reaction and consequently on the activation energy found. Concluding, it is important to emphasize the huge influence of the isotherm parameters on the kinetic constants found. Therefore, it is important to pay attention to both the isotherm parameters and the kinetic constants during fitting of the reaction rates.

Verification of rate expression

The found rate expressions are verified by use of the mathematical model presented in section 2.2.6. Comparing Figures 2.20 and 2.21 it seen that the Toth rate equation with this works isotherm (set B) predicts the experiment better than the Toth rate equation for set A. However, the error in prediction for the Veneman parameters (set A) is an error in prediction of the equilibrium capacity since the initial rate is correctly predicted. This is confirmed when looking at the SSE of all experiments in Table 2.S4 of the Supporting Information. When fitting to 100 seconds no clear distinction can be made between the two isotherm sets. This shows that initial reaction rate is predicted correctly for both isotherm sets. However, looking at the SSE for the fit until 1000 seconds a clear effect of prediction of the equilibrium capacity is seen. For temperatures below 25°C the isotherm from this work (set B) predicts the experiments better. However, in line with the parity plots presented in Figure 2.S1, the Veneman et al. isotherm (set A) predicts the experiments better at higher temperatures. In consequence, for longer times the isotherm parameters predicting equilibrium capacity are more important than the kinetic parameters

Figure 2.20 | Experimental (100mbar and 20°C) and model (Particle Model, section 2.2.6) with Veneman et al. parameters, set A.

Figure 2.21 | Experimental (100mbar and 20°C) and model (Particle Model, section 2.2.6) with this work isotherm parameters, set B.

for a good fit of experimental data.

Summary

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The analysis above showed that the pseudo-first order LDF equation is not able to fit the data. The pseudo-second order LDF fits the temperature dependency of the adsorption rate. However, the pressure influence is not correctly described.

The Toth reaction rate equation describes both the temperature and pressure dependencies. The goodness-of-fit parameters for both sets of isotherm parameters (A & B, Table 2.3) are close. The quality of prediction of the initial reaction rate is independent of the isotherm and kinetic parameters. For longer times, however, the prediction of loading is strongly dependent on the prediction of the equilibrium capacity by the isotherm parameters used.

2.4.4. Experimental method verification

The particle model is used to verify that indeed intrinsic kinetics are measured and that heat and mass transfer limitations have been eliminated. The model presented in section 2.2.6 has been used with the rate equation of Toth using the Veneman isotherm parameters. A worst case scenario for external heat transfer is assumed by using $Nu=2$ for a stagnant gas around at particle. However, in the experiment most of the particles are in contact with the thermostated bottom of the reactor, which improves heat transfer by conduction.

In Figure 2.22 the maximum temperature increase in the particle centre is shown for a fast, mediocre and slow experiment. It seen that the maximum temperature increase is about 8K for the fastest experiment performed. However, at the start of the fitting interval at 5s the temperature is almost back to the initial temperature. This shows that the effect of the temperature increase on the fit will be minimal. Especially, because the effects are smaller for the slower experiments and heat transfer is expected to be under predicted by the model.

Additionally, the radial profiles for the fastest experiment are studied in Figure 2.23. In Figure 2.23 can be seen that there is no radial temperature profile in the particle. This shows that heat transfer is externally limited, which might be an effect of the assumption of $Nu=2$. However, as discussed before the external heat transfer might be larger in the experimental setup. Consequently, with increased external heat transfer the maximum temperature increase will be lower.

The concentration profile in Figure 2.24 shows that in the first second a significant radial concentration profile is present. However, after 5 seconds the concentration inside the particle is almost equal to the bulk concentration. Therefore, it is not

Figure 2.22 | Maximum temperature increase in particle centre for a fast, mediocre and slow experiment. Symbols are added to increase distinction between lines.

Figure 2.23 | The radial temperature profile inside the particle for a fast experiment at 200mbar and 40°C. Symbols are added to increase distinction between lines.

Figure 2.24 | The radial concentration profile inside the particle for a fast experiment at 200mbar and 40°C. Symbols are added to increase distinction between lines.

expected that the diffusional resistance will influence fit results.

The above results from the particle model confirm that intrinsic kinetics are measured in this study. The influence of the initial mass and heat transfer limitations on the reaction rate are clearly negligible.

2.5. Conclusion

To measure the intrinsic reaction kinetics for CO₂ adsorption on a solid amine sorbent an experimental method has been developed and applied. To ensure the absence of transport limitations, the influences of supply rate, heat and mass transfer on the adsorption rate have been evaluated. Supply rate limitations of CO₂ have been eliminated by the use of a bypass valve. By using pure CO₂ limitations related to external mass transfer and molecular diffusion into the sorbent pores have been removed. Experimental analysis of the particle diameter showed that influence of heat transfer and internal mass transfer is minimal and mathematical modelling of the convection, diffusion and reaction rate inside the particle confirmed the absence of mass and heat transfer limitations and, hence, confirmed the measurement of intrinsic kinetics.

Analysis of the experimental data showed that the pseudo-first order and pseudo-second order linear driving force equations are not able to describe the experiments. Especially, the pseudo-first order linear driving force is not able to describe the strong non-linear behaviour of the particle loading in time. The Toth isotherm based rate equation was found to predict the experiments well. The found kinetic parameters show a strong correlation with the isotherm parameters used, especially for partially loaded sorbents. The above results show that for prediction of both the initial and equilibrium loading a rate based isotherm equation is necessary for consistent description of both kinetics and equilibrium.

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2.6. Supporting Information

2.6.1. Material properties and model symbols.

Table 2.S1 | Material properties and model symbols.

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Symbol	Value	Unit	Meaning	Ref.
b		bar^{-1}	Toth isotherm equilibrium parameter	
C		mol m_g^{-3}	Gas concentration	
C_{p,CO_2}	0.85	$\text{kJ kg}^{-1} \text{K}^{-1}$	CO_2 heat capacity	[194]
$C_{p,s}$	1.58	$\text{kJ kg}^{-1} \text{K}^{-1}$	Sorbent heat capacity	[62]
D		$\text{m}_g^2 \text{s}^{-1}$	Diffusion coefficient	
d_s	0.2	mm	Particle diameter	
k			Kinetic constant	
M	0.044	kg mol^{-1}	Molar mass CO_2	[194]
n		mole	Number of moles	
NSD			Normalised standard deviation	
P		bar	Pressure	
q		mol kg_s^{-1}	Particle loading	
q_e		mol kg_s^{-1}	Equilibrium loading at present conditions	
q_s		mol kg_s^{-1}	Absolute maximum particle loading	
R	8.314	$\text{J mole}^{-1} \text{K}^{-1}$	Gas Constant	
R_{ads}		$\text{mol kg}_s^{-1} \text{s}^{-1}$	Adsorption rate	
r_{pore}	12.5	nm	Pore radius	[55]
r		m	particle radius	
SSE			Sum of squared errors	
t		s	time	
t_h			Toth isotherm heterogeneity parameter	
T		K	Temperature	
V		K	Volume	
Greek Symbols				
χ			Toth isotherm parameter	
$\Delta_r H$	75	kJ mol^{-1}	Reaction heat	[62]
ε	0.23	$m_{\text{pore}}^3 m_s^{-3}$	Particle voidage	[55]

(table continues)

Table 2.S1 | Continued

Symbol	Value	Unit	Meaning	Ref.
λ_{CO_2}	0.016	$W\ m^{-1}K^{-1}$	CO ₂ thermal conductivity (1 bar, 293K)	[194]
λ_s	0.43	$W\ m^{-1}K^{-1}$	Sorbent thermal conductivity	App. B
μ_{CO_2}	$1.5 \cdot 10^{-5}$	$Pa\ s^{-1}$	CO ₂ viscosity (1 bar, 293K)	[194]
ρ_s	880	$kg\ m_s^{-3}$	Sorbent density	[184]
ρ_{CO_2}	1.8	$kg\ m_g^{-3}$	CO ₂ density (1 bar, 293K)	[194]
τ	2.3	$m_g\ m_s^{-1}$	Pore tortuosity	[184]
Subscripts				
ads			Adsorption	
des			Desorption	
g			Gas	
LDF1			Pseudo-first order Linear	
			Driving Force	
LDF2			Pseudo-second order Linear	
			Driving Force	
p			Pore	
s			Sorbent	
Toth			Toth isotherm	

2.6.2. Error analysis

Error analysis has been performed on the loading determined during the experiments. The method of propagation of errors have been used as shown in equation 2.S1 for loading q [186].

2

$$\delta q = \sqrt{\left(\frac{\sqrt{\delta n_{\text{buf},0}^2 + \delta n_{\text{buf},t}^2 + \delta n_{\text{reac},t}^2}}{|n_{\text{buf},0} - (n_{\text{buf},t} + n_{\text{reac},t})|} \right)^2 + \left(\frac{\delta m_{\text{sorbent}}}{|m_{\text{sorbent}}|} \right)^2} \cdot |q(t)| \quad (2.S1)$$

In which the error in number of moles δn_i is calculated using equation 2.S2. The initial amount of moles in the reactor is neglected because the value is very small because of the vacuum pressure.

$$\frac{\delta n_i}{|n_i|} = \sqrt{\left(\frac{\delta V_i}{|V_i|} \right)^2 + \left(\frac{\delta P_i}{|P_i|} \right)^2 + \left(\frac{\delta T_i}{|T_i|} \right)^2} \quad (2.S2)$$

The error in the $\delta m_{\text{sorbent}}$ is calculated by equation 2.S3. The errors in wet sorbent mass $\delta m_{\text{sorbent}}$ and the moisture content $\delta \text{MC}_{\text{sorbent}}$ are determined as explained in the main text section 2.2.5 error analysis.

$$\delta m_{\text{sorbent}} = \sqrt{\left(\frac{\delta \text{MC}_{\text{sorbent}}}{|\text{MC}_{\text{sorbent}}|} \right)^2 + \left(\frac{\delta m_{\text{sorbent,wet}}}{|m_{\text{sorbent,wet}}|} \right)^2} \cdot |m_{\text{sorbent}}| \quad (2.S3)$$

2.6.3. Goodness of fit

In the Table 2.S2 an overview of the results for the linear driving force rate equations is given for the experiments included in the Arrhenius plot in section 2.4.3. In the Table 2.S3 the same overview is given of for the Toth rate equation with parameters set A and B (section 2.4.3) In the last Table 2.S4 an overview is given of the SSE of the particle model versus the experimental values for both parameters sets.

Table 2.S2 | Experimental conditions, found kinetic rate constant and Goodness-of fit parameters R^2 and SSE for pseudo-first order linear driving force and pseudo-second order linear driving force equation using the isotherm B.

Temperature °C	Pressure (mbar)	Pseudo-first order LDF			Pseudo-second order LDF		
		k_{LDF1}	SSE	R^2	k_{LDF2}	SSE	R^2
5.3	50.1	0.080	8.008	0.922	0.037	4.421	0.957
5.8	100.5	0.053	13.429	0.914	0.025	6.257	0.960
5.0	100.6	0.052	13.448	0.911	0.025	6.416	0.958
5.5	100.5	0.052	12.155	0.922	0.025	5.524	0.964
5.9	200.6	0.035	18.906	0.919	0.018	6.436	0.972
10.2	50.1	0.095	10.671	0.911	0.046	5.507	0.954
11.2	100.5	0.061	16.067	0.911	0.031	6.615	0.963
11.1	100.5	0.062	17.093	0.906	0.032	7.049	0.961
11.3	200.9	0.040	22.200	0.916	0.022	6.268	0.976
12.0	200.7	0.039	20.935	0.916	0.021	6.255	0.975
15.0	50.1	0.112	14.118	0.900	0.058	6.564	0.954
14.9	100.5	0.071	20.562	0.899	0.039	7.631	0.962
15.5	100.6	0.069	17.821	0.910	0.038	6.406	0.968
15.0	100.5	0.069	19.173	0.903	0.037	7.224	0.963
15.0	200.8	0.042	23.804	0.908	0.023	6.761	0.974
15.3	200.7	0.043	23.159	0.912	0.024	6.164	0.977
22.2	50.0	0.143	17.043	0.900	0.085	6.299	0.963
20.6	100.5	0.082	22.824	0.896	0.049	7.247	0.967
20.4	100.5	0.083	23.053	0.895	0.049	7.194	0.967
21.0	200.7	0.056	37.135	0.880	0.036	8.108	0.974
21.4	200.7	0.052	29.155	0.894	0.034	6.422	0.977
25.8	100.5	0.099	27.335	0.883	0.066	7.153	0.969
31.1	50.1	0.198	22.095	0.885	0.146	5.709	0.970
30.5	100.5	0.116	29.932	0.874	0.087	6.331	0.973
30.2	100.5	0.116	30.566	0.872	0.087	6.523	0.973
30.2	200.9	0.069	32.619	0.885	0.056	4.190	0.985
30.4	200.4	0.069	34.605	0.866	0.057	5.571	0.978
40.6	50.2	0.273	33.754	0.793	0.267	8.164	0.950
39.4	100.6	0.154	32.860	0.835	0.156	5.025	0.975
41.5	200.8	0.092	38.744	0.801	0.104	5.006	0.974

Table 2.S3 | Experimental conditions, found kinetic rate constant and Goodness-of fit parameters R^2 and SSE for the Toth rate equations fitted with isotherms from Table 2.3 in the main manuscript

Temperature °C	Pressure (mbar)	Isotherm B			Isotherm A		
		k_{toth}	SSE	R^2	k_{toth}	SSE	R^2
5.3	50.1	5.35	0.076	0.999	8.45	0.272	0.997
5.8	100.5	5.07	0.434	0.997	8.39	1.053	0.993
5.0	100.6	5.04	0.338	0.998	8.21	0.871	0.994
5.5	100.5	5.03	0.545	0.996	8.28	1.203	0.992
5.9	200.6	5.24	2.360	0.990	9.09	4.061	0.983
10.2	50.1	5.93	0.046	1.000	10.26	0.291	0.998
11.2	100.5	5.46	0.413	0.998	10.03	1.285	0.993
11.1	100.5	5.76	0.351	0.998	10.63	1.200	0.993
11.3	200.9	5.73	2.632	0.990	11.20	5.107	0.981
12.0	200.7	5.25	1.962	0.992	10.34	4.089	0.984
15.0	50.1	6.65	0.021	1.000	12.50	0.311	0.998
14.9	100.5	6.42	0.312	0.998	12.76	1.366	0.993
15.5	100.6	6.13	0.370	0.998	12.30	1.437	0.993
15.0	100.5	5.81	0.333	0.998	11.46	1.381	0.993
15.0	200.8	5.19	1.603	0.994	10.79	3.929	0.985
15.3	200.7	5.49	1.874	0.993	11.55	4.370	0.983
22.2	50.0	8.08	0.025	1.000	17.27	0.396	0.998
20.6	100.5	6.83	0.158	0.999	15.05	1.277	0.994
20.4	100.5	7.02	0.175	0.999	15.47	1.332	0.994
21.0	200.7	7.03	1.408	0.995	16.69	4.739	0.985
21.4	200.7	6.78	0.842	0.997	16.33	3.303	0.988
25.8	100.5	8.05	0.025	1.000	19.60	0.955	0.996
31.1	50.1	10.14	0.322	0.998	25.20	0.126	0.999
30.5	100.5	8.97	0.127	0.999	23.79	0.545	0.998
30.2	100.5	9.01	0.109	1.000	23.81	0.574	0.998
30.2	200.9	8.38	0.292	0.999	24.12	2.534	0.991
30.4	200.4	8.50	0.035	1.000	24.71	1.103	0.996
40.6	50.2	10.96	4.861	0.970	31.00	1.463	0.991
39.4	100.6	10.38	2.504	0.987	32.28	0.242	0.999
41.5	200.8	8.74	3.560	0.982	30.84	0.409	0.998

Table 2.S4 | Experimental conditions and SSE for loading curve of the particle model versus experimental values. Results shown for Toth rate equation with isotherms from Table 2.3 in the main manuscript.

Temperature °C	Pressure (mbar)	SSE Isotherm A		SSE Isotherm B	
		t=100s	t=1000s	t=100s	t=1000s
5.3	50.1	8.6	731.4	15.1	390.1
5.8	100.5	146.9	1746.9	146.2	1011.3
5.0	100.6	149.4	1502.6	148.7	828.9
5.5	100.5	153.8	223.2	153.0	187.4
5.9	200.6	157.0	300.9	148.5	230.1
10.2	50.1	6.2	403.5	14.3	222.9
11.2	100.5	142.1	1057.4	139.9	422.1
11.1	100.5	4.2	1251.8	5.6	486.0
11.3	200.9	12.0	2509.7	4.7	1140.4
12.0	200.7	161.5	2019.6	156.3	866.4
15.0	50.1	4.4	22.7	14.2	18.1
14.9	100.5	142.6	1079.3	141.3	404.6
15.5	100.6	3.4	726.3	4.5	158.3
15.0	100.5	167.0	189.7	162.4	164.6
15.0	200.8	167.6	217.2	164.8	174.6
15.3	200.7	166.9	215.2	161.6	170.4
22.2	50.0	140.1	415.4	152.5	226.6
20.6	100.5	144.2	423.3	140.6	147.2
20.4	100.5	121.8	399.0	119.5	129.2
21.0	200.7	166.7	1320.8	149.7	363.5
21.4	200.7	158.5	807.7	148.1	187.0
25.8	100.5	3.6	86.4	8.8	125.7
31.1	50.1	12.2	84.7	48.5	467.7
30.5	100.5	124.5	158.5	126.7	547.7
30.2	100.5	137.9	165.4	139.6	506.9
30.2	200.9	9.3	77.8	1.5	206.1
30.4	200.4	152.1	199.0	141.4	415.5
40.6	50.2	186.0	220.3	207.0	292.3
39.4	100.6	3.9	143.6	26.7	991.1
41.5	200.8	6.7	10.8	20.3	67.6

Figure 2.S1 | Parity plot for Veneman [85] Toth isotherm (Set A, Table 2.3).

Figure 2.S2 | Parity plot for this work Toth isotherm (Set B, Table 2.3).

CO₂ DESORPTION

II

3

Evaluating regeneration options of solid amine sorbent for CO₂ capture

Abstract

The regeneration conditions of a solid amine sorbent are evaluated by experiments and equilibrium modelling. Theoretically, pressure swing adsorption without purge flow is the most energy efficient method (1.9 MJ/kg CO₂). It was found that when using a purge flow the desorption rate is strongly influenced by the equilibrium between the gas and adsorbed phase. Because of the strong dependency of the isotherm on temperature, heat transfer is an important design parameter. With elevated temperature (>80°C) both the working capacity and the productivity increase significantly. Therefore, most important design considerations are heat transfer and the trade-off between the sorbent working capacity and energy consumption for sorbent heating.

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3.1. Introduction

For large scale CO₂ capture, the ease of regeneration and the stability of the sorbent are important parameters in determining the efficiency, the cost and the feasibility of a process [86]. Therefore the objective of this chapter is to evaluate the various regeneration methods. First, the boundary operating conditions for each regeneration method are identified. Within these constraints, the effect of different process parameters on the degree of desorption and corresponding energy use are determined. In this chapter the regeneration of solid sorbents is studied while in the next chapter the production of pure CO₂ will be determined.

3.2. Experimental section and methods

3.2.1. Materials

The sorbent used in this chapter is a commercial sorbent Lewatit VP OC 1065 from Lanxess. The sorbent has a support of spherical polystyrene beads with primary benzyl amine functional units. The Toth isotherm of this sorbent has been investigated in chapter 2. The effect of CO₂ pressure and temperature on the isotherm equilibrium loading are shown in Figure 2.4 and is used to evaluate the desorption performance. In Table 3.S1 more details about the properties of the materials used are given.

3.2.2. Equipment

The setup used for the adsorption-desorption experiments consisted of a N₂/CO₂ gas supply, a temperature controlled reactor and CO₂ analysis equipment. A simplified sketch of the setup is shown in Figure 3.1. This setup can be operated at different temperatures, using a water bath (Julabo F32/F25) or electrical heating (600W heat tracing controlled by Eurotherm 2132). The pressure can be altered from atmospheric pressure to reduced pressures using a vacuum pump (Vacuubrand PC-510NT).

The fixed bed reactor has a diameter of 13mm and a length of 600mm. The fixed bed reactor was filled with 30g of wet Lewatit sorbent for all experiments. This equals about 19g of dry sorbent after removal of pre-adsorbed water and carbon dioxide. The dry mass of sorbent is used in the calculations of the sorbent loading. The location of the adsorbent bed in the reactor is changed by a spacer such that a K-type thermocouple (TI-4, Fig 3.1) is in the axial and radial centre of the bed (T_{bed} in the results section). Another K-type thermocouple (TI-5, Fig 3.1) is placed at the

Figure 3.1 | Experimental set-up for fixed bed experiments of CO₂ capture

outside reactor wall (T_{wall} in the results section).

High purity (Grade 5.0) CO₂ and N₂ were used in the experiments and the flow rates were controlled with Brooks mass flow controllers (SLA 5850 series). The reactor outlet stream can be diluted with nitrogen, so that the CO₂ concentration is in the measurement range of the CO₂ gas analyzer and a constant flow through the vacuum pump – if operational – is maintained. The concentration of CO₂ in the outlet stream was measured with a CO₂ infrared gas analyser (Sick Maihak S700) with range of 0-50% and a detection limit of 0.5%. The relative humidity of the gas can be analysed using relative humidity sensors installed before the reactor and after the reactor and CO₂ analyser.

3.2.3. Procedure

The fresh sorbent was pre-treated by heating to 150°C under nitrogen flow before the start of the experimental series. Thereby, any pre-adsorbed CO₂, H₂O or other components were removed. Each experimental cycle consisted of three steps: 1) adsorption, 2) desorption, 3) regeneration of the sorbent. For all experimental cy-

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cles, adsorption was performed at 45% CO₂ at atmospheric pressure, 40°C and with a total feed gas flow rate of 215NmL/min. Using 45% of CO₂ allowed for faster successive screening of the desorption conditions compared to air capture conditions. When the measured outlet concentration of CO₂ was equal to the inlet concentration, the adsorption step was stopped. The adsorption loading of the sorbent is calculated by integrating the inlet molar flow of CO₂ and subtracting the integrated outlet molar flow of CO₂. For the desorption loading, the integrated outlet molar flow of CO₂ is subtracted from the adsorption loading.

The procedure of the desorption step is dependent on the chosen method of desorption. For the temperature swing, the pressure swing, and the combined pressure-temperature swing experiments, the reactor inlet was closed after ending the adsorption step. Next, the pressure was reduced using the vacuum pump and/or the reactor was heated. When using combined pressure and temperature swing, the pressure was reduced before the reactor was heated. If a nitrogen or air purge was used, the purge flow was started after the adsorption was stopped and the heating was started simultaneously. When a reduced overall pressure was used, first the reactor was evacuated and next the purge flow was started. After the desorption step, the sorbent was fully regenerated at 150°C under nitrogen flow in order to make sure that all adsorbed components are removed and the sorbent was clean and ready for the next adsorption.

3.2.4. Error analysis

All experiments have been performed with the same sample of sorbent. This allowed quick successive experimentation and also gave an indication of degradation of the sorbent. In Figure 3.2 the adsorption loading of all experiments are presented. The average of the experimental equilibrium adsorption loading (40% CO₂, 40°C) is 2.6 ± 0.1 mol/kg. All shown errors in this article are defined via one standard deviation. The result in Figure 3.2 shows that the reproducibility of the adsorption experiments is good. The first two experiments in Figure 3.2 show a lower adsorption loading. Note that in those experiments also the loading after regeneration is below zero. Therefore, it is concluded that the sorbent was not completely empty before the adsorption was started. Within these 55 experiment, no signs of degradation have been observed within the experimental error. Performing a t-test at 95% significance level using the first 27 and last 28 experiment showed that statistically these two group have the same mean value.

Another error analysis on the experiments can be made by examining the mass balance. In Figure 3.2 the mass balance closure is expressed as the loading after regeneration. Since all adsorbed CO₂ should be removed in the combined desorp-

Figure 3.2 | Adsorption equilibrium loading (sphere) and loading after regeneration (triangle) for all experiments performed.

tion and deep regeneration step, the theoretical loading after regeneration should be zero. The average error on the mass balance is 0.1 ± 0.2 mol/kg.

In general, it is noted that the experiments at lower desorption temperatures have a larger error. For example, the three points in the N_2 purge section with an error around 0.5 mol/kg are performed at 40°C desorption temperature. Because of the lower desorption temperature the desorption rate is lower which results in CO_2 outlet concentrations at/below the detection limit of the CO_2 analyser. Consequently, CO_2 is removed from the reactor while not detected.

The set of air purge experiments was performed using instrumental air. During a measurement it was noted that the CO_2 content in the instrumental air was fluctuating between 50 and 250 ppm. Therefore, a value of 150 ppm in the instrumental air was assumed for the calculations. However, because the CO_2 content is estimated, the error in the CO_2 loading after regeneration is increased as is clearly visible in Figure 3.2.

3.2.5. Energy calculations

In order to evaluate the regeneration of solid amine sorbent in more detail energy calculations have been performed. The total amount of energy needed for desorp-

Figure 3.3 | Overview of energy flows included in the calculations.

tion has been calculated for the experiments without purge flow. In the section below the equations needed are discussed in more detail and the material properties are given in Table 3.S1.

In the calculations the sensible heat of the sorbent and the produced CO₂ are included. Next to that, the reaction heat and – if necessary – the energy for adiabatic compression are added. In Figure 3.3 an overview of the energy flows included is given.

First of all, the sensible heat of the sorbent ($Q_{\text{sensible,sorbent}}$ [J/kg_{CO₂}]) is calculated using equation (3.1). Where $T_{\text{desorption}}$ and $T_{\text{adsorption}}$ are the desorption and adsorption temperature respectively.

$$Q_{\text{sensible,sorbent}} = m_{\text{sorbent}} \cdot C_{P,\text{sorbent}} \cdot (T_{\text{desorption}} - T_{\text{adsorption}}) \quad (3.1)$$

The sorbent mass m_{sorbent} is calculated by the amount of dry sorbent mass needed to capture 1 kg of CO₂ using the molar mass of CO₂ (MW_{CO_2}) and the working capacity (Δq_{exp}) of the corresponding experiment:

$$m_{\text{sorbent}} = \frac{1}{\Delta q_{\text{exp}} \cdot MW_{\text{CO}_2}} \quad (3.2)$$

Because the desorption reaction of the CO₂ from the amine is endothermic, energy is required for the reaction. The amount of energy required per kg of CO₂ is

calculated by dividing the reaction heat ($\Delta_r H$) by the molar mass (MW_{CO_2}):

$$Q_{\text{reaction heat}} = \frac{\Delta_r H}{MW_{CO_2}} \quad (3.3)$$

The sensible heat of the CO_2 released is calculated by:

$$Q_{\text{sensible}, CO_2} = C_{P, CO_2} \cdot (T_{\text{desorption}} - T_{\text{adsorption}}) \quad (3.4)$$

In case of a pressure swing regeneration, energy is required to create a reduced pressure in the reactor during desorption while delivering the CO_2 produced at atmospheric pressure. Adiabatic compression [195] is assumed and the required energy is calculated by equation (3.5) for the cases without purge flow. The efficiency of compression η is assumed to 0.75 and the ratio of C_p/C_v is $k = 1.3$ [196]. In equation 3.5, P_1 is the suction pressure of the compressor whereas P_2 is the discharge pressure which is assumed to be 1 bar.

$$Q_{\text{adiabatic compression}} = \frac{1}{\eta} \cdot \frac{k}{k+1} \cdot \frac{1}{MW_{CO_2}} \cdot RT_{\text{desorption}} \cdot \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right] \quad (3.5)$$

3.2.6. Equilibrium model

The influence of equilibrium on desorption is investigated by a simple equilibrium fixed bed model. The gas phase has been modelled as an ideal PFR as shown in equation (3.6). In this equation is C_g (mol m^{-3}) the gas phase concentration, q_e and q (mol kg^{-1}) the equilibrium sorbent loading and the actual sorbent loading respectively, u_g (m s^{-1}) the superficial gas velocity, ε (–) the bed voidage and ρ_s (kg m^{-3}) the sorbent density (see also Table 3.1).

$$\frac{\partial C_g}{\partial t} = \frac{u_g}{\varepsilon} \frac{\partial C_g}{\partial z} - k_1 (q_e - q) \rho_s \frac{(1 - \varepsilon)}{\varepsilon} \quad (3.6)$$

The mass transfer between the gas and solid phase has been modelled using the linear driving force model. Local equilibrium is ensured between the gas and solid phase by using a sufficient large linear driving force constant (k_1 , equation (3.7)).

$$\frac{\partial q}{\partial t} = k_1 (q_e - q) \quad (3.7)$$

The experimental increase in the bed temperature is approached using a segmented linear temperature increase as shown in Figure 3.10. The equations used are shown in equation (3.8) when the temperature is increasing. The slope $\frac{\Delta T}{\Delta t}$ is determined from the experimental temperature increase. Equation (3.9) is used when the temperature is constant. Using this method, the experimental temperature profile is approached without extensive modelling of heat transfer phenomena.

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$$\frac{\partial T}{\partial t} = \frac{\Delta T}{\Delta t} \text{ for } t < t(T_{\text{constant}}) \quad (3.8)$$

$$\frac{\partial T}{\partial t} = 0 \text{ for } t \geq t(T_{\text{constant}}) \quad (3.9)$$

The equations are solved using the ODE15s solver in Matlab. The differential $\frac{\partial C_g}{\partial z}$ is manually discretized, while the differential $\frac{\partial C_g}{\partial t}$ is solved by the ODE15s solver.

Table 3.1 | Values of parameters in equilibrium model

Symbol	Value	Unit	Meaning
ε	0.38	–	Bed voidage
k_1	1e9	s ⁻¹	Linear driving force constant
ρ_s	880	kg m ⁻³	Sorbent density

3.3. Results and discussion

3.3.1. Stability of SAS

The first step is to check the temperature stability of the sorbent to set the boundaries of utilized process conditions. The sorbent manufacturer recommends an operating temperature in the range of -20°C -100°C [55] and several studies have reported urea-bridge formation in the presence of CO₂ at high temperature. [61, 86] Because air is the cheapest option of purge gas, a quick test of oxidative stability of the sorbent was carried out at 80°C and 100°C for 1 hour, which showed degradation of 5-6% of capacity, but insignificant degradation at 60°C. These results are in line with findings of Yu et al. [61] that show that in the presence of oxygen the sorbent is only stable up to approximately 70°C due to oxidative degradation. However, without the presence of CO₂ and O₂, the thermal stability of the sorbent can be maintained up to 150°C. In the presence of CO₂ the sorbent stabil-

ity/regenerability is less well studied, but appears to be stable up to 130°C, above which urea formation might occur [56, 61].

From stability tests, it was decided to perform TSA at a maximum temperature of 120°C when CO₂ is present. When air is used as purge gas, the temperature is limited to 60°C to prevent oxidative degradation. So far, no significant degradation has been observed or reported for regeneration methods using reduced absolute pressure.

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3.3.2. Pressure Temperature Swing Adsorption

First, experiments without purge flow were executed, the results are shown in Figure 3.4. The 30 minutes working capacity is defined as difference between the adsorption equilibrium capacity and desorption loading after 30 minutes of desorption. The final working capacity is defined as the difference between the adsorption loading and the loading at the end of the desorption step ($t > 40$ min). By integration of the outlet CO₂ mole flow during the regeneration step the residual loading is found. In Figure 3.7 the working capacities are illustrated.

Pure pressure swing experiments have been performed at the adsorption temperature of 40°C. This would enable a more or less isothermal adsorption/desorption process. This method of desorption is not very effective, as shown in Figure 3.4. Even at a low system pressure of 10 mbar, only 40% of the adsorption loading is removed during desorption. Increasing the temperature is more effective in cleaning the sorbent as is shown by the temperature swing experiments in Figure 3.4. This observation is in line with Lewatit VP OC 1065 being a chemical sorbent, where energy is needed to break the chemical bond between the sorbent and absorbed species.

Moreover, the effect of temperature is larger than the effect of pressure due to the shape of the isotherm (see Figure 2.4 in chapter 2). The isotherm is very steep in the region of low pressure of CO₂ (< 5 kPa). Consequently, the system pressure must be lowered to a significant lower pressure (< 1 Pa) in order to evacuate the sorbent completely at a temperature of 40°C. Combination of pressure and temperature swing (PTSA) leads to higher working capacities at lower temperatures and higher pressure compared to pure TSA or PSA.

In order to get more insight in the most optimal desorption method, a comparison of energy consumption is made. The required sensible heat for the sorbent and the produced CO₂ are calculated. The compression cost is estimated by adiabatic compression of the produced CO₂. Using the experimental determined working capacities from Figure 3.4, the amount of sorbent required to produce one kilogram

Figure 3.4 | Residual CO₂ loading (mol/kg) on the sorbent after 30 minutes and at the end of desorption step without purge flow. Desorption was varied between the methods: PSA was performed at 40°C, PTSA at 100mbar and TSA at 1 bar.

Figure 3.5 | Energy use (MJ/kg CO₂) of the cases presented in Figure 3.4 based on the reaction heat, the adiabatic compression and the sensible heat of the sorbent and the produced CO₂.

of CO₂ per cycle is calculated. A more detailed description of these calculations can be found in section 3.2.5.

The energy comparison showed a more favourable result for the PSA as shown in Figure 3.5. Merely since for PSA energy is only added to the CO₂ product while for TSA energy is added to both the product gas and sorbent. The lowest energy requirement is found for the PSA case with the highest pressure (100mbar). Of course, compression energy can be further reduced by a lower reduction in pressure although this will also further reduce the working capacity. Low working capacity require a lot of adsorption/desorption cycles to produce one kilogram of CO₂. This leads to larger equipment size and consequently investment costs. At higher temperature the working capacity will increase on the cost of an increase in sensible heat. This will reduce investment cost but increase the operational cost because of increased energy requirement. Application of both an increase in temperature and reduction in pressure (PTSA) show good working capacity with medium sensible heat requirement. Therefore, PTSA show good potential to be the most optimal conditions.

In short, it can be concluded that temperature swing is needed to reach a noteworthy working capacity, and pressure swing can be used to lower the required sensible heat for the same working capacity. The trade-off between these is subject of economic optimization depending on cost and availability of utilities.

3.3.3. Temperature effect on capacity when using a purge flow

Instead of reducing the CO₂ pressure by reducing the system pressure, a purge gas flow can be used to lower the CO₂ partial pressure. An effective purge gas should be inert, abundantly available, inexpensive and preferably condensable. In literature [61, 86, 94, 184] nitrogen is considered an effective purge gas and is evaluated in this paper. Alternatively, especially for larger scale operation, air might be a cheaper purge gas, although less inert due to the oxygen content. It should be noted that by using a inert, non-condensable purge gas the sorbent can be (fully) regenerated, but the produced CO₂ is only available at lower concentration.

From the isotherm of Lewatit (see Figure 2.4), it is clear that an increase in temperature will lead to an increase in working capacity. This effect is clearly seen in Figure 3.6 as the 30 minute working capacity increases from 1 mol/kg at 40°C to the full capacity of 2.5 mol/kg above 100°C. The significant faster desorption above 80°C is in line with results of Serna-Guerrero et al. [94].

In contrast to what the theory predicts, Figure 3.6 shows a significant final loading is present for the 40°C and 60°C N₂ purge cases. In Figure 3.7 it is shown that

Figure 3.6 | Effect of temperature on residual CO₂ loading on the sorbent after 30 minutes and at the end of desorption step with a purge flow of 226mL/min.

Figure 3.7 | Experimental loading versus time for the 40°C, 226mL/min N₂ purge case. The dashed line illustrates the decrease in loading when the CO₂ concentration was below the detection limit of the analyzer.

a kind of equilibrium (at 0.9 mol kg^{-1}) is reached for the 40°C case after 7h of the desorption. In the next 9h, no significant ($<0.5\%$ CO_2 , below detection limit) CO_2 was measured in the outlet of the reactor. In the following regeneration step only 0.4 mol kg^{-1} was desorbed although 0.9 mol kg^{-1} was expected. It seems plausible that the missing 0.5 mol kg^{-1} (shown as 'unaccounted capacity' in Figure 3.6) was desorbed during the last 9h of the desorption step, at a concentration level below the detection limit. This opinion is supported by the fact that the subsequent adsorption step of the next experiment showed again full adsorption capacity (see Figure 3.2).

Additionally, in Figure 3.6 the nitrogen purge is compared with the air purge experiments. As seen, the working capacities after 30 minutes for the nitrogen purge and air purge are almost equal. Therefore, it can be concluded that the CO_2 present in air does not have a significant effect on the desorption rate in the first 30 minutes. This hypothesis is confirmed when the average outlet CO_2 molar fraction is calculated (average $x_{\text{CO}_2} = 0.06$ for 40°C N_2 purge case). It can be noticed that the average outlet concentration is not significantly changed by 400 ppm ($x_{\text{CO}_2} = 0.0004$) of CO_2 in air.

Moreover, it is shown in Figure 3.6 that the CO_2 in air has a significant effect on the final loading. This is predicted by theory, since the isotherm value at 150 ppm of CO_2 in the instrument air used and 40°C is 0.5 mol kg^{-1} . However, this also shows that the presented final loading is not the equilibrium loading. Note that the unaccounted capacity is small for the 40°C air purge experiment because it was stopped after 3.8 hours of desorption when the CO_2 outlet concentration was below the detection limit, instead of running the experiment 17 hours as for the 40°C nitrogen purge.

3.3.4. Temperature effect on the desorption rate

In Figure 3.6 it can be observed that the desorption *rate* is increasing with temperature, since the difference between the 30 minute and the final working capacity is reduced with increasing temperature. Desorption of CO_2 will only happen when the equilibrium loading at the local conditions is lower than the actual loading. This effect is analysed in Figure 3.8 by plotting the bed-average experimental loading (1) versus time. The experimental loading is compared to the Toth isotherm loading, evaluated at the CO_2 concentration at the reactor outlet. For the Toth isotherm both the loading assuming the bed temperature (2) and assuming the outside wall temperature (3) are reported.

In Figure 3.8 is shown that both the isotherm lines lay above the experimental line

Figure 3.8 | Experimental bed-average loading (1) at 40, 80, 120°C and 226NmL/min N₂ purge. Additionally, the Toth isotherm values evaluated at the outlet CO₂ concentration and the bed temperature (2) or the outside wall temperature (3) are shown.

for the 40°C experiment. Based on this observation desorption is not expected. However, it should be realized that the isotherm lines are evaluated at the CO₂ outlet concentration, which is the highest CO₂ concentration in the column. Because CO₂-free nitrogen is entering the column, the local CO₂ concentration at the entrance side of the bed will be lower. Therefore, locally desorption will happen in the beginning of column first. This supported by the fact that the isotherm is extremely favourable for adsorption, and will be unfavourable for desorption. This will lead to a steep mass transfer zone as described by Ruthven [197] and Seader et al.[198].

On the other hand, the experimental loading for the 120°C case is higher than the isotherm line evaluated on the wall temperature for all times (see Figure 3.8). This means that, at least around the wall, desorption is possible along the whole length of the column. Therefore, the desorption front will be less distinct for the 120°C experiments. As a consequence of desorption occurring in a larger fraction of the column compared to 40°C the desorption rate will be higher for the 120°C. Additionally, the isotherm line evaluated at the bed temperature suggest that the experimental loading is in equilibrium with the outlet gas concentration.

The large difference in isotherm value for the wall and the bed shown in Figure 3.8

for the 120°C case is a result of the large radial temperature gradient of 35°C seen during the experiments. A large radial temperature gradient is present due to the low thermal conductivity of the sorbent. Consequently, there might be a large radial gradient in local loading. E.g. the sorbent might be 'empty' at the wall but still contain CO₂ in the centre of the bed. The low thermal conductivity of the sorbent is an important factor for the design of an up-scaled system because too large column diameters might lead to large radial temperature gradients. As a result, large temperature gradients might cause excessive regeneration times to remove all CO₂ from the column and thereby reduce column productivities.

3

The above results suggest that desorption rate is strongly influenced by the equilibrium between the gas and the adsorbed phase. For the 40°C this seems to be more locally at the desorption front, whereas for the 120°C situation this seems to be along (most of) the total length of the column. This effect will be further studied using the equilibrium PFR model introduced in section 3.2.6.

In Figure 3.9 it is shown that the prediction of the trend in sorbent loading by the equilibrium PFR model matches quite well with the experimental trend. Thereby it is also shown that excessive modelling of the temperature profile (see Figure 3.10) is not necessary to describe the experiments. From the model can be concluded that the desorption rate is strongly influenced by the equilibrium between the gas and solid phase as hypothesized above. Because the isotherm is strongly dependent on temperature also the desorption rate depends strongly on temperature. This implicates that heat transfer is an important factor when designing the adsorption/desorption system. Better heat transfer will raise reactor temperature faster and thereby increase the desorption rate.

In Figure 3.9 it is seen that the model predicts the two extremes in temperatures (40°C and 120°C) the best. Surprisingly, the predictions for the temperatures in between are worse. It is expected that slight imperfections of the isotherm might influence the model results. Additionally, the influence of the produced CO₂ on the gas velocity is not taken into account in the modelling. The desorption rate might be under-predicted for this reason since the gas velocity will increase when the produced CO₂ is taken into account.

It can be concluded that the desorption rate of the sorbent is strongly determined by the isotherm and the rate of transport of CO₂ out of the reactor. At 40°C and 60°C the desorption rate is too slow to reach equilibrium without excessive (above 3h) regeneration times. Above 100°C the sorbent is completely clean within half an hour of desorption.

Figure 3.9 | Experimental loading and predicted values by the equilibrium model for the nitrogen purge experiments presented in Figure 3.6

Figure 3.10 | Experimental temperature and predicted values by the equilibrium model for the nitrogen purge experiments presented in Figure 3.6

3.3.5. Effect of purge gas flow rate on desorption rate

The effect of purge gas flow rate also depends on the temperature, as shown in Figure 3.11. While at 60°C there is a significant influence of the purge flow, at 120°C there is only a minimal increase in desorption rate. For the 60°C experiments, especially in the first 30 minutes a strong effect of flow on the desorption rate is seen. In the following two hours of the experiment it seems that the desorption rates have the same order of magnitude. This can be seen in Figure 3.11, because the difference between the 30 minute loading and the residual loading is almost independent of the flow rate, especially for the two lowest flow rates.

In Figure 3.12 this effect is also clearly visible, in the first 600 seconds the desorption is influenced by the flow rate while after 600 seconds the desorption rate appears to be approximately the same for all flow rates at 60°C. This shows that in the first 600 seconds the desorption rate is strongly influenced by the gas concentration. Desorption of CO₂ will only happen when the equilibrium loading at the local conditions is lower than the actual loading. Initially, the desorption rate will be higher for a higher flow rate because the gas concentration is lower. Therefore, a larger fraction of the adsorbed CO₂ can desorb from the bed before reaching equilibrium between the gas and adsorbed phase. Resulting in a lower sorbent loading. After 600 seconds, albeit having lower a gas concentration also the local loading is lower for the higher flowrate. Therefore, after 600 seconds the effect of a lower gas concentration at higher flow rate is cancelled by the effect of lower local loading. Consequently, the desorption rate is approximately the same.

For the high temperature experiments, it is shown in Figure 3.12 that the difference in desorption rate is minimal. Due to the high desorption rates, the CO₂ concentrations are high (>25%) during the experiment. Because of the high temperature and CO₂ concentration, the isotherm is in the flat region (see Figure 2.4). Consequently, the effect of a reduction in CO₂ concentration is small and therefore the influence of flow is minimised. Additionally, Figure 3.10 indicates that after 700 seconds the sorbent reaches 120°C whereas the sorbent is also fully regenerated after 700 seconds. Consequently, the desorption rate might be increased by increasing the heating rate. It supports the idea that ensuring good heat transfer to the sorbent is important when designing a solid amine sorbent CO₂ capture system.

3.3.6. Air purge at different system pressures

Since the maximum temperature using air purge is limited to 60°C due to oxidative degradation [61], the effect of lowering the system pressure while using an air purge is investigated. Due to lower CO₂ pressure, a lower final loading is expected

Figure 3.11 | Effect of purge gas flow rate [NmL/min] and temperature on residual CO₂ loading on the sorbent after 30 minutes and at the end of desorption step at 60°C and 120°C.

Figure 3.12 | Experimental loading and predicted values by the equilibrium model for the nitrogen purge experiments presented in Figure 3.11.

Figure 3.13 | Effect of pressure on residual CO₂ loading on the sorbent after 30 minutes and at the end of desorption step at temperature of 60°C and an air-purge flow of 226NmL/min.

for a lower system pressure. Comparing the residual loadings in Figure 3.13, this effect can be clearly seen.

Next to the lower final working capacity, the difference between the working capacity after 30 minutes and at the end of the desorption step is also reduced with decreasing pressure. This increase in desorption rate might be due to enhanced mass transfer as a result of an increased diffusivity of CO₂. Additionally, since the volume flow is set in normal liters per minute and held constant during the experiments, the gas velocity will increase with decreasing pressure. This will increase both the mass transfer from the particle to the bulk and the CO₂ removal from the reactor. In general, it can be said that the working capacity and the desorption rate are increased with decreasing pressure. However, additional optimization (e.g. economics) has to be performed in order to determine the most optimal desorption case.

3.4. Conclusion

In this paper the regeneration conditions of a solid amine sorbent have been evaluated. Without purge flow, pressure swing adsorption is the most favourable option based on energy usage only. However, because of the low working capacity, pres-

sure swing adsorption alone is most likely not economic and should be combined with an increase in temperature (PTSA).

When a purge gas is used, it was found that sorbent regeneration is dominated by heat transfer and local equilibrium conditions. Because of stability issues air can be used at lower temperatures, at the expense of lower working capacities and reduced desorption productivity. At higher temperatures (>80°C) the working capacity increases drastically, but sensible heat requirements become significant. Therefore, most important design considerations are heat transfer and the trade-off between the sorbent working capacity and energy consumption for sorbent heating. Optimization of capex and opex cost will dictate the optimum conditions.

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3.5. Supporting Information

Table 3.S1 | Material properties

Symbol	Value	Unit	Meaning	Reference
$C_{P,\text{sorbent}}$	1.58	$\text{kJ kg}^{-1} \text{K}^{-1}$	Sorbent heat capacity	[62]
C_{P,CO_2}	0.85	$\text{kJ kg}^{-1} \text{K}^{-1}$	CO ₂ heat capacity	[194]
C_{P,N_2}	1.04	$\text{kJ kg}^{-1} \text{K}^{-1}$	N ₂ heat capacity	[194]
C_{P,O_2}	0.92	$\text{kJ kg}^{-1} \text{K}^{-1}$	O ₂ heat capacity	[194]
$C_{P,\text{steel}}$	0.50	$\text{kJ kg}^{-1} \text{K}^{-1}$	Steel heat capacity	[199]
μ_{N_2}	$1.2 \cdot 10^{-5}$	Pa s	Kinematic viscosity nitrogen	[199]
d_p	520	μm	Average particle diameter	[55]
ρ_{sorbent}	880	kg m^{-3}	Sorbent density	[184]
ρ_{N_2}	1.2	kg m^{-3}	Density nitrogen	[199]
MW_{CO_2}	0.044	kg mol^{-1}	Molar mass CO ₂	
$\Delta_r H$	75	kJ mol^{-1}	Reaction heat	[62]

Production of high purity CO₂ from air using solid amine sorbents.

Abstract

For CO₂ capture from air on a supported amine sorbent, the effects of water co-adsorption and steam purge on the CO₂ working capacity and energy requirement for CO₂ desorption are studied. Working capacities are studied by fixed bed operation for changing temperature, pressure and amount of steam purge. Results show that for pressure-temperature swing adsorption a temperature above 100°C and a pressure below 200mbar as desorption conditions are required to maximize CO₂ working capacity and reduce energy requirement for desorption. Co-adsorption of water reduces energy requirement due to an increased CO₂ working capacity. Application of a steam purge increases the CO₂ working capacity and hence reduces sorbent inventory required. However, the net energy requirement per kilogram CO₂ does not decrease due to the latent heat of water. Concluding, steam purge regeneration for air capture does not reduce opex but might reduce capex.

This chapter is based on the following publication:

M.J. Bos, S. Pietersen, D.W.F. Brilman, *Production of high purity CO₂ from air using solid amine sorbents.*, Accepted for publication in **Chemical Engineering Science**: X, doi:10.1016/j.cesx.2019.100020

4.1. Introduction

One of the goals of this thesis is to capture CO₂ from air and produce CO₂ with high enough purity for the production of methanol. In this chapter the regeneration options of Lewatit VP OC 1065 to produce high purity CO₂ are studied. The energy consumption of regeneration options based on experimental data will be evaluated. Especially, the influence of a steam purge on the desorption energy requirement is studied. Next to that, the effect of co-adsorption of water during the adsorption on the working capacity and energy requirement is studied.

4

4.2. Experimental section

4.2.1. Experimental Setup

The setup used is discussed in chapter 3.2.2. However, three changes have been made. First, the 0-50 vol.% CO₂ analyser is replaced by a 0-2 vol.% [LI-COR LI-840A] and a 0-15 vol.% [Sick Maihak Sidor S700] CO₂ analyser for increased accuracy at low partial pressures of CO₂. The 0-2 vol.% analyser is used during adsorption and the 0-15 vol.% CO₂ during desorption and regeneration. Second, a gas humidifier is added to the system to be able to perform co-adsorption experiments of H₂O with CO₂. Gas humidity is measured using humidity sensors [Galltec LKK3.0S.F101.C05.00G] in the inlet and outlet. Third, a steam injection system is installed. Liquid water is injected by a syringe pump to an inline heater where the steam is generated. The amount of steam injected and the injection rate are controlled by the syringe pump. For convenience a schematic overview of the setup is given in Figure 4.1.

In this study the fixed bed reactor was filled with 53.6 grams of wet Lewatit sorbent as supplied by the manufacturer for all experiments. After removal of pre-adsorbed moisture and CO₂ this equals about 30.4 grams of dry sorbent. The amount of pre-adsorbed moisture and CO₂ for the batch of sorbent used is determined using TGA analysis. The dry sorbent mass is used for normalization of the sorbent loading.

4.2.2. Experimental method

Desorption capacity measurements are performed in three steps. In the first step, the adsorption is performed at 20°C with simulated air of 400 ppm of CO₂ in nitrogen until the sorbent equilibrium capacity is reached. Also, experiments are performed with 5000ppm of CO₂ allowing for faster successive adsorption – des-

Figure 4.1 | Experimental set-up for fixed bed experiments of solid amine sorbent desorption.

orption cycles in the experiments. Additionally, 5000ppm might represent CO₂ levels in enclosed environments such as submarines or spacecraft's [95]. Therefore, these experiments are relevant for reducing CO₂ concentrations in such enclosed environments. The adsorption step is performed until the equilibrium capacity of the sorbent is reached.

After completion of the adsorption step, the second step, desorption, is performed. First the heater is switched on directly followed by the vacuum pump. The steam purge – when applied – is applied as soon as the reactor temperature is above the boiling point of water to prevent condensation of water on the sorbent. Condensation of water on the sorbent and into the pores will effect the adsorption rate in the consecutive adsorption step. In screening experiments it was seen that liquid water on the sorbent significantly reduced the adsorption rate in a consecutive adsorption step unless the sorbent was fully dried prior adsorption. For this reason, rapid heating by condensing steam on the sorbent is not possible and heating by steam can only be applied indirectly. The desorption step is run until the CO₂ concentration – mixed with the dilution stream (see Figure 4.1) – in the analyser is below 0.05 vol% CO₂.

The final step is to fully regenerate the sorbent by purging nitrogen at 100°C to ensure a clean sorbent for the next adsorption. It should be noted that this step is only performed to fully clean the sorbent for the next adsorption step. In an industrial process only the adsorption and desorption will be performed, since the use of purge gas is too expensive and will lead to dilution of the CO₂ produced.

4.2.3. Error analysis

All experiments are performed with the same batch of sorbent. This ensured quick successive screening of the working capacities for various conditions during desorption. In Figure 4.2 the adsorption capacity of CO₂ is analysed for signs of sorbent degradation and repeatability of adsorption experiments. As shown, no sign of degradation is seen over more than 60 experiments with varying desorption conditions. However, it should be noted that during earlier screening experiments – which are not included in the results presented here – degradation of the sorbent was seen when operating at temperature above 120°C during desorption and regeneration. These results are in line with data presented by Yu et al. [61] and therefore high temperatures should be prevented.

The adsorption experiments show great reproducibility as the average adsorption loading is $1.64 \pm 0.03 \text{ mol kg}^{-1}$ for the 5000ppm CO₂ dry adsorption experiments. The adsorption experiments at 400ppm show the same reproducibility as the standard deviation ($1.06 \pm 0.03 \text{ mol kg}^{-1}$) is equal to the standard deviation for 5000ppm. The equilibrium loading itself is lower because it is a function of the CO₂ partial pressure. Another measure of the reliability of the experiments is the loading after regeneration. With perfect mass balance closure this loading should be zero. As seen in Figure 4.2 the CO₂ loading after regeneration approaches zero and therefore shows great accuracy.

Whereas for CO₂ the mass balance closure in the experiments is excellent, the closure of the mass balance for water is less good. The closure of the mass balance for H₂O is 79.0% on average. Source of the poor mass balance closure is the limited accuracy of the relative humidity sensors used. The accuracy of the sensors ranges from $\pm 3\% \text{RH}$ at 10 – 40°C and 30 – 80%RH to $\pm 8\% \text{RH}$ at 90°C and $< 30\% \text{RH}$. Especially, during desorption the accuracy of the relative humidity sensors is too low because of high temperature and low relative humidity caused by the dilution flow needed for good CO₂ mass balance closure. As will be shown in the results section, despite the uncertainty in the water balance, the trends in the CO₂ recovery in the presented data are beyond the uncertainty due to the water balance. Conclusions in this article are therefore not influenced by this imperfect closure of the H₂O mass balance.

Figure 4.2 | Loading after adsorption (square) or regeneration (rounds) as a function of experiment number. Striped lines show the average loading including one standard deviation for the dry adsorption experiments and the average after regeneration. Average numbers for co-adsorption experiments are not included because of changing relative humidity.

All the error bars shown in the study present one standard deviation (68% confidence interval) unless mentioned otherwise. The error in loading shown in the results section is the error in mass balance of the experiment, that is the loading after regeneration. The error in the energy requirement for desorption is determined by propagation of the errors in the experimental values. The main contributors to the error in energy requirement are the errors in the working capacity of both CO_2 and – if present – H_2O . For the cases with low working capacity and high loading after regeneration consequently a large relative error in working capacity is found. This might result in large error – up to 25% – in the energy requirement for desorption, as seen in the results section.

4.2.4. Energy calculations

In the results section the energy requirement for desorption of CO_2 from the solid amine sorbent is shown. The calculations are given in more detail below. Included in the evaluation are the sensible heat of the sorbent, CO_2 , water and the reaction heat of CO_2 and adsorbed water. Next to that, the latent heat of water for steam generation and the compression energy required for the vacuum production are

included.

First of all, the sensible heat of the sorbent ($Q_{\text{sensible,sorbent}}$ [J/kg_{CO₂}]) is calculated using equation (4.1). Where T_{des} and T_{ads} are the desorption and adsorption temperature respectively. The amount of sorbent to capture one kilogram of CO₂ is calculated by the experimental working capacity Δq_{exp} and the molar mass of CO₂ MW_{CO_2} .

$$Q_{\text{sensible,sorbent}} = \frac{1}{\Delta q_{\text{exp}} \cdot MW_{\text{CO}_2}} \cdot C_{P,\text{sorbent}} \cdot (T_{\text{des}} - T_{\text{ads}}) \quad (4.1)$$

4

The sensible heat of the CO₂ ($Q_{\text{sensible,CO}_2}$ [J/kg_{CO₂}]) is calculated by equation (4.2):

$$Q_{\text{sensible,CO}_2} = C_{P,\text{CO}_2} \cdot (T_{\text{des}} - T_{\text{ads}}) \quad (4.2)$$

The energy required for the desorption reaction of CO₂ ($Q_{\text{reaction heat}}$ [J/kg_{CO₂}]) is given by equation (4.3) and is calculated by dividing the reaction heat $\Delta_r H$ by the molar mass MW_{CO_2} . Similar, the energy required for desorption of H₂O is found. The 'reaction heat' for H₂O is equal to the vaporization enthalpy [85].

$$Q_{\text{reaction heat}} = \frac{\Delta_r H}{MW_{\text{CO}_2}} \quad (4.3)$$

The amount of energy needed to heat the co-adsorbed water or steam purge – when used – is determined by the sensible heat of water and steam ($Q_{\text{sensible,H}_2\text{O}}$ [J/kg_{CO₂}]) in equation (4.4). The latent heat of water ($Q_{\text{latent,H}_2\text{O}}$ [J/kg_{CO₂}]) is found by equation (4.5).

$$Q_{\text{sensible,H}_2\text{O}} = m_{\text{H}_2\text{O}} [C_{P,\text{H}_2\text{O}} \cdot (T_{\text{sat}} - T_{\text{ads}}) + C_{P,\text{steam}} \cdot (T_{\text{des}} - T_{\text{sat}})] \quad (4.4)$$

$$Q_{\text{latent,H}_2\text{O}} = m_{\text{H}_2\text{O}} \cdot \Delta_{\text{vap}} H_{\text{H}_2\text{O}} \quad (4.5)$$

The amount of H₂O per kilogram of CO₂ ($m_{\text{H}_2\text{O}}$ [kg_{H₂O}/kg_{CO₂}]) can be found by equation (4.6). The molar ratio H₂O : CO₂ is defined by equation (4.7) when using humid feed gas and by equation (4.8) when applying a steam purge. If applicable the combination of both is used.

$$m_{\text{H}_2\text{O}} = \text{ratio H}_2\text{O} : \text{CO}_2 \cdot \frac{MW_{\text{H}_2\text{O}}}{MW_{\text{CO}_2}} \quad (4.6)$$

The ratio $\text{H}_2\text{O} : \text{CO}_2$ with humid feed gas is defined as the ratio between the working capacities of H_2O and CO_2 during desorption, see equation (4.7).

$$\text{ratio } \text{H}_2\text{O} : \text{CO}_2 = \frac{\Delta q_{\text{H}_2\text{O},\text{exp}}}{\Delta q_{\text{CO}_2,\text{exp}}} \quad (4.7)$$

In the case of steam purge the ratio $\text{H}_2\text{O} : \text{CO}_2$ can be determined using the volume of H_2O ($V_{\text{H}_2\text{O},\text{exp}}$) added during the experiment. In equation (4.8) $\rho_{\text{H}_2\text{O}}$ is the density of H_2O and $m_{\text{sorb},\text{exp}}$ the amount of sorbent used during the experiment.

$$\text{ratio } \text{H}_2\text{O} : \text{CO}_2 = \frac{V_{\text{H}_2\text{O}} \cdot \rho_{\text{H}_2\text{O}} \cdot \text{MW}_{\text{H}_2\text{O}}^{-1}}{\Delta q_{\text{CO}_2,\text{exp}} \cdot m_{\text{sorb},\text{exp}}} \quad (4.8)$$

4

For the creation of vacuum adiabatic compression [195] is assumed and the required energy is calculated by equation (4.9). The efficiency of compression η is assumed to 0.75 and the ratio of C_p/C_v is $k = 1.3$ [196]. In equation (4.9), P_1 is the suction pressure of the compressor whereas P_2 is the discharge pressure which is assumed to be 1.5 bar.

$$Q_{\text{adiabatic compression}} = \frac{1}{\eta} \cdot \frac{k}{k-1} \cdot \frac{1}{\text{MW}_{\text{CO}_2}} \cdot RT_{\text{desorption}} \cdot \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right] \quad (4.9)$$

Symbols and values used in the equations above are summarized in Table 4.S1.

4.3. Results and discussion

4.3.1. PTSA dry adsorption

One of the ways to produce high purity CO_2 is desorption without the use of a purge medium. The effect of pressure and temperature on the working capacity is shown in Figure 4.4 for pressure temperature swing adsorption (PTSA) operation without any purge flow during desorption. Example profiles for temperature and loading during a desorption experiment at 200mbar and a bed temperature set-point of 100°C are given in Figure 4.3. As seen in Figure 4.3, the temperature at the wall is significantly higher than the set point temperature. The reason for this is the fact that the power input via the heating coil around the reactor is controlled by the temperature as measured in the center of the adsorbent bed. Therefore, in this study a volume averaged temperature as defined in equation 4.10 is used for interpretation.

In this equation $T(r)$ is defined as a linear radial profile between $T(r = 0) = T_{\text{bed}}$ and $T(r = \frac{1}{2}d_r) = T_{\text{wall}}$, where d_r is the reactor diameter (13mm).

$$T_{\text{avg}} = \frac{2\pi \int_0^r T(r) r dr}{\frac{1}{4}\pi d_r^2} \quad (4.10)$$

The definition of working capacities used in this article are visualized in Figure 4.3. Δq_{600} is the working capacity 600s after the start of the desorption operation. The working capacity is the difference between the adsorption loading and the loading after desorption, in this case after 600s. Analogue is Δq_{900} the working capacity after 900s of desorption operation. When the CO₂ concentration – mixed with the dilution stream, see setup Figure 4.1 – in the analyser is below 0.05 vol% the desorption step is stopped. The capacity at this time is defined as residual loading q_{res} with final working capacity (Δq_{fin}).

In Figure 4.4 the working capacities as a function of pressure and temperature are shown. First, experiments with 5000ppm of CO₂ are performed leading to an adsorption loading around 1.6mol kg⁻¹. Additionally, experiments with 400ppm of CO₂ – resulting in an adsorption loading of 1.1mol kg⁻¹ – are performed at those pressures leading to a positive working capacity. As seen, the final loading after desorption is independent of the adsorption loading. Although, it seems that for the 91°C experiments there is somewhat more variation in the data for the final loading. This might be an effect of slower desorption kinetics at lower temperature. This implicates that not all experiments have reached their equilibrium capacity as soon as the CO₂ concentration is below 0.05vol.% (including dilution) and the desorption step was stopped.

Additionally, it can be seen that the two experiments with the highest pressure at 91°C have a very small working capacity. This is in line with isotherm predictions, as the isotherm predicts a loading above 1.6mol kg⁻¹ when considering 100% CO₂ and a pressure above 700mbar at 91°C. The small working capacity observed might be due to some residual nitrogen present in the reactor from the adsorption step. Moreover, the loading reached falls within the accuracy of the isotherm. It can be concluded that in order to reach reasonable working capacities low pressure (<300mbar) at 116°C or really low pressure (<100mbar) at 91°C have to be used.

The energy evaluation using Δq_{900} in Figure 4.5 confirms the need for high temperature and low pressure to increase working capacity and thereby lowering the energy requirements. The experiments with a low working capacity at 900s in Figure 4.4 show high energy requirement in Figure 4.5. Major reason is the increased amount of sorbent needed to capture one kilogram of CO₂. With increased sorbent

Figure 4.3 | Example loading and temperature profiles versus time. Set point temperature 100°C for the bed temperature ($T_{\text{avg}} = 116^\circ\text{C}$) and pressure 200mbar. The definition of the working capacity after 600s (Δq_{600}), 900s (Δq_{900}) and at the end (Δq_{fin}) are shown. Note the break in x-axis in the adsorption stage to give more emphasis to the desorption stage.

Figure 4.4 | Experimental working capacities as a function of temperature and pressure (on x-axis in mbar) reported after 600s (Δq_{600}), 900s (Δq_{900}), at the end (Δq_{fin}) and residual capacity (q_{res}). Adsorption at 20°C and 5000 ppm or 400 ppm of CO_2 . Error bars show the loading after regeneration.

Figure 4.5 | Energy requirement for desorption for the experimental conditions presented in Figure 4.4 calculated with the working capacity after 900s. *Other* in the legend includes the sensible heat of CO₂ and compression energy. Error bars show the propagated experimental error.

mass, the sensible heat for the sorbent increases linearly. It can be seen in Figure 4.4 that for the experiments with low working capacity the error is larger than the working capacity itself. Consequently, in Figure 4.5 considerable error bars for the experiments with low working capacity are found due to error propagation.

Pressures below 200mbar are needed to have a energy requirement for desorption below 10MJ/kg_{CO₂}. Moreover, if the CO₂ concentration is 400ppm also a higher temperature is needed. At 91°C the 400ppm experiments lead to high energy requirements due to the low working capacities. However, the energy requirement might easily be halved by extending the desorption phase and reaching the final working capacity instead of the working capacity at 900s. As shown in Figure 4.4 the working capacity at 400ppm is significantly increased from 900s to the final capacity, especially at 91°C.

Moreover, the achieved adsorption loading of 1.1mol kg⁻¹ is at 20°C and under absolute dry conditions. Lowering the temperature or increasing the relative humidity will increase the adsorption loading and thereby the working capacity [85]. However, in an air capture process the environmental conditions will determine the adsorption conditions and thus cannot be optimized separately. Pre-treating air is too costly because of the enormous amount of air – minimal 1400m³ – to be pro-

cessed to capture one kilogram of CO₂.

A temperature higher than 116°C might increase working capacities even more. However, increasing the temperature above 120°C may lead to degradation of the sorbent [61]. Therefore, it can be concluded that in order to reach sufficient high working capacities without the use of a purge gas, the air capture equipment should be able to reach a pressure below 200mbar and temperatures higher than 100°C during the desorption step. Otherwise, energy requirement for desorption might significantly increase.

4.3.2. PTSA humid adsorption

As mentioned in the previous section, the incoming air during CO₂ air capture will be humid and water will co-adsorb on the sorbent. Moreover, the CO₂ equilibrium capacity is increased by co-adsorption of H₂O. Both of these effects are described by Veneman et al. [85]. In Figure 4.6 the increase in CO₂ capacity and co-adsorption of H₂O is confirmed. With increasing relative humidity in the gas feed, both the CO₂ and H₂O capacity are increased. The CO₂ working capacity after 900s is increased by two effects with increasing relative humidity. To illustrate, the adsorption capacity is increased by 0.4mol kg⁻¹ at from 0%RH to 79%RH.

Second, because of the desorption of water the CO₂ partial pressure is reduced during desorption. This leads to a 0.15mol kg⁻¹ lower CO₂ loading at 79%RH after 900s compared to 0%RH. Overall, the working capacity of CO₂ after 900s is increased from 0.6mol kg⁻¹ at 0%RH to 1.3mol kg⁻¹ at 79%RH. The large error in the H₂O loading can clearly be seen by the error bars in Figure 4.6. Moreover, the duplicate measurements at 400ppm and 68%RH show large variation in loading. As discussed before, the error bars are significantly larger for H₂O compared to CO₂.

The increase of the CO₂ working capacity has a strong impact on the energy requirement of desorption as shown in Figure 4.7 for 5000 ppm experiments. Although the co-adsorption of water raises an energy penalty for the adsorption enthalpy and sensible heat of water, the total energy requirement reduces because of the increased working capacity of CO₂. When considering the error bars the decreasing trend with increasing relative humidity is less pronounced. However, an energy saving compared to dry adsorption is seen for all relative humidities. For the 400ppm experiment the reduction of energy requirement is more clear. Even though the ratio H₂O to CO₂ is significantly higher. The increased ratio is a result of a reduced CO₂ working capacity with constant H₂O working capacity. From 44%RH onwards the total energy requirement remains constant due to increasing

Figure 4.6 | Experimental working capacities for CO₂ and H₂O reported after 600s (Δq_{600}), 900s (Δq_{900}), at the end (Δq_{fin}) and residual capacity (q_{res}) as function of the adsorption at 20°C and RH on x-axis and 400 or 5000 ppm of CO₂. Desorption at 500 mbar and $T_{avg} = 116^\circ\text{C}$. Error bars show the loading after regeneration.

Figure 4.7 | Energy requirement for desorption for the experimental conditions presented in Figure 4.6 calculated with the working capacity after 900s. In the reaction heat bar the ratio H₂O:CO₂ [mol mol⁻¹] – see equation 4.7 – is given. *Other* in the legend includes the sensible heat of CO₂ and H₂O and the compression energy. Error bars show the propagated experimental error.

ratio of H_2O to CO_2 . This is a result of the fact that the working capacity of H_2O is increasing faster compared to the working capacity of CO_2 . From this, it can be concluded that the co-adsorption of H_2O does not lead to an increased energy penalty and, on the contrary, even might reduce the energy requirement. An energy reduction is clearly shown for 400ppm experiments. Moreover, water will be co-harvested from air during air capture of CO_2 using a solid amine sorbent and will be a secondary product.

4.3.3. Steam purge with dry adsorption

Amount of steam

Steam is often suggested as a purge medium to produce pure CO_2 because it is easily separated from CO_2 by condensation. Therefore, in this work the effect of the amount of steam injected (in $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) during desorption is evaluated in Figure 4.8 and 4.9. Three stages of desorption can be identified in the figures. First, the heating stage is seen for $t = 0 - 250$ seconds. In this phase only the heating elements are switched on and the bed temperature is increased. This stage could be considered a temperature swing adsorption. As seen in Figure 4.8, little desorption is occurring at $T_{\text{avg}} = 91^\circ\text{C}$ which is in line with isotherm predictions at 91°C and 100% CO_2 . A slight decrease in loading can be observed in Figure 4.9 due to the higher reactor temperature.

The second stage is seen after approximately 250s when the vacuum pump and water injection are started. A decrease in loading is seen due to the decrease in CO_2 pressure with total pressure. The third stage starts at approximately $t=600\text{s}$ where a strong decrease in loading is observed as a result of reduced partial pressure of CO_2 due to the steam injected. This peak is not instantaneously because of the residence time of the water and steam in the evaporation system.

Using a steam purge does not always lead to a positive effect on the working capacity as seen in Figures 4.8 and 4.9. Amounts of steam injected up to 0.03kg kg^{-1} even have a slight negative effect on the working capacity, when compared to the 0kg kg^{-1} PTSA experiment. An explanation can be found in the water capacity of the sorbent. Because the adsorption is performed with dry feed gas as soon as steam is injected it adsorbs on the sorbent. Veneman et al. [85] showed adsorbed water will increase the CO_2 capacity and hence a negative effect on the working capacity is seen for water volumes up to 0.03kg kg^{-1} .

Another effect of the adsorption of water is that it will not lower the partial pressure of CO_2 in the reactor. Veneman et al. [85] showed that the water capacity on the sorbent is a function of relative humidity. Evaluating the maximum rela-

Figure 4.8 | Effect of the amount of steam purge added ($\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) at $T_{\text{avg}} = 91^\circ\text{C}$, $P = 300\text{mbar}$ and an injection rate of $1\text{kg}_{\text{steam}}/\text{h}$ on the desorption rate and working capacity. Adsorption at 5000ppm, 20°C and 0%RH.

Figure 4.9 | Effect of the amount of steam purge added ($\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) at $T_{\text{avg}} = 116^\circ\text{C}$, $P = 500\text{mbar}$ and an injection rate of $1\text{kg}_{\text{steam}}/\text{h}$ on the desorption rate and working capacity. Adsorption at 5000ppm, 20°C and 0%RH.

tive humidity in the reactor – 41% and 29% respectively – a water capacity of 3.9 and 2.6 mol kg^{-1} was found for the conditions of $T_{\text{avg}} = 91^\circ\text{C}$ & $P = 300 \text{ mbar}$ and $T_{\text{avg}} = 116^\circ\text{C}$ & $P = 500 \text{ mbar}$ respectively. These capacities correspond to 0.07 and 0.05 kg kg^{-1} of steam added. Consequently, adding more than 0.05 kg kg^{-1} of steam at 116°C would reduce the CO_2 partial pressure and accordingly the loading. In Figure 4.9 this effect is confirmed as from 0.07 kg kg^{-1} onward a significant improvement in working capacity is seen. However, for the low temperature (Figure 4.8) the 0.07 kg kg^{-1} line unexpectedly has an improved working capacity. This might be an effect of the radial temperature gradient inside the reactor resulting in lower maximum relative humidity locally. Moreover, the local partial pressure of H_2O can be reduced due to desorbing CO_2 also resulting in lower relative humidity.

The energy requirement for desorption as a function of the amount of steam added is shown in Figure 4.10. The absolute amount of energy required is not reduced by introducing the steam purge. The latent heat for evaporation of water raises the energy requirement significantly. Therefore, it is important to reduce the ratio $\text{H}_2\text{O}:\text{CO}_2$ as defined in equation 4.8 and shown on the inside of the x-axis in Figure 4.10. The ratio can be lowered by adding less water or by increasing the working capacity of CO_2 with the same amount of water. However, the working capacity for CO_2 can only be increased by increasing the temperature or reducing the pressure. Practically, the temperature cannot be increased because of stability issues [61]. Moreover, reducing the pressure would also lower the relative humidity and thereby the adsorption of water. As discussed above, this should improve the effectiveness of the purge.

On the other hand, reducing the amount of steam added reduces the CO_2 working capacity as displayed in Figures 4.8 and 4.9. Hence, reducing the amount of steam at the current pressure is not an option. Therefore, the amount of water should be minimized while the CO_2 working capacity is maximized. This effect is clearly seen in Figure 4.10 as the 0.10 kg kg^{-1} case of the 116°C experiments has the lowest energy requirement for the highest temperature. Adding more water will not increase CO_2 working capacity and hence is a waste of energy. On the other hand, for the 91°C case increasing the water amount above 0.13 kg kg^{-1} might increase the CO_2 working capacity even more and thereby reduce energy requirement.

Comparing PTSA and steam purge, it should be noted that although the total energy requirement is not reduced, the temperature level of the heat required can be reduced. Since, the total pressure of the system is reduced the latent heat of water can be supplied by low temperature heat. The boiling point of water at 300 and 500 mbar is 69 and 81°C respectively, which is significant lower than the reactor

Figure 4.10 | Energy requirement for desorption as a function of the amount of steam purge added (in kg_{steam}/kg_{sorbent}) injected. The CO₂ working capacity at 900s in Figures 4.8 and 4.9 is used. The ratio H₂O:CO₂ [mol mol⁻¹] – see equation 4.8 – is shown inside of the x-axis. *Other* in the legend includes the sensible heat of CO₂ and H₂O and the compression energy. Error bars show propagated error.

Figure 4.11 | The effect of the injection rate of steam (kg_{steam}/h) on the working capacity for two injection amounts (in kg_{steam}/kg_{sorbent}). Adsorption at 5000ppm, 20°C and 0%RH. Desorption at 500mbar and T_{avg} = 116°C.

temperature. Thereby, a reduction of energy requirement at a higher temperature level can be achieved. This opens extra opportunities for heat integration and thereby options for energy savings on process level. Moreover, by using the steam purge the working capacity is increased which means that less sorbent is required to capture the same amount of CO₂. This results in smaller adsorption equipment and thereby possibly a reduction in associated capex costs. The reduction depends on the balance between the capex cost of the steam generator and for the combined sorbent and reactor cost.

Injection rate

The effect of the injection rate of steam on the working capacity is shown in Figure 4.11. It can be seen that the injection rate does not have an effect on the final loading. Only the 0.07 kg kg⁻¹ at 2.0 kg h⁻¹ injection has a slight increase in working capacity. A clear effect of the residence time of the water in the evaporation system can be seen by the 'breakthrough' of the steam purge. The difference in breakthrough between 2.0 and 1.0 kg h⁻¹ and 1.0 and 0.5 kg h⁻¹ is approximately 100 and 200 s respectively. Because the working capacity of CO₂ is not affected by the injection rate the energy requirement for desorption will not change with the injection rate. It can be concluded that injection rate is mainly influencing the time needed for desorption. Thereby, a higher injection rate increases equipment productivity.

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4.3.4. Steam purge with humid adsorption

In the previous section it was concluded that the ratio of water and CO₂ should be reduced to have a reduction in energy requirement when applying a steam purge. Moreover, in section 4.3.3 it was shown that the steam injected partly adsorbs on the sorbent. However, since water will co-adsorb from air during air capture of CO₂ it is expected that less steam will adsorb. This might effectively reduce the amount of steam needed to increase the working capacity of CO₂. In Figure 4.12 the effect of the amount of steam purged on the CO₂ loading is shown for an adsorption feed gas with 66% RH. The corresponding water loading is shown in Figure 4.S1. Both the 0.02 and 0.03 kg kg⁻¹ experiments have a positive effect on the working capacity in Figure 4.12. For adsorption with 0% RH adsorption feed gas a positive effect was only seen from feeding 0.05 kg kg⁻¹ of steam onwards, as shown in Figure 4.9. However, the increase of working capacity by adding 0.03 kg kg⁻¹ is only limited to 0.1 mol kg⁻¹ and might not justify the cost involved in installing extra equipment.

The effect of the steam purge on the energy requirement is shown in Figure 4.13.

Figure 4.12 | Effect of the amount of steam purge added (in $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) at an injection rate of $1.0 (\text{kg}_{\text{steam}}/\text{h})$, $T_{\text{avg}} = 116^\circ\text{C}$ and 500mbar on the desorption rate and working capacity. Adsorption at 5000ppm, 20°C and 66%RH.

Figure 4.13 | Energy requirement for desorption as a function of the amount of steam purge added (in $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) injected for 5000 ppm CO₂ adsorption. The CO₂ working capacity at 900 s in Figure 4.12 is used. The ratio H₂O:CO₂ [mol mol^{-1}] is shown inside of the x-axis and is the combined ratio of H₂O adsorbed and purged (eq. 4.7 and 4.8). *Other* in the legend includes the sensible heat of CO₂ and H₂O and the compression energy. Error bars show propagated errors.

Figure 4.14 | Effect of the amount of steam purge added (in $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) at an injection rate of $1.0 \text{ kg}_{\text{steam}}/\text{h}$, $T_{\text{avg}} = 116^\circ\text{C}$ and 500 mbar on the desorption rate and working capacity. Adsorption at 400ppm, 20°C and 66%RH.

Figure 4.15 | Energy requirement for desorption as a function of the amount of steam purge added (in $\text{kg}_{\text{steam}}/\text{kg}_{\text{sorbent}}$) injected for 400ppm CO_2 adsorption. The CO_2 working capacity at 900s in Figure 4.14 is used. The ratio $\text{H}_2\text{O}:\text{CO}_2$ [mol mol^{-1}] is shown inside of the x-axis and is the combined ratio of H_2O adsorbed and purged (eq. 4.7 and 4.8). *Other* in the legend includes the sensible heat of CO_2 and H_2O and the compression energy. Error bars show propagated errors.

Adding a steam purge does increase the working capacity of CO₂, but the total energy requirement is not reduced. The counteracting effects of energy required for desorption of co-adsorbed water and the increase in the working capacity for CO₂ is already discussed in section 4.3.2. Comparing the effect of steam purge for dry and humid adsorption it can be seen that the effect on the working capacity in case of humid adsorption is reduced. As an example, for the 0.1kg kg⁻¹ experiment at 900s the increase in working capacity by the addition of steam is reduced from 0.75 to 0.45mol kg⁻¹, when comparing for the dry and humid adsorption experiments. The effect of the steam purge is reduced and as a consequence a reduction of energy requirement is not achieved.

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In Figure 4.14 the working capacity of CO₂ as a function of the steam purge added is shown for adsorption using 400ppm of CO₂. As shown, the desorption capacities of CO₂ are more or less equal to the capacities for the 5000ppm experiments. This means the working capacity for CO₂ is significantly reduced as the adsorption loading is much lower for the 400 ppm experiments compared to the 5000ppm experiments. Similar to the 5000ppm an effect of the steam purge is seen from 0.03kg kg⁻¹ of steam purge added. Looking at the energy requirement for desorption in Figure 4.15 it is seen that the energy requirement is higher for the 400ppm adsorption because of the reduced working capacity. Again, the application of the steam purge does not reduce the total energy requirement. However, as discussed in section 4.3.3 the temperature level of the heat required is reduced and equipment productivity increased because of the increase in CO₂ working capacity.

4.3.5. Multi cycle experiment

All experiments up to this point have been performed using a clean sorbent, where all previously adsorbed CO₂ and H₂O is removed by a deep regeneration step at the end of the previous experiment using a hot nitrogen purge. Of course, in an envisaged industrial process the regeneration step should be removed because it is cost and equipment inefficient. Therefore, experiments have been performed without this deep regeneration step. After the first desorption step, a new adsorption is directly started using the same conditions. In Figure 4.16 it is shown that the CO₂ working capacity is reaching a constant value. Also all the measured desorption CO₂ working capacities are equal. This confirms that the working capacity found for the first cycle is relevant for the following cycles. Due to a lower measurement accuracy, the working capacities of H₂O show more variation. However, after the first cycle the adsorption working capacities of H₂O show constant values. Therefore, these adsorption capacities are used in the energy evaluation below. Note that the desorption working capacity of H₂O for the steam purge experiment is

Figure 4.16 | Final working capacities for successive adsorption-desorption cycles without a regeneration step. Desorption at 116°C and pressure + steam purge shown on x-axis. Adsorption at 5000ppm, 20°C and 66%RH.

Figure 4.17 | Energy requirement for desorption using the average final working capacity for the experiments shown in Figure 4.16. The ratio H₂O:CO₂ [mol mol⁻¹] is shown inside of the x-axis and is the combined ratio of H₂O adsorbed and purged (eq. 4.7 and 4.8). *Other* in the legend includes the sensible heat of CO₂ and H₂O and the compression energy. Error bars show propagated errors.

higher because of the steam injected.

In Figure 4.17 the energy requirement for desorption is shown using the average final working capacities from Figure 4.16. Once again, it can be concluded that adding a steam purge does not reduce the energy requirement. Moreover, by comparing the 500mbar experiment shown here and shown in Figure 4.7 it can be seen that the energy requirement is larger when using the final working capacity instead of the working capacity after 900s. This is a result of the increased ratio of H₂O to CO₂. When obtaining high H₂O to CO₂ ratios in the product gas, a water condensation step prior to recompression of the gas should be considered when upscaling the process.

4

4.4. Conclusion

High purity CO₂ can be produced from air using solid amine sorbent. The high purity CO₂ can be produced by applying either a pressure temperature swing or by purging steam. In case of a pressure temperature swing operation a temperature above 100°C and a pressure below 200mbar should be reached in order to maximize CO₂ working capacity and reduce the energy requirement for desorption. Co-adsorbed water will increase the CO₂ working capacity and, counter intuitive, reduce the energy requirement for desorption.

Application of a steam purge during desorption will increase the sorbent CO₂ working capacity. However, the energy requirement for desorption per unit of CO₂ does not decrease due to latent heat for water evaporation. On the other hand, the sorbent mass required to capture a kilogram of CO₂ reduces. This implies a reduction in equipment size and consequently in capex costs.

The global minimum of the energy requirement should be found by an optimization of the complete system including the adsorption and desorption conditions, cycle times and equipment sizes.

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4.5. Supporting Information

Table 4.S1 | List of symbols and material properties

Symbol	Value	Unit	Meaning	Ref.
C_{P,CO_2}	0.85	$\text{kJ kg}^{-1} \text{K}^{-1}$	CO ₂ heat capacity	[194]
C_{P,H_2O}	4.18	$\text{kJ kg}^{-1} \text{K}^{-1}$	H ₂ O heat capacity	[194]
$C_{P,sorbent}$	1.58	$\text{kJ kg}^{-1} \text{K}^{-1}$	Sorbent heat capacity	[62]
$C_{P,steam}$	2.05	$\text{kJ kg}^{-1} \text{K}^{-1}$	Steam heat capacity	[194]
DAC	-	—	Direct air capture	
d_p	0.7	mm	Average particle diameter	[55]
d_r	13	mm	Reactor diameter	
k	1.3	—	Ratio of C_p/C_v	[196]
m_{H_2O}	-	$\text{kg}_{H_2O}/\text{kg}_{CO_2}$	mass of H ₂ O per kilogram of CO ₂	
m_{sorb}	30.4	g	Dry sorbent mass	
MW_{CO_2}	0.044	kg mol^{-1}	Molar mass CO ₂	
MW_{H_2O}	0.018	kg mol^{-1}	Molar mass H ₂ O	
P	-	Pa	Pressure	
$PTSA$	-	—	Pressure temperature swing adsorption	
Q	-	J/kg_{CO_2}	Energy requirement	
r	-	m	Reactor radius	
R	8.314	$\text{J mol}^{-1} \text{K}^{-1}$	Gas constant	
RH	-	%	Relative humidity	
T	-	K	Temperature	
V_{H_2O}	-	$\text{m}^3 \text{s}^{-1}$	Volume flow of steam injection	
Greek Symbols				
$\Delta_r H$	75	kJ mol^{-1}	Reaction heat	[85]
$\Delta_{vap} H$	41	kJ mol^{-1}	H ₂ O vaporization enthalpy	[194]
Δq	-	mol kg^{-1}	Working capacity	
η	0.75	—	Compressor efficiency	
ρ_{H_2O}	998	kg m^{-3}	H ₂ O density	[194]

4.5.1. H₂O loading

The H₂O loading during desorption is shown Figure 4.S1. This is the corresponding H₂O loading to the CO₂ loading in Figure 4.12. The loading is determined by integration of the difference in H₂O inflow and outflow.

The lines in Figure 4.S1 imply that the loading is significantly increased by steam injection. However, the shown loadings are too high in our opinion and a result of the uncertainty in the H₂O mass balance. At the 116°C and 500 mbar the maximum relative humidity is 29% corresponding to a loading of 2.6 mol kg⁻¹ according to literature [85]. Therefore, it is far-fetched that a loading of 7 mol kg⁻¹ is actually reached even despite local variations in pressure and temperature. Because of the uncertainty in the H₂O loading no conclusions can be made about the precise H₂O loading.

4

Figure 4.S1 | Effect of the amount of steam purge added (in kg_{steam}/kg_{sorbent}) at an injection rate of 1.0 (kg_{steam}/h), $T_{\text{avg}} = 116^{\circ}\text{C}$ and 500mbar on the desorption rate and working capacity. Adsorption at 5000ppm, 20°C and 66%RH.

CO₂ CONVERSION TO METHANOL

III

5

A novel Liquid Out Gas In Concept (LOGIC) reactor for CO₂ to methanol conversion

Abstract

A novel reactor concept for the conversion of CO₂ and H₂ to methanol is developed. Conversion limitations because of thermodynamic equilibrium are bypassed via in situ condensation of a water/methanol mixture. Two temperatures zones inside the reactor ensure optimal catalyst activity (high temperature), automatic gas circulation by natural convection and full conversion by condensation at a lower temperature in a separate zone. Experimental work confirmed full carbon conversion (>99.5%) and high methanol selectivity (>99.5% on carbon basis). Because of full gas conversion there is no need for an external recycle of unconverted reactants.

This chapter is based on the following publication:

M.J. Bos, D.W.F. Brilman, *A novel condensation reactor for efficient CO₂ to methanol conversion for storage of renewable electric energy*. **Chemical Engineering Journal**, 2015, **278**, pp.527-532, doi:10.1016/j.cej.2014.10.059

5.1. Introduction

In section 1.5 advanced CO₂ to methanol conversion methods to circumvent thermodynamic limitations are discussed. One of the ways to avoid equilibrium limitations is the condensation of product vapours. In this chapter a novel methanol reactor concept using two temperature zones is introduced and an experimental proof of concept is demonstrated.

5.2. Theoretical considerations

5.2.1. Methanol synthesis

During methanol synthesis the methanol formation reactions – equations 5.1 and 5.2 – are in equilibrium with the water gas shift reaction, see in equation 5.3. Due to the exothermic character of the methanol formation reactions and the decrease of the number of moles during the reaction the equilibrium is more advantageous at high pressure and low temperature.

Chemical equilibria during the methanol synthesis are calculated using the equilibrium constants presented by Graaf et al. [200]. Nonideality of the gas mixture is taken into account by including the fugacity coefficients in the equilibrium constants, see equation 5.4 and 5.5 where K_i is the equilibrium constant, T the temperature (K), ϕ_i the fugacity coefficient, y_i the gas phase mole fraction and P the pressure (bar). The fugacity coefficients are calculated by the modified Soave-Redlich-Kwong (mSRK) equation as described by Bennekom et al.[201] Since the original SRK equation is developed for hydrocarbon and slightly polar systems, the modified version for polar systems by Mathias [202] is used.

$$K_1 = 10^{\frac{5139}{T} - 12.621} = \left[\frac{\phi_{\text{CH}_3\text{OH}}}{\phi_{\text{CO}} \phi_{\text{H}_2}^2} \right] \left[\frac{y_{\text{CH}_3\text{OH}}}{y_{\text{CO}} y_{\text{H}_2}^2 P} \right] \quad (5.4)$$

$$K_2 = 10^{-\frac{2073}{T} + 2.029} = \left[\frac{\phi_{\text{CO}} \phi_{\text{H}_2\text{O}}}{\phi_{\text{CO}_2} \phi_{\text{H}_2}} \right] \left[\frac{y_{\text{CO}} y_{\text{H}_2\text{O}}}{y_{\text{CO}_2} y_{\text{H}_2}} \right] \quad (5.5)$$

The equilibrium methanol yield is a function of pressure, temperature and feed composition, see Figure 5.1 and Figure 5.2. With increasing temperature the product composition is shifting from methanol rich to CO rich mixtures. Thereby, decreasing the equilibrium yield of methanol. The same trend is seen with decreasing pressure. Although the effect of decreasing pressure is small compared to the effect of increased temperature.

The equilibrium methanol yield of syngas based systems – see Figure 5.1 – is significantly higher than for CO₂ feeds systems at the same conditions, see Figure 5.2. If full conversion of reactants using CO₂ as feedstock is pursued, the increased recycling of unreacted components will increase operational and capital costs of the process. In this chapter, a novel reactor design achieving full CO₂ and H₂ conversion at low pressure is proposed. Full conversion at low pressure is achieved by condensation of product vapours using a temperature gradient and internal circulation inside the reactor.

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5.2.2. Dew point temperature

To initiate condensation, the temperature of the condensation zone inside the reactor should lower than the dew point temperature. Therefore, phase equilibria calculations are performed using the mSRK Equation of State [201, 202]. During phase equilibrium the fugacity of the liquid phase must be equal to the fugacity of the vapor phase, see equation 5.6 where y_i is gas phase mole fraction, ϕ_i^V the gas phase fugacity coefficient, x_i is liquid phase mole fraction and ϕ_i^L the liquid phase fugacity coefficient, in all cases for the component i . The dew point temperature is the highest temperature for which equation 5.6 is valid for a certain gas composition and pressure.

$$y_i \phi_i^V = x_i \phi_i^L \quad (5.6)$$

In Figure 5.3 it is shown that at high pressure (>100 bar) and low reaction temperature (473K) condensation of the chemical equilibrium mixture can happen at the reaction temperature. However, with increased reaction temperature a significant higher pressure (>150 bar) is needed to condensate the equilibrium mixture at the reaction temperature. At relatively lower pressures (e.g. 50 bar) a decrease in temperature is needed to initiate condensation because the dew point temperature (403-413K) is below the reaction temperature (473-533K). Therefore, a temperature gradient should be present inside the reactor in order to initiate in-situ condensation of product vapors.

Figure 5.1 | Chemical equilibria in methanol synthesis from syngas feed. Syngas feed: H₂/CO/CO₂ 75.9/16.9/7.2 (mol fractions).

Figure 5.2 | Chemical equilibria in methanol synthesis from CO₂ feed. Syngas feed: H₂/CO/CO₂ 75.0/0/25.0 (mol fractions).

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Figure 5.3 | Dew point of the equilibrium mixture generated at a reaction temperature of 473/498/523K as a function of pressure. (CO_2 feed: H_2 : CO_2 3:1 molar ratio.)

Figure 5.4 | Relative density ($\rho(T)/\rho(573K)$), calculated for the equilibrium composition generated at 503 K and respectively 25/50/100 bar (CO_2 feed: H_2 : CO_2 3:1 molar ratio.).

5.2.3. Natural Convection

A significant temperature gradient should be present for product condensation inside the reactor. This could result in a significant density gradients inside the reactor. Thereby, the reactor productivity can possibly be enhanced by a natural convection flow between condensation and reaction zones. Therefore, the density ρ of the equilibrium mixture generated at 503 K and 25/50/100 bar is calculated as a function of temperature T (K) using the mSRK Equation of State [201, 202], see equation 5.7 where P is the pressure (Pa), Z the compressibility and MW_i (kg mol⁻¹) the mole weight of component i .

$$\rho(T) = \frac{P}{ZRT} \cdot \sum_{i=1}^n (y_i \cdot MW_i) \quad (5.7)$$

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In Figure 5.4 it can be seen that density is doubled when decreasing the temperature from 573 to 273K. Furthermore, a 35% density difference between a typical reaction temperature (503K) and a typical condenser temperature of 373K is present. The change in density is increasing with increased pressure due to increased non-ideality of the gas. Thereby, the difference in the compressibility factor (Z) is larger at high pressure than at low pressure. Since a temperature difference of at least 70K between the reaction section – minimal 473K in view of reaction kinetics – and the condensation section – maximal 403K at 50bar due to the dew point temperature, see Figure 5.3 – should be present in the reactor, it is expected that the reactor design could benefit from natural convection phenomena.

5.2.4. Liquid-Out Gas-In Concept

According to the findings above a novel reactor design was designed and developed. In the novel reactor design two temperature zones are created inside the reactor in order to shift the chemical equilibrium. The catalyst zone operates at a higher temperature (473-533K) to ensure optimal catalyst performance. In the second zone the temperature is lowered below the dew point temperature to condensate the products. In Figure 5.5 is shown that the cold section is placed in top of the reactor, while reaction section is placed in the bottom of the reactor. In this way an optimal configuration is obtained to benefit from natural convection flow. However, to be able to study the effect of gas circulation independent of the temperature levels applied a fan is included.

The reactor is designed to operate in the so-called *Liquid-Out, Gas-In Concept* (LOGIC) modus. The gaseous reactants are fed and converted inside the reactor and accord-

ingly the product vapours are condensed in-situ and extracted as liquid product from the reactor. In this way full conversion of gaseous H_2 and CO_2 reactants to the liquid products methanol and water can be achieved. Additionally, this concept makes possible carbon selectivity loss to CO in the reaction zone irrelevant, as CO will not leave the reactor as long as it is in the gas phase.

5.3. Experimental

5.3.1. Materials

Feed gas was supplied in a premixed bottle by Praxair, the Netherlands. Purity of the mixture was $24.8 \text{ vol}\% \pm 2\% \text{rel.} CO_2$ in H_2 (Feed gas 1) in the first experimental series and $24.9 \text{ vol}\% \pm 2\% \text{rel.} CO_2$ in H_2 (Feed gas 2) in the second experimental series. The catalyst used was a commercial Cu/ZnO/Al₂O₃ catalyst (CP-488) provided by Johnson Matthey. The catalyst was used as received as cylindrical tablets with 6mm diameter and 5mm length.

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5.3.2. Set-up description

The setup consists of a buffer vessel, a reactor including an oven and a cooler with a water bath to regulate cooling temperature. A schematic overview of the setup is given in Figure 5.6. Feed gas is fed to a 3.8L buffer vessel (a) to a maximum pressure of 100 bar, which is measured by a pressure indicator (PI-1) [GE Druck, Unik PTX-5072-TB-A1-CA-H1-PA, 0-100bar]. The pressure inside the reactor is measured by a pressure indicator (PI-2) [GE Druck, Unik PTX-5072-TB-A1-CA-H1-PA, 0-250bar] and regulated by a pressure reducer (PCV-1) between the buffer vessel and the reactor.

The catalyst is placed in the annular spacing (b, see fig 5.6) of the bottom section of the reactor. The catalyst section has an inner diameter of 24mm, an outer diameter of 48mm and a length of 72mm. The catalyst section is surrounded by a temperature controlled [Eurotherm, 2132] heating jacket (h). The current to the oven is measured by a current indicator (CI-1) [Phoenix Contact, MACX MCR-SL-CAC-5-I-UP]. The gas temperatures just before (TI-3) and after (TI-2) the catalyst bed is measured by K-type thermocouples [B+B sensors]. The pressure drop over the catalyst bed is measured by a differential pressure indicator (dP-1) [GE Druck, LPM-9481].

A fan (c) of 38mm diameter is installed to ensure circulation inside the reactor. The fan is powered by a 30W magnetic coupled motor (M) to ensure a gas-tide power transmission. The cooler (d) is placed in the inner part of the top section and it is

constructed from spiral wound stainless steel tubing. Gas temperatures of the cooler inlet (TI-5) and outlet (TI-4) are measured by K-type thermocouples [B+B sensors]. The cooler is operated with water and the temperature is regulated by a water bath (g) [Julabo F34-HE]. The water flow is measured by a flow indicator [POM B.I.O-Tech Becker 52.01 in combination with Red Lion IFMA 0035] and the water inlet (TI-7) and outlet temperature (TI-6) is measured by K-type thermocouples [B+B sensors]. Liquid product is collected inside the reactor in a collection cup with a volume of approximate 6mL. The product is tapped from the reactor into an ice-cooled collection bucket (e) outside the reactor.

5.3.3. Experimental procedure

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The reactor was filled with catalyst and activated according to the procedure provided by the manufacturer. In between experiments the reactor is stored under a reducing environment. Before an experiment the buffer vessel was filled with feed gas from the gas bottle and the reactor is purged with the feed gas. After purging the reactor it was pressurized and heated, the catalyst outlet temperature was regulated by the temperature of the oven. The cooler was turned on and the cooler outlet temperature was controlled by the flow and temperature of the cooling water. The fan was switched on and the fan speed was controlled by the voltage supplied.

The experiments were performed in semi-continuous mode, feed gas was continuously fed from the buffer vessel to the reactor in order to maintain the reactor pressure at 50 bar, as the pressure in the reactor will decrease due to reaction and condensation. At every two bar of pressure drop in the buffer vessel the condensate was tapped from the reactor resulting in approximate 4 mL of condensate. The productivity of the reactor was measured by the liquid production per unit of time. Productivity was determined over a minimum of 5 condensate samples under stable conditions.

During the condenser temperature experiments the condenser temperature is varied between 358K and 413K. The reactor pressure is kept constant at 50 bar and the catalyst outlet temperature is regulated at 483K. The fan speed was adjusted (via power supply voltage, between 8 and 10V) to maintain a constant pressure drop over the catalyst bed of 0.15 mbar. It is expected that a constant pressure drop over the catalyst bed reflects a constant circulation flow inside the reactor. However, no method of direct flow measurement was present at the reactor.

The fan speed was varied between 0 and 10V during the fan speed experiments. The catalyst bed outlet temperature was regulated at 468K and the cooler outlet

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Figure 5.5 | LOGIC reactor with catalyst section in the bottom annulus spacing and condenser in the top section.

Figure 5.6 | Schematic overview of the setup: (a) Buffer vessel, (b) Catalyst Section (annulus), (c) Fan, (d) Cooler, (e) Liquid Outlet, (f) Purge, (g) water bath, (X-1) oven temperature controller, (TI) Temperature Indicator, (PI) Pressure Indicator, (CI) Current Indicator, (dP) differential Pressure Indicator, (FI) Flow Indicator, (PCV) Pressure Control Valve, (V) Valve.

temperature was 363K. The reactor pressure was maintained at 50 bar.

The liquid product was analyzed in a HPLC [Agilent Technologies 1200 Series] using RID detection and 300 mm x 7.7 mm Hi-Plex H column equipped with a pre-column. The injected volume was 10 μ L, the temperature 65°C and the mobile phase 5mM H₂SO₄ at 0.6mL/min. Calibration curves were obtained by injecting mixtures of known composition in the range of interest before the samples.

5.4. Results and discussion

Two series of experiments have been performed. In the first set the condenser section outlet temperature has been varied, while in the second set the fan speed is varied. The goal of the first set of experiments is the ‘proof of concept’ of the Liquid-Out Gas-In concept, showing full conversion and high selectivity. In the second set of experiments the effect of fan speed is tested, showing the performance under natural convection gas circulation.

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5.4.1. Condenser temperature

In Figure 5.7 is shown that the reactor productivity increases with a decreasing condenser temperature. At a lower condenser temperature a larger fraction of the product vapours will condense and thereby a larger conversion per pass can be achieved in the catalyst section. The productivity reaches zero for a condenser temperature of about 418K which approaches the calculated dew point temperature of the equilibrium composition as shown in Figure 5.3. Accordingly, it is shown that the system reaches the equilibrium composition for high condenser temperatures.

The condensate composition is found to be 48.4 $\pm$ 2.0 mole% of methanol in water, whereas the expected theoretical ratio is 50 mole% methanol in water. However, as methanol is more volatile than water, we expect that possibly some methanol is evaporated during sampling. Additionally, extra water can be produced by the water gas shift when some gas (possible containing CO) is lost during liquid sampling. No significant changes in liquid composition are seen for changes in condenser temperature. At the prevailing conditions in the catalyst zone, the formed methanol is for more than 99.5 mol% pure and only traces of ethanol, 1-propanol and formic acid are found.

Because no gas phase is subtracted from the reactor a very high carbon yield of larger than 99.5% is found. Mass balances based on the pressure decrease in the buffer vessel and the recovered condensate are consistent (within few percent).

Figure 5.7 | Reactor productivity as a function of condenser outlet temperature. (P=50 bar, Catalyst bed outlet temperature =483K, Catalyst bed pressure drop=0.15mbar, Feed gas 1)

5.4.2. Fan speed

The novel design is able to produce methanol condensate at a significant production rate without forced convection by the fan, see the productivity at 0V in Figure 5.8. Thereby, proving that the concept can operate without moving parts inside the reactor. This opens the potential for a simple small-scale and standalone methanol producing vessel. This set of experiments achieved the same high carbon yield to methanol as the previous set. The average methanol concentration is 47.5 ± 0.6 mole% of methanol in water, again only traces of ethanol and formic acid are detected leading to a methanol purity of $>99.8\%$.

It should be mentioned that determination of the absolute gas circulation flows inside the reactor was not possible. The pressure drop over the catalyst bed was too low (<0.1 mbar) to measure with the available equipment. Therefore, relative fan speed in the form of the applied voltage to the fan is presented in the figures below.

At low fan speeds the productivity is increased in comparison to natural convection. This is probably the effect of enhanced mass transfer from and to the catalyst and condenser by forced convection. Thereby, the catalyst is used more efficiently. However, further enhancement of mass transfer by increased fan speed showed

decreasing productivity. A reason for this behaviour can be found when the gas temperatures of the inlet and outlet of the catalyst bed are compared, see Figure 5.9. It is seen that at higher flows the gas temperature of catalyst bed inlet drops significant, thereby reducing the average catalyst temperature and consequently reducing the reaction rates. Apparently, at lower fan speed internal heat transfer is sufficient to preheat the gas to the catalyst bed to a temperature close to the catalyst bed outlet temperature (which is used as set point for the catalyst heater). At higher flow rates additionally heat transfer is necessary to preheat the gas and increase catalyst efficiency. To improve radial heat transfer from the catalyst bed to the inner tube – containing the cold recycling gas returning to the catalyst – one may consider the use of conducting structured catalyst as discussed by Montebelli et al [203]. Additionally, it is seen that the condenser outlet temperature still matches its set value thereby suggesting that cooling rates are still sufficient at high flow rates.

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At high fan speed it is seen that the flow inside the reactor is too high to maintain catalyst temperature and reaction kinetics. Additionally, it is seen that in the previous set of experiments – presented in Figure 5.7 – the flow was also too high since the catalyst inlet temperature was relatively low (393-413K). An effect of the catalyst bed outlet temperature is seen when comparing the productivity at high fan speed in Figure 5.8 (2 mmole MeOH gcat⁻¹ hr⁻¹, catalyst out 468K) with the higher productivity in Figure 5.7 at the same condenser temperature of 363K (3-4 mmole MeOH gcat⁻¹ hr⁻¹, catalyst out 483K).

It is clear that reactor productivity can be further enhanced by optimizing flow and catalyst temperature. By increasing the catalyst inlet temperature the productivity of the reactor is increased. Because the average catalyst temperature will increase and thereby reaction rates increase. In the current setup optimal productivity is found at low flow rates. However, it is expected that the optimal flow will increase with increase temperature. Thereby reactor productivity will be enhanced. It can be concluded that optimization of the reactor conditions is clearly subject of further study.

5.4.3. Energy efficiency

The reactor energy efficiency is decreasing with increased fan speed (see Figure 5.10) because more energy input is needed while the productivity is decreasing. The difference between the cooler and oven duty is a measure of the heat loss (123±45W) of the lab reactor. The maximum produced reaction heat is 8.5W and not very significant compared to the oven duty in this laboratory setup.

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Figure 5.8 | Reactor productivity as a function of fan speed. (P=50 barg, Catalyst bed outlet temperature=468K, Condenser outlet temperature=363K, Feed gas 2)

Figure 5.9 | Gas temperatures at the catalyst and condenser inlet/outlet as a function of fan speed. (P=50 barg, Catalyst bed outlet temperature=468K, Condenser outlet temperature =363K, Feed gas 2)

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Figure 5.10 | Oven and cooler duty as a function of fan speed. (P=50 barg, Catalyst bed outlet temperature=468K, Condenser outlet temperature=363K, Feed gas 2)

Figure 5.11 | Energy input per kg of methanol as a function of fan speed. (P=50 barg, Catalyst bed outlet=468K, Condenser outlet temperature=363K, Feed gas 2)

In this small lab setup, the energy input per kilogram of methanol is too high under the current conditions (see Figure 5.11), because it is about three times the higher heating value of methanol (22.4MJ/kg [117]). However, this energy input includes heat loss to the environment and the loss by the cooling duty. If the heat loss to environment is neglected (to be achieved by an improved design) and 50% of the condenser duty is used to reheat the cold gas, the energy input at low fan speeds is already reduced to the higher heating value of methanol. This underlines the importance of further work on heat exchange in this reactor design.

5.5. Conclusion

A novel reactor concept to circumvent equilibrium limitations during methanol synthesis is developed. By the creation of two temperature zones, in-situ condensation of the products vapors is possible at low pressure thereby shifting the equilibrium. The design of the reactor comprises a cold condensation zone in the top and a hot reaction zone in the bottom of the reactor in order to benefit from natural convection phenomena.

Experimental results showed that indeed methanol was produced with the novel 'Liquid Out Gas In Concept' reactor. The expected 50/50 molar ratio of water / methanol was approached in the produced condensate. The carbon yield to methanol was very high (above 99.5%), since the obtained methanol contained only traces of ethanol, 1-propanol and formic acid.

Additional experiments with varying fan speed showed that indeed a significant methanol production was found without forced convection, opening the potential for a simple small-scale and standalone methanol producing vessel.

The energy efficiency of the current lab scale setup is too low to produce methanol with a positive energy balance. Therefore more work is needed in optimizing the conditions inside the reactor, heat exchange between the hot and cold section inside the setup and minimizing heat loss to the surroundings.

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6

Characterization of the LOGIC reactor for CO₂ to methanol conversion

Abstract

A novel condensing reactor for conversion of CO₂ to methanol is characterized under forced convective conditions, both experimentally and by modelling. The goal of the study is to optimize the operation conditions and identify limitations of the reactor concept. Experimental results show that productivity is limited by reaction equilibrium and mass transport at high temperature (>250°C), while reaction kinetics limit productivity at low temperature (<220°C).

Further analysis of the LOGIC concept is performed by an adiabatic 1D-reactor model in combination with an equilibrium flash condenser model. To enable autothermal operation heat exchange is required and it was found that a condenser temperature below 70°C is required to prevent excessive heat exchange area. Most important design parameter is found to be the conversion per pass over the catalyst bed. Increasing dimensions of the catalyst section, and thus overall reactor size, will increase the conversion per pass, until equilibrium is reached. On the other hand, the recycle ratio is decreased and thus less heat exchange and condenser area is required, decreasing overall reactor size. With the model developed, overall reactor performance can be optimized by finding the most optimal combination of reaction and condenser conditions.

This chapter is the basis of the following publication:

M.J. Bos, Y. Slotboom, S.R.A. Kersten, D.W.F. Brilman, *Characterization of a condensing CO₂ to methanol reactor*, Submitted to peer reviewed journal

6.1. Introduction

In the previous chapter 5 [204] a new reactor concept for CO₂ hydrogenation to methanol has been introduced. In this reactor the reaction equilibrium is shifted towards completion by the use of two temperature zones. One zone operates at reaction conditions and the other zone at reduced temperature to condensate the products in situ.

In the previous chapter, experimental methanol yields were determined to be higher than 99.5%. While showing great potential, the reactor was operated as a black box. Feed gas is fed to the reactor and only liquid products are extracted. Thereby, little is known about the internal flow and gas compositions, making it difficult to optimize and upscale the concept. Therefore, in this chapter the condensing CO₂ to methanol reactor is studied in more detail. Effort is taken to determine the internal gas composition and flow experimentally.

First, the experimental details will be discussed, followed by the equations of the constructed model. In the discussion section, the results of the model for the experimental conditions under forced convection will be discussed. Subsequently, the LOGIC concept will be discussed in more general way.

6

6.2. Experimental section

6.2.1. Materials

The pre-mixed feed gas is supplied from a bottle provided by Linde, the Netherlands. Purity of the mixture was $23.9\% \pm 2\% \text{rel.}$ of CO₂ in H₂.

The catalyst is a commercial Cu/ZnO/Al₂O₃ (CP-488) methanol catalyst supplied by Johnson Matthey. The catalyst is used, as supplied, in cylindrical tablets with diameter 6 mm and height 5 mm. Before first use, the catalyst is activated by hydrogen according to the procedure of the manufacturer. The amount of catalyst present in the reactor is 52.2g.

6.2.2. Liquid-Out Gas-In Concept reactor and setup

In Figure 6.1 the reactor is shown which is operated in the so-called LOGIC modus: Liquid Out Gas In Concept. Feed gas is fed from the buffer vessel into the central tube of the reactor. Next, the gases react on the catalyst bed in the annulus spacing of the reactor. Following, the products are condensed on the spiral condenser in top of the reactor. Liquid products are collected in the 'basket' and can be removed

from the reactor by the tube inserted in the basket. Non condensed gases are recycled to the catalyst. The theoretical background of concept is discussed in more detail in chapter 5.

For interpretation and discussion of the results it is important to note the location and name definition of the various thermocouples. Four thermocouples measure the in and outgoing temperatures for both the condenser and catalyst section. The catalyst inlet ($T_{\text{cat,in}}$, TI-2, Fig.6.1) and catalyst outlet ($T_{\text{cat,out}}$, TI-3, Fig.6.1) temperature are measured just before and after the catalyst bed. The condenser inlet ($T_{\text{cond,in}}$, TI-5, Fig.6.1) thermocouple is located between the top of the reactor and condenser, for a better view see Figure 6.S1 in the Supporting Information. The condenser outlet temperature ($T_{\text{cond,out}}$, TI-4, Fig.6.1) is measured at the inlet of the central tube. Note that this location is not directly below the condenser and therefore the measured temperature might not represent the true temperature at the end of the condenser. Next to that, the temperature of the cooling water inlet ($T_{\text{cw,in}}$, TI-6, Fig.6.2) and outlet ($T_{\text{cw,out}}$, TI-7, Fig.6.2) are measured.

Compared to the setup of the previous chapter a few changes have been made. To be able to determine the internal gas flow rate the pressure drop over the catalyst section has been increased by adding 1 mm spherical stainless steel particles (see Figure 6.1). Now, the pressure drop can be determined using a differential pressure sensors (dP-1, Fig 6.2). Previously, the pressure drop over the catalyst bed was too small to measure. A gas chromatograph (downstream of V-201/V-202) is connected to the gas samples points of the reactor to determine the internal gas composition. The liquid products are removed from the reactor by opening V-203. Closing of V-203 is automated by the use of a conductivity sensor. As soon as gas breakthrough occurs conductivity of the product stream will decrease and the valve is closed by the software.

The pressure in the reactor is controlled by a pressure control valve (PCV-1, Fig 6.2). The temperature of the catalyst section is controlled by a electric oven (E-3, Fig 6.2). The condenser is cooled using water. The temperature of the water is regulated by a water bath (E-6, Fig 6.2). The water flow is controlled by a needle valve in a bypass line (see detailed PFD in Figure 6.S2). More details about the other equipment is given in section 5.3.2.

6.2.3. Experimental method

Before each experiment the reactor is purged using the feed gas and subsequently the buffer vessel is pressurized with feed gas mixture. Next, the reactor is heated and pressurized up to the experimental conditions. The experiments are run in

Figure 6.1 | Schematic overview of the LOGIC reactor (E2 in Fig. 6.2). Important for discussion of the results are the locations of the temperature indicators of the catalyst in (TI-2), catalyst out (TI-3), condensor in (TI-5) and condensor out (TI-4). Note that the catalyst is randomly packed in reality.

Figure 6.2 | Process flow diagram of the setup. Equipment on the PFD: Buffer vessel (E-1), LOGIC reactor (E-2), Electric heater blocks (E-3), Fan (E-4) and cooling water bath (E-6). Indicators installed: Temperature indicators (TI-1 to TI-7), Pressure indicators (PI-1/PI-2), Flow indicator (FI-1) and differential Pressure indicator (dP-1).

semi-continuous mode. Gas will be fed continuously to keep the reactor pressure constant, as the reactor pressure decreases due to the reaction and condensation of the products. Liquid products are removed from the collection basket periodically. The time between samples is constant per experiment and depending on the production speed. The production speed can be foreseen by keeping track of the pressure of the buffer vessel. It is known that 2 bar of pressure drop in the buffer vessel means that the liquid basket is almost full. Productivity of the reactor is determined by the liquid production over time. Productivity is determined over minimal five liquid samples under steady state conditions.

6.2.4. Chemical analysis

Gas composition was determined using gas chromatography (Varian 450-RGA). The GC is equipped with three channels. Channel 1 analyses hydrogen using TCD detection on a Hayesep Q column (Agilent CP1305) and a Molsieve 5A column (Agilent CP1306) using N_2 as carrier gas. Channel 2 detects permanent gases using TCD detection on a Hayesep Q column (Varian CP1308), Hayesep N column (Varian CP1307) and a Molsieve 13X column (Varian CP1309) using helium as carrier gas. Channel 3 detects hydrocarbons using FID detection on a CP-Sil 5CB column (Varian CP1310) and a Select Al_2O_3 /MAPD column (Varian CP7433) using helium as carrier gas. The reactor is directly connected to the GC and the tubing between the GC and setup are flushed using N_2 between gas samples. Any N_2 detected is therefore considered to be purge gas and, if present, removed from the gas composition. Calibration of the GC is performed with gas mixtures from gas bottles containing predefined gas mixtures.

The liquid product was analysed in a HPLC (Agilent Technologies 1200 Series) using RID detection and GROM Resin H+ IEX column equipped with a pre-column. The injected volume was 10 μ L, the temperature 65°C and the mobile phase 5 mM H_2SO_4 at 0.6 mL min⁻¹. Calibration curves were obtained by injecting mixtures of known composition (Sigma Aldrich HPLC grade Methanol and milliQ ultrapure water) in the range of interest.

6.2.5. Error analysis and reproducibility

In the results section error bars are shown for the altered parameter and for productivity. The error in the altered parameter is represented by error bars and are two standard deviations (95% confidence interval) determined over the experimental steady state period. The error in productivity is composed of two errors. First, an experiment at $T_{cat,out} = 200^\circ C$, $T_{cond,out} = 100^\circ C$, $T_{cw,in} = 60^\circ C$ and $v_s = 0.019 \text{ m s}^{-1}$

Figure 6.3 | Schematic overview of the LOGIC reactor. The reactor internals are symbolized within the striped box.

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has been performed three times. The average value in productivity of these three experiments is found 14.0 ± 0.9 mmol/g_{cat}h. Second, the standard deviation of the measured productivity is taken into account. However, this standard deviation of the measured samples is usually small (about 0.2 mmol/g_{cat}h). The total error in productivity is the sum of the error in the triplet experiment and the error in the measured samples. The error in the superficial velocity is a result of error propagation of the standard deviation in the measured pressure drop.

6.3. Reactor model

Up to the start of this study the LOGIC reactor was a black-box as illustrated by the dashed box in Figure 6.3. Only, the amount of gas fed and liquid produced and four internal temperatures (see Figure 6.1) were measured. However, internal gas compositions and flows were unknown. In the experimental section, the changes to the setup to measure the internal gas flow and composition are discussed. By construction of a reactor model more insight into the dynamics and internal phenomena are acquired. The model consists of three main parts: (1) a fixed bed model for the catalyst section, (2) a condenser model calculating vapour liquid equilibria and (3) equations to calculate the recycle and feed flow. In the Figure 6.3 a schematic overview of the model is given. In the section below the model sections are discussed in more detail.

6.3.1. Reaction section

Three reactions are occurring in the system: equation (6.1) the CO₂ hydrogenation to methanol, equation (6.2) the CO hydrogenation to methanol and equation (6.3) the reverse water gas shift (RWGS) reaction. The most widely used equilibrium constants for the reactions are determined by Graaf et al. [143]. Recently, Graaf and Winkelman published a reassessment [144] using over 300 experimental data points of the equilibrium constants. The equilibrium constants are determined for equation (6.2) and (6.3). By combination of these two the equilibrium constants of equation (6.1) can be found. The recent values from Graaf and Winkelman [144] have been used in this study.

Methanol kinetics have been widely studied in literature. However, consensus about reaction pathways is not reached. Bozzano and Manenti [157] gave an overview of kinetics models in literature. The most widely used models are the kinetic rate equations of Graaf et al. [143, 159] and Bussche and Froment [149]. In recent work (see Appendix C) we critically analysed steady state kinetic models for methanol synthesis by re-evaluation on a set of 234 experiments. The 6-parameter model presented in Appendix C is used in this work, unless mentioned otherwise. Fugacities are applied to incorporate component partial pressures in the rate equations. Intra particle resistances are included by the effectiveness factor calculated by a Thiele modulus approach, as discussed by Lommerts et al. [205]. For more details see the Supporting Information section 6.7.3.

The catalyst section is modelled by a set of 2D-pseudo-homogeneous equations as shown in Table 6.1. Mass fractions are used to account for the change in the amount of moles during the reaction [206]. Radial dispersion is taken into account and calculated by the recommended equation in the review by Delgado [207]. The effective thermal conductivity of the combined gas and solid phase is calculated by a Zehner/Bauer/Schlunder type of equation [208] in which the thermal conductivity of both gas and solid phase, the effect of particle size, pressure and the heat transport by radiation and convection are included [208, 209]. More details about the radial dispersion coefficient and thermal conductivity can be found in the Supporting Information section 6.7.3. The equations in Table 6.1 are solved using the built-in Matlab function PDEPE. The outlet properties (temperature and mass fractions) of the reaction section are volume-averaged and used as input for the condenser section.

Table 6.1 | Catalyst section equations

Equations	
$\frac{\phi_m}{A_r} \frac{\partial w_i}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left(\rho_g D_r r \frac{\partial w_i}{\partial r} \right) + M_{w_i} \sum_{j=1}^2 v_{i,j} R_j$	(6.1.1)
$\frac{\phi_m}{A_r} C_{p_g} \frac{\partial T}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_r r \frac{\partial T}{\partial r} \right) + \sum_{j=1}^2 R_j \cdot \Delta_r H_j$	(6.1.2)
$R_j = \eta_j \rho_{\text{cat}} (1 - \epsilon_{\text{bed}}) r_j$	(6.1.3)
Boundary Conditions	
$T _{x,r=r_{\text{inner}}} = Y_1 \cdot T_{\text{cond,out}} + (1 - Y_1) T_{\text{cat,in}}$	(6.1.4)
$T _{x,r=r_{\text{outer}}} = Y_2 \cdot T_{\text{oven}}$	(6.1.5)
$\left. \frac{\partial w_i}{\partial x} \right _{x,r=r_{\text{inner}}} = \left. \frac{\partial w_i}{\partial x} \right _{x,r=r_{\text{outer}}} = 0$	(6.1.6)
$T _{x=0,r} = T_{\text{cat,in}}$	(6.1.7)
$w_i _{x=0,r} = w_{i,\text{cat,in}}$	(6.1.8)

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Figure 6.4 | Schematic overview of the catalyst section model including boundary conditions.

Table 6.2 | Condenser section equations

Differential equations	
$\phi_{V_{cw}} C_{P_{water}} \rho_{water} \frac{\partial T_{cw}}{\partial x} =$	(6.2.1)
$\alpha_g A_{tubes} (T_g - T_{cw}) + \alpha_{wall} \pi d_{cond} (T_{wall} - T_{cw})$	
$\frac{\partial U_g}{\partial x} = -\alpha_g A_{tubes} (T_g - T_{cw})$	(6.2.2)
Constant enthalpy equilibrium flash	
$y_i \Phi_{V_i} = x_i \Phi_{L_i}$	(6.2.3)-(6.2.7)
$\underbrace{\chi_{EQ} y_{i-1}}_{\text{Gas out}} + \underbrace{(1 - \chi_{EQ}) x_{i-1}}_{\text{Liquid out}} = \underbrace{\chi_0 y_{0_{i-1}}}_{\text{Gas in}} + \underbrace{(1 - \chi_0) x_{0_{i-1}}}_{\text{Liquid in}}$	(6.2.8)-(6.2.11)
$\sum_{i=1}^{N_c} y_i = 1, \sum_{i=1}^{N_c} x_i = 1$	(6.2.12), (6.2.13)
$U_g + P \phi_V = h_g(T_g) \phi_{N,g} + h_l(T_g) \phi_{N,l}$	(6.2.14)
Boundary Conditions	
$T_{cw} _{x=0} = T_{cw,in}$	(6.2.15)
$U_g _{x=0} = h_f(T_{cond,in}) \phi_{N,in} - P \phi_{V,in}$	(6.2.16)

Figure 6.5 | Schematic overview of the condenser model including boundary conditions.

6.3.2. Condenser section

The condenser section is modelled by a combined differential enthalpy balance and a constant enthalpy equilibrium flash at every differential position [210]. The set of equations and boundary conditions are shown in Table 6.2. The condenser is modelled as a co-current heat exchanger between the gas phase and cooling water. However, in reality the condenser is partially co-current and counter-current. The differential equations 6.2.1-2 are solved using a forward-Euler discretization algorithm.

The gas and liquid compositions at every differential position are assumed to be in phase equilibrium at the current temperature and pressure. The Vapour Liquid Equilibria (VLE) are calculated using the fugacities by the Soave-Redlich-Kwong (SRK) Equation of State (EoS) as described by van Bennekom et al.[201]. Because of the presence of polar components a polarity correction parameter [202] is used. Enthalpies of the streams are calculated using the standard enthalpy of formation and the gas phase heat capacity. Included is the enthalpy correction calculated by the Equation of State [211]. For detailed equations see Appendix A.4.

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The flash calculation has, in our case, twelve unknowns. That is, the gas phase composition (5 unknowns), the liquid phase composition (5 unknowns), the vapour fraction and the gas temperature. These unknowns are solved by twelve equations as shown in Table 6.2. Setting the gas fugacity to the liquid fugacity gives five equations (eq. 6.2.3-7). The mass balance per component (n-1) gives four equations (eq. 6.2.8-11). The mass balance of the fifth component is determined indirectly by the two equations summing the gas and liquid fractions to unity (eq. 6.2.12-13). Finally, the gas temperature is found by solving the internal energy balance (eq. 6.2.14). The flash equations are solved using the `fmincon` function in MATLAB.

The gas to cooling tube heat transfer coefficient α_g is determined by a Nusselt correlation for cross flow over a tube bundle. The wall to cooling water heat transfer coefficient α_{wall} is fitted to a constant value of 255 W m⁻² K⁻² for all experiments. The volume flow is determined by the gas density calculated by the equation of state.

6.3.3. Gas flow

The internal gas flow rate is determined by the pressure drop over the catalyst section as discussed in section 6.2.2. The pressure drop over the catalyst section is converted to a gas velocity by the Stokes-Ergun composite solution [212]. In Figure 6.6 the importance of using the composite solution compared to the normally used Ergun equation is shown. The pressure drop in Figure 6.6 is calculated using

Figure 6.6 | Pressure drop versus superficial flow rate over the stainless steel particles. Composition and properties for catalyst out temperature of 200 °C. The composition is [CO₂, CO, H₂, CH₃OH, H₂O] = [0.626, 0.125, 0.107, 0.110, 0.032] in mass fraction.

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the conditions of a typical experiment. In our experiments, Reynolds numbers of 1-200 have been seen. Thereby, using the Ergun equation only would give a significant under-prediction of the velocity as shown in Figure 6.6. For the velocity calculation, it is assumed that the pressure drop is fully generated by the stainless steel particles while pressure drop over the catalyst particles is negligible. Detailed equations are given in Supporting Information section 6.7.3.

The amount of feed gas flow is controlled by the pressure controller in the experiments. In the model a PID-type of control loop ensures a constant pressure by changing the feed gas flow rate of the model while ensuring numerical stability. For this, the number moles in the reactor are evaluated at the conditions of the catalyst outlet. The composition after the mixing point is based on the mass averaged composition of the condenser and feed gas. In section 6.7.3 of the Supporting Information more detailed equations are shown.

6.3.4. Energy analysis

For analysis of the energy efficiency of the reactor concept, the heat flows involved are calculated. The heat analysis is performed using enthalpy balances. In Figure 6.7 the definitions of the enthalpies are shown. The equations to determine the

heat flows are summarized in Table 6.3. The condenser outlet temperature and catalyst inlet are controlled parameters and are therefore known. The required heating of the feed gas and recycle gas from the condenser is shown by equations 6.3.1 and 6.3.3. In the heat analysis, the reactor is assumed to operate adiabatically and thereby the catalyst outlet temperature can be calculated by the standard reaction heat. For analysis purposes, the gases are cooled to the condenser outlet temperature in a virtual cooler. For the cooler duty, only the sensible heat of the gas is included and latent heat is extracted in the condenser completely. In reality, the cooler and condenser are combined into one piece of equipment.

When the heat exchanger is evaluated, the duty of the heat exchanger is assumed equal to the heater duty of the recycle gas. Since the catalyst outlet temperature is known because of adiabatic operation, the condenser inlet temperature can be calculated based on the heat exchanger duty, see equation 6.3.6. The condenser duty will include both the sensible and latent heat of the gas stream out of the heat exchanger.

6.3.5. Material properties

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In the model the gas phase density is determined by the mSRK Equation of State by the molar volume. The liquid density is calculated by the COSTALD method [213]. Note that, for correct prediction of the liquid density, the polarity correction factor ω for water is – only for liquid density calculations – taken from Hankinson and Thomson [213] instead of van Bennekom et al [201]. The enthalpy of the mixture is determined by the mSRK equation of state [211]. The pure component standard enthalpies are taken from Gmehling [214]. The heat capacities are determined by Shomate equations for which the constants are taken from Gmehling [214] for the liquid phase and from Yaws [215] for the gas phase.

The material properties for the mixed components are determined by mixing rules. The mixed viscosity [189, 216] and thermal conductivity [217] are determined by semi-empirical equations. The pure components are taken from NIST Webbook [218] for the conditions at 200°C and 50 bar. More details are given in Supporting Information section A.3.

6.3.6. Validation of model sections

The two fundamental building blocks of the reactor model – the kinetics of methanol synthesis and the equation of state – have been validated against experimental data.

The kinetic models for methanol synthesis by Graaf et al. [159] and Bussche and

Figure 6.7 | Schematic overview of enthalpies for heat flow analysis of the LOGIC reactor. Proposed heat exchange between gas from the condenser and catalyst section is shown by the dashed line.

Table 6.3 | Equations for heat analysis

Heat analysis	
$Q_{\text{feed}} = \Phi_{\text{m},\text{in}} (h_2 - h_1)$	(6.3.1)
$Q_{\text{reaction}} = \sum (\Phi_{\text{m},i} \Delta_r H_i)$	(6.3.2)
$Q_{\text{heater}} = (\Phi_{\text{m}} - \Phi_{\text{m},\text{in}}) (h_7 - h_6)$	(6.3.3)
$Q_{\text{cooler}} = (\Phi_{\text{m}} - \Phi_{\text{m},\text{in}}) (h_{4b} - h_3)$	(6.3.4)
$Q_{\text{cond}} = ((\Phi_{\text{m}} - \Phi_{\text{m},\text{in}}) h_6 + \Phi_{\text{m},\text{in}} h_5) - \Phi_{\text{m}} h_{4b}$	(6.3.5)
$h_{4a} = h_3 + \frac{Q_{\text{hex}}}{\Phi_{\text{m}}}$	(6.3.6)
$Q_{\text{cond,hex}} = ((\Phi_{\text{m}} - \Phi_{\text{m},\text{in}}) h_6 + \Phi_{\text{m},\text{in}} h_5) - \Phi_{\text{m}} h_{4a}$	(6.3.7)

Froment [149] have analysed in Appendix C. A set of 234 experiments have been used to refit the parameters of the model. A new kinetic model is developed to fulfil recent physical evidence in literature and reduce over-parametrisation of rate equations. The predictions of the new kinetic model (Slotboom et al, Appendix C) and the models of Graaf et al. [143] and Bussche and Froment [149] with refitted parameters are shown in Figure 6.8.

The experiments shown in Figure 6.8 are performed in a separate single-pass fixed bed setup. It is seen that prediction by the Slotboom et al. model has good agreement with the experiments for both, conversion and selectivity. The prediction of the refitted models of Graaf et al. and Bussche and Froment have slightly worse agreement with experimental data. The accuracy of prediction for all models is sufficient for engineering purposes. The Slotboom et al. kinetic model has been selected to be used in the rest of this chapter, unless mentioned otherwise. For more details about the methanol kinetics the reader is referred to Appendix C.

The Vapour-Liquid Equilibria (VLE) diagram for methanol-water is calculated and validated on experimental data of Gmehling et al.[219] in Figure 6.9. It is shown that for all temperatures the prediction of VLE is in good agreement with experimental data. Consequently this validates the correct implementation of the Soave-Redlich-Kwong (SRK) Equation of State (EoS) as described by van Bennekom et al. [201]. In Figures 6.S3 and 6.S4 in the Supporting Information the VLE diagrams of methanol-water at higher temperatures and methanol-hydrogen are shown. Both figures show good agreement of prediction by the equation of state and experiments.

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6.3.7. Parameter overview

An overview of the model parameters is given in Table 6.4. For the catalyst section, the boundary conditions including the values used in the base model are given. The values of Y_1 and Y_2 will be changed in a sensitivity study in section 6.4.4. For the condenser section, the inlet gas temperature is taken from the experiment and the outlet temperature is calculated. The cooling water flow is regulated to match the model and experimental value of the condenser water outlet temperature. The direct heat transfer by radiation from the oven to the cooling water is included by the α_{wall} parameter.

Figure 6.8 | CO_2 conversion and methanol selectivity as function of the reaction temperature. Single pass fixed bed experiments (spheres) at $P=40$ bar, $\text{GHSV} = 3032 \text{ h}^{-1}$ and $\text{CO}_2:\text{H}_2$ ratio = 1:3. Lines show the equilibrium by Graaf and Winkelman [144] (dash) and the prediction by the (re)fitted kinetic models of Slotboom et al. (solid), Graaf et al. (dash-dot) and Bussche and Froment (short-dash).

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Figure 6.9 | VLE diagram of methanol - water for 333K, 373K and 423K. Symbols are experimental data by Gmehling et al. [219] and lines the SRK EoS predication with parameters of van Bennekom et al.[201].

Table 6.4 | Overview of the parameters for the model and values of the base model.

Variable		Base Model
$T_{\text{cat,in}}$	Experiment	
$T_{\text{cat,out}}$	Calculated	
T_{oven}	Experiment	
$T _{x,r=r_{\text{inner}}}$	Assumption ($Y_1 T_{\text{cond,out}} + (1 - Y_1) T_{\text{cat,in}}$)	$Y_1=0.5$
$T _{x,r=r_{\text{outer}}}$	Calculated, fitted ($Y_2 T_{\text{oven}}$)	$Y_2=0.92$
$T_{\text{cond,in}}$	Experiment	
$T_{\text{cond,out}}$	Calculated	
T_{wall}	Assumption ($Y_3 T_{\text{oven}} + (1 - Y_3) T_{\text{cond,in}}$)	$Y_3=0.5$
$T_{\text{cw,in}}$	Experiment	
$T_{\text{cw,out}}$	Experiment	
$\phi_{V_{\text{cw}}}$	Calculated, fitted (α_{wall})	$\alpha_{\text{wall}} = 255 \text{ W m}^{-2} \text{ K}^{-1}$
v_s	Experiment	$v_s = 0.019 \text{ m s}^{-1}$

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6.4. Results and discussion

6.4.1. Catalyst temperature

The reactor productivity as a function of the catalyst temperature is shown in Figure 6.10. The experiments have been performed by increasing the catalyst outlet gas temperature from 180°C to 240 °C by steps of 10°C. The catalyst outlet temperature is increased by increasing the oven temperature. The condenser outlet temperature is regulated at a constant value of 100°C by changing the cooling water flow. The productivity in Figure 6.10 is plotted as function of the catalyst inlet temperature because the calculated catalyst outlet temperature does not necessarily match with the experimental value.

Because of increased reaction kinetics with temperature, an increase in reactor productivity is seen with temperature. However, an optimum in productivity can be identified in Figure 6.10. The equilibrium conversion at high temperatures is lower, thereby reducing methanol production. At the same time, increased reaction kinetics at high temperature ensure equilibrium is reached faster. Moreover, the selectivity of the CO₂ conversion reaction is shifting from methanol to CO at high temperature. Thereby, the fraction of methanol in the outlet gas is reduced. Consequently, at constant condenser temperature the portion of methanol condensed is lower. As a result the reactor productivity is reduced. It can be con-

cluded that productivity is increased initially, due to improved reaction kinetics. At higher temperature, limitations by equilibrium and loss in selectivity reduce productivity.

The line of the base model in Figure 6.10 shows that the trend in productivity is predicted in reasonable agreement with the experimental data. Increase in productivity by increased kinetics and reduction in productivity due to equilibrium limitations are predicted correctly. However, the absolute numbers do not match with experiments. While at low catalyst temperature, the productivity is under-predicted by the model, at high temperature the productivity is over-predicted. This indicates that the local temperatures as calculated by the model are not correct. When the volume-averaged outlet temperature of the model is compared with the measured gas temperature this hypothesis is confirmed. It is seen that the model calculates too low gas temperatures for the first three experiments, while for the last four experiments the temperature have been calculated too high. To conclude, the temperature in the catalyst zone is not predicted correctly. To speculate, the factor (Y_2) – determining the outer wall temperature – might be an function of the oven temperature.

At first sight, the catalyst temperature seems low enough ($<230^\circ\text{C}$) to ignore intraparticle mass transfer. However, a clear increase in reactor productivity is seen in Figure 6.10 by assuming an effectiveness factor of unity. A closer look into the reactor temperatures reveal that significant higher temperatures are present in the catalyst bed. While the experimental gas temperatures are relatively low ($<240^\circ\text{C}$), the oven temperature is significantly higher ($>260^\circ\text{C}$). This results in a high outer wall ($r=0.024\text{m}$) temperature, as shown in Figure 6.11 for a typical experiment. For this reason, close to the outer wall kinetics are fast and diffusion inside the particle limits overall production rates.

Moreover, in Figure 6.11 it can be seen that the temperature of the inner wall ($r=0.012\text{m}$) is low because of cold gas returning from the condenser. As a consequence, part of the catalyst bed is inactive in the methanol synthesis. Because of the hot outer wall and cold inner wall a strong radial temperature gradient is present in the catalyst section. Although, the gradient is predicted steep due to the assumptions for the boundary values, in reality the gradient might be less steep. Due to radiative heat the inner wall might have a higher temperature and heat transfer between the oven and reactor might be worse, resulting in a lower outer wall temperature. Consequently, the temperature gradient will be less steep. The temperature gradient makes optimization of the catalyst temperature difficult, as either the outside wall is too hot or the inside wall too cold. Therefore, such a temperature gradient should be prevented in a next generation reactor. Increasing

Figure 6.10 | Productivity as a function of the catalyst inlet temperature. (Catalyst outlet temperature varies between model and experiments). The effect of intra-particle mass transfer resistance is shown by the effectiveness factor. Lines are added for guidance of the eye. Experimental conditions: $T_{\text{cond,out}} = 100^\circ\text{C}$, $T_{\text{cw,in}} = 60^\circ\text{C}$, average $v_s = 0.019\text{ m s}^{-1}$.

Figure 6.11 | Typical radial temperature profiles in catalyst section at different axial positions.

$T_{\text{cat,in}} = 165.4^\circ\text{C}$, $T_{\text{oven}} = 298^\circ\text{C}$, $T_{\text{cat,out}} = 201^\circ\text{C}$, $T_{\text{cond,in}} = 158^\circ\text{C}$, $T_{\text{cond,out}} = 100^\circ\text{C}$, average $v_s = 0.019\text{ m s}^{-1}$

Figure 6.12 | Typical axial temperature profile in the condenser for low and high velocity experiment. $T_{\text{cat,in}} = 165^\circ\text{C}$, $T_{\text{oven}} = 298^\circ\text{C}$, $T_{\text{cat,out}} = 201^\circ\text{C}$, $T_{\text{cond,in}} = 158^\circ\text{C}$, $T_{\text{cond,out}} = 100^\circ\text{C}$, average $v_s = 0.019\text{ m s}^{-1}$

the radial heat transfer rate by a highly heat conductive catalyst material [203, 220] might be a solution. Another improvement could be raising the temperature of the returning nonconverted gases from the condenser, consequently raising the temperature of the inner wall. Heat exchange between hot gases leaving the catalyst section and cold gases returning from the condenser could be an effective way of increasing the inner wall temperature. This heat exchange concept is further discussed in section 6.5.2.

6.4.2. Condenser temperature

Initially, the effect of the condenser outlet temperature was measured by changing the cooling water flow and temperature, while keeping the measured gas outlet temperature of the catalyst constant. However, at a cooling water temperature of 75°C the oven temperature needed to be increased to maintain a constant measured catalyst outlet temperature. In Figure 6.13 is shown that the increase in oven temperature had a strong effect on the productivity of the reactor. Therefore, the experimental points with increased oven temperature have also been remeasured with a constant oven temperature, consequently reducing catalyst outlet gas temperature. In Figure 6.13 the productivity is plotted against the cooling water outlet temperature as it enables comparing experimental and model values. The gas condenser outlet temperature differs significantly between experimental and model values, which will be discussed in more detail below.

The effect of the condenser temperature on the reactor productivity is shown in Figure 6.13. With a reduced condenser temperature the productivity of the reactor is increased because a larger fraction of methanol is condensed. For the constant oven temperature series the productivity levels around $16 \text{ mmol g}^{-1} \text{ h}^{-1}$, at low condenser temperature. This indicates that the maximum production rate – limited by kinetics – in the catalyst section is reached, as condensing more methanol does not increase productivity. For the current design, the productivity levels off for condenser temperatures below 80°C, although by increasing the length of the catalyst bed this point will be found at a lower condenser temperature. Limitations by kinetics are also confirmed by the series with increased oven temperature. Due to increased catalyst temperature the kinetics increase and the reactor productivity increases significantly.

When looking at the temperature profile in the condenser in Figure 6.12 it is seen that the cooling capacity is not limiting productivity. For the low flow experiment, at one third of the condenser length the final gas temperature is already reached. This indicates that, in the current experimental reactor the condenser section is not limiting production, since more cooling capacity is available. Note that the

gas is reheated by the direct radiative heat from the oven to the condenser. Due to the assumptions made for the condenser model (i.e. all the radiative heat by the oven is directly adsorbed by the water) the gas and water temperature cross, although being modelled as co-current heat exchange. Moreover, it is shown that the condenser gas outlet temperature is lower than the experimental measured gas temperature (100°C). As discussed in the experimental section, this is a result of the location of the thermocouple. The thermocouple (TI-4, Fig.6.1) is not located directly at the condenser outlet. Consequently, the gas might already be reheated – due to radiative heat from the oven – at the point of measuring in the experimental setup.

The model predicts the trend in experimental data with fair agreement in Figure 6.13, although absolute values do not match for the whole range of condenser temperatures. For both series, the slope of the model line is larger than for the experimental data. Comparing experimental and model temperatures, it was found that the catalyst outlet temperature is higher than the experimental temperatures for all points. The difference between experimental and model values decreases with increasing cooling water temperature. At the same time, the predicted condenser outlet gas temperature by the model is lower than the experimental value for all points. Again, the difference in model and experimental values decreases with increasing cooling water flow. Therefore, it is not possible to pin-point the error in temperature prediction to one section of the model, based on this experimental series.

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6.4.3. Internal flow

The gas flow rate in the reactor has been changed by the rotational speed of the fan at the bottom the reactor. The effect of flow rate on the reactor productivity can be seen in Figure 6.14. In line with results from the previous chapter (Figure 5.8) the productivity reduces at higher flow rates. This is mainly an effect of reduction in catalyst inlet temperature at higher velocity. The reduction in inlet temperature results in a lower average temperature of the catalyst section. Due to reduced kinetics, the production of methanol is lower.

The strong decrease in catalyst inlet temperature by increased flow is a results of the design of the experimental setup. Since no heat exchanger is included in the reactor, no effective means of reheating the gas from the condenser before entering the catalyst section is present. However, when installing a heat exchanger in a next generation reactor, heat transfer will be function of gas flow rate. Therefore, even in a reactor with more effective heat transfer, the catalyst inlet temperature might be a function of gas flow rate. Hence, during design of a next generation

Figure 6.13 | Productivity as a function of the condenser temperature with constant oven temperature. The effect of increasing the oven temperature to maintain a constant measured catalyst outlet temperature is shown by the gray series. Experimental conditions: $T_{cat,out} = 200^{\circ}C$, $T_{cw,in} = 60^{\circ}C$, $T_{cw,in} = 60^{\circ}C$.

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Figure 6.14 | The effect of superficial velocity over the catalyst bed on the productivity. Experimental conditions: $T_{cat,out} = 200^{\circ}C$, $T_{cond,out} = 100^{\circ}C$, $T_{cw,in} = 60^{\circ}C$.

reactor a broad range of flow rates should be investigated.

Moreover, by an increase of velocity the residence time in the catalyst and condenser is reduced. This might lead to reduced conversion in the catalyst section, especially in combination with lower temperatures due to increased flow. Of course, also the residence time in the condenser is decreased. However, as shown for the high velocity in Figure 6.12 the experimental cooling rate in the condenser is still sufficient.

Increase in heat transfer rate during experiments by increasing velocity is seen by the oven temperature required to maintain the same experimental catalyst outlet temperature. At high gas flow rate the oven temperature had to be reduced, which is unexpected since more power is required because of the higher flow rate.

The trend in model predictions is in agreement with experimental data. However, the absolute values predicted by the model are lower than the experimental productivity. Once again, the prediction of the temperature profile in the catalyst seems to raise an error. While the experimental catalyst outlet temperature is kept constant at 200°C, the model predicts volume-averaged catalyst outlet temperatures from 228°C at the lowest flow to 176°C at the highest flow. A more thorough description of heat transfer is required to match the absolute values for the productivity.

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6.4.4. Sensitivity study

From the section above it can be concluded that the predicted productivity by the model is strongly correlated with the temperature profile in the catalyst zone. Therefore, a sensitivity study is performed on the assumption of both wall boundary conditions.

The effect of the temperature of the inner wall of the catalyst section can be seen in Figure 6.15. With a lower temperature the productivity is decreased and with a higher temperature the productivity is increased. However, although not clearly visible in the graph, also the slope of the lines changes. Compared to base model line, the slope increases (+16%) when the wall is hotter and reduces (-9%) when the wall is colder. The slope of the line for the lowest temperature is closest to the experimental value (-50%, compared to base model), although the absolute values do not match. For this reason, the inner wall temperature is not reduced in the model despite having a better prediction of the trend. The sensitivity on the catalyst outer wall shows the same trends. Lower temperature leads to lower productivity and higher temperatures to higher productivity. Again, the slope of the lines changes ($\pm 7\%$) with temperature of the outer wall.

A sensitivity of the condenser water outlet temperature is performed. Effectively this is a sensitivity on the condenser outlet gas temperature as the gas and water temperatures are (almost) at equilibrium. In Figure 6.17 is shown that changing the condenser temperature leads to a shift in productivity. The trend in model prediction however remains the same. Consequently, if productivity is matched at low catalyst temperature, the mismatch at higher temperature becomes larger. Therefore, it can be concluded that changing the water outlet temperature will not improve the model predication.

However, also a model run was performed where the condenser was flashed at the experimental condenser outlet gas temperature. In this run no detailed condenser model is used but only a phase equilibrium flash calculation is performed. As shown by the fourth line in Figure 6.17 the trend for this run is in better agreement with the experiments. However, again the absolute values do not match the experiments. This might be a results of the location of the thermocouple as discussed above. A match of absolute values might be found when a temperature difference between the experimental gas temperature and the flash temperature is applied.

The productivity predicted by the (re)fitted kinetic models of Slotboom et al. [6-parameter, Appendix C], Graaf et al.[143] and Bussche and Froment [149] are shown in Figure 6.18. The predicted productivity by different kinetic models varies up to 50% between the models, despite reasonable consistent results in describing kinetic experiments, as shown in Figure 6.8 and Appendix C. The residence time in the catalyst section is a major difference in conditions in the LOGIC reactor (GHSV 20,000 to 150,000) and in the kinetics study (GHSV 2,000 to 10,000). While in the LOGIC reactor model the initial reaction rate is important, the kinetics fitted might present a kinetic rate averaged over a longer residence time.

6.4.5. Summary

Experimental results show that an optimum in productivity can be found when increasing the catalyst temperature. Advantageous are increased kinetics at higher temperatures, but equilibrium limitations limit productivity. Lower condenser temperatures increase productivity, although for the current reactor design, below 80°C the experimental productivity is limited by the methanol production rate in the catalyst section. Depending on catalyst bed and condenser dimensions other optimal temperatures might be found. At increased flow rate, productivity is reduced because of reduction in catalyst inlet temperature. This shows the importance of considering heat exchange during design. By heat exchange, the catalyst inlet temperature can be increased and consequently productivity is increased.

Figure 6.15 | Sensitivity on catalyst inner wall temperature ($T_{w,i}$).

Figure 6.16 | Sensitivity on catalyst outer wall temperature ($T_{w,o}$).

Figure 6.17 | Sensitivity on condenser temperature (T_{cw} =cooling water temperature). Note that the fourth line is flashed at the experimental gas temperature.

Figure 6.18 | Sensitivity on the kinetic models by Slotboom [App.C], Graaf et al. [143] and Bussche and Froment [149].

The model is able to predict the trends in experimental data correctly. However, matching absolute values is difficult because of the description of the temperature gradient in the catalyst section. Moreover, the sensitivity study showed that the prediction of the absolute numbers is strongly related to the assumptions made. In particular, the quality of the kinetic model was found to be of great importance.

6.5. Concept Optimization

The LOGIC reactor will be further analysed under forced convection conditions in the section below. In the previous section, it is confirmed that the reactor model describes trends in productivity correctly. The radial temperature gradient complicates analysis and should be avoided in a next version of the reactor. Therefore, for further analysis and concept optimization, a simpler approach is taken. The reactor is modelled as an 1D-fixed bed reactor, either isothermal or adiabatic. The dimensions of the catalyst section are kept equal to the one in the current experimental setup. The condenser will be modelled by a phase equilibrium flash at a certain temperature. In this way, the reactor concept can be analysed independent of limitations in the current experimental setup.

6.5.1. Operating conditions

Operating the catalyst section adiabatic or isothermal has an effect on the optimal catalyst inlet temperature, as shown in Figure 6.19. For isothermal operation the optimal productivity is reached for catalyst inlet temperatures between 250 and 270°C, depending on the condenser temperature. The amount of methanol in the catalyst inlet is dependent on the condenser temperature, therefore the equilibrium conversion will change with the condenser temperature. While operating adiabatically, the highest productivity is reached for inlet temperatures between 210 and 240°C. The productivity reaches a maximum at different inlet temperatures because of accumulation of the reaction heat when operating adiabatically. Therefore, the difference between adiabatic and isothermal operation is smaller at a condenser temperature of 100°C, because less reaction heat is released at a lower conversion.

Lower productivity at high condenser temperatures is also seen in Figure 6.20. Moreover, at low catalyst inlet temperatures the productivity is limited because of slow kinetics at all condenser temperatures. The productivity at high catalyst inlet temperature levels off at low condenser temperature because the system is limited in the catalyst section. Condensation of a larger fraction of the methanol does not increase productivity because the maximum production is achieved in the cata-

Figure 6.19 | Productivity for an adiabatic and isothermal 1D-reactor model with phase equilibrium flash as condenser model given as a function of the catalyst inlet temperature for three different condenser temperatures. $P=50\text{bar}$ and $v_s = 0.019\text{m s}^{-1}$

Figure 6.20 | Productivity as a function of condenser temperature for an adiabatic 1D-reactor model for five catalyst inlet temperatures. $P=50\text{bar}$ and $v_s = 0.019\text{m s}^{-1}$. Symbols added to increase distinction between lines.

Figure 6.21 | Single pass conversion over the catalyst bed as a function of the catalyst inlet temperature, for two condenser temperatures. $P=50\text{bar}$ and $v_s = 0.019\text{m s}^{-1}$

Figure 6.22 | Heat flows as function of the condenser temperature. $P=50\text{bar}$, $T_{\text{cat,in}} = 240^\circ\text{C}$ and $v_s = 0.019\text{m s}^{-1}$. Symbols added to increase distinction between lines.

lyst section already. The condenser temperature at which the production levels off, depends on the dimensions of the catalyst bed. At constant conditions, with an increase in residence time in the catalyst section the conversion will be higher and a lower condenser temperature is required to condensate all methanol. Therefore, productivity will increase with longer residence time in the catalyst section and lower condenser temperature, as long as the equilibrium conversion is not reached.

Overall, it can be concluded that, when operating adiabatically and for the current dimensions of the catalyst section, at 50 bar a catalyst inlet temperature of 230-250°C combined with an condenser temperature below 70°C ensures optimal productivity. Moreover, it is seen that high catalyst outlet temperatures limit productivity in the reactor. Therefore, (partial) removal of the reaction heat from the catalyst bed might be beneficial for productivity of the reactor.

6.5.2. Conversion and heat flows

The per pass and equilibrium conversion as a function of catalyst inlet temperature for adiabatic operation are shown in Figure 6.21. The equilibrium conversion is evaluated at the catalyst outlet temperature. It is seen that with lower condenser temperature the equilibrium conversion is increased. Since more methanol is condensed at lower condenser temperature, a larger equilibrium conversion can be achieved. Moreover, it is seen that – for the current experimental catalyst bed dimensions – the equilibrium conversion is reached between 250 and 260°C. The selectivity to methanol is, at steady state, above 99.7% for all temperatures. Selectivity loss to CO is only a result of CO dissolved in the condensate. Increasing residence time in the catalyst section would further enhance conversion per pass, if not limited by equilibrium. Increasing conversion per pass over the catalyst, would decrease heat exchange and cooler duty because of reduced recycle ratio. Therefore, increasing the dimensions of the catalyst section (and increase conversion pass) would reduced the dimensions of the heat exchange and condenser section. Therefore, the operating conditions could be optimized by considering the combined dimensions of heat exchanger and catalyst section and optimize total reactor dimensions.

The heat flows, as defined in section 6.3.4, in the reactor as function of the condenser outlet temperature are shown in Figure 6.22 for a simulation at a catalyst inlet temperature of 240°C. The amount of heat required to reheat the gas from the condenser to the catalyst inlet temperature is shown by the heater line. Because the heater duty is significantly larger than the reaction heat (1.5MJ kg^{-1}), without heat exchange an external heater is required to keep the system running. How-

ever, since the reaction is exothermal, this not an preferred situation and would be unnecessary use of energy. Therefore, adding an heat exchanger to exchange heat between hot gas from the catalyst section and cold gas from the condenser is required.

It is seen that for all temperatures the cooler duty is larger than the heater duty. This shows that – in theory – heat exchange is possible for all condenser temperatures. Analysing the temperature approach of the proposed heat exchanger it is seen that a condenser temperature of maximal 100°C can be used. Thereby, a minimal temperature approach – that is the difference between catalyst inlet and outlet temperature – in the heat exchanger of 10°C is ensured. However, when operating at 70°C the difference between catalyst inlet and outlet temperature is already more than 30°C. Therefore, it is expected that the heat exchanger can operate efficiently inside the reactor.

Looking at the heat flows in Figure 6.22 it can be seen that the required heat exchanger duty per kilogram of methanol stabilizes below 70°C. For condenser temperatures above 70°C the single pass conversion decreases significantly, thereby increasing recycle ratios and heat exchanger duties. Therefore, it is advised to operate at condenser temperatures below 70°C to prevent unreasonable large heat exchange areas. Moreover, the duty of the heat exchanger and condenser are in the same order of magnitude. Accordingly, it is not expected that adding a heat exchanger would increase reactor dimensions excessively.

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Further heat integration in the reactor can be performed by integration of the feed heater. As shown in Figure 6.22, below 70°C, the difference between the heater and cooler duty is larger than the feed heater duty. This shows that the cooler duty is large enough to heat the recycle gas and the fresh feed. Combining both heaters can easily be done by feeding the feed stream after the condenser but before the heat exchanger and would only increase the required area for heat exchange.

Using both opportunities for heat exchange it is clear that the reactor concept can operate without external heat input. Only during start-up external heat input might be required to start the reaction. For optimal heat exchange areas, condenser temperatures below 70 °C are required. Optimization of dimensions of the catalyst section and heat exchanger can be done by tuning the catalyst inlet temperature and conversion per pass.

Figure 6.23 | Illustrations on the effect of heat exchange on natural convection flow. Catalyst section in left bottom and condenser in right top. red=high temperature, blue=low temperature, orange=medium temperature.

6.5.3. Natural convection

In the two subsections above the LOGIC concept is evaluated under forced convective conditions. However, ideally the reactor is operated under natural convection conditions. Thereby, the need for moving parts in the reactor is absent, significantly reducing complexity of reactor construction. Moreover, no external recycle loop is required thereby saving on opex and capex for a recycle compressor.

However, implementing heat exchange, as discussed in the section above, would affect the driving force for gas circulation flow under natural convection. When the average temperature in the reactor increases, the difference in density between the cold and hot tubes in the reactor will become smaller. In Figure 6.23A the situation without heat exchange is shown. The tube above the catalyst section is at high temperature and low density, while the tube below the condenser is at low temperature and high density. In this situation the driving force for natural convection is at its maximum.

When heat exchange is applied between the up and down going gases directly, the average temperature in the hot tube will become lower. At the same time, the temperature in the cold tube becomes higher. This situation is illustrated in Figure 6.23B. Because, the average density in hot tube is increased, while the density in the cold tube is decreased, the driving force for natural convection will be re-

duced. Therefore, the flow rate will be lower compared to the situation without heat exchange. Depending on the amount of heat exchange, the flow by natural convection can become minimal. Moreover, additional pressure drop by the heat exchanger will decrease flow further.

Therefore, heat exchange should be performed carefully without losing the driving force for natural convection and without excessive heat exchange area. One solution can be to apply heat exchange in the horizontal section between the tubes. This method is illustrated in Figure 6.23C as external heat exchange. In this way the driving force for natural convection is similar to the situation without heat exchange. However, the flow will be lower because of the increase in pressure drop due to the heat exchange area required. A disadvantage of this method is the need for an external heat transport medium. To design and optimize a reactor performing with the combination of heat exchange and flow by natural convection more research is needed. Especially, more research on the effect of heat exchange and design of the heat transfer method on natural convection flow is required.

6.5.4. Other design considerations

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Since only gas is fed to the reactor and only liquid is removed, any gaseous inert will build up in the reactor. Therefore, gaseous inerts should be removed upstream of the reactor. If the inert is condensable, it might be fed to the reactor. In this case the inert will condense and leave the reactor with the condensate product. It should then be removed from the condensate downstream of the reactor. If any gaseous impurity is accumulating a (periodic) small gas purge will solve the issue.

Co-feeding of carbon monoxide is not a problem for the reactor concept. As long as the stoichiometric number of the reactor feed is met, both CO and CO₂ will be fully converted to methanol. Of course, during design the composition of the feed should be taken into account. For example, increasing CO content in the feed will increase equilibrium conversion in the catalyst section. Also the dew point of the mixture is influenced because of the reduction of the water content in the gas.

Another issue is the significant higher solubility of CO₂ in the condensate compared to H₂. Therefore, more CO₂ leaves reactor by the condensate, when compared to H₂. Consequently, stoichiometry in the reactor is shifted and some build up of hydrogen will occur. A solution is to feed slightly more CO₂ to the reactor than required by stoichiometry to compensate for CO₂ losses through the condensate. A method to recover the CO₂ from the condensate might be stripping with the hydrogen feed [221].

6.6. Conclusion

A model has been developed to describe the current experimental LOGIC reactor with gas circulation between a catalyst and condenser section. Experimental results show that an optimum in productivity can be found with increasing the catalyst temperature. Advantageous are increased kinetics at higher temperatures but equilibrium limitations may limit productivity. It should be noted that, although in the current experimental setup the catalyst temperature can be controlled, in a proposed autothermal concept only the condenser temperature can be controlled and the catalyst temperature is a result of heat exchange. Lower condenser temperatures increase productivity, although below 80°C the experimental productivity is limited by the methanol production rate in the catalyst section. At increased flow rate, the reactor productivity is reduced because of lower average catalyst temperature. This effect can be reduced by sufficient heat exchange in a next generation design.

The model is able to predict the trend in experimental data correctly. However, matching absolute numbers of productivity needs refinement of the model. By modelling it was found that a radial temperature gradient is present in the catalyst section, complicating optimization and leaving scope for design improvements. A sensitivity study showed that the prediction of absolute numbers strongly depends on the assumptions for temperature boundary conditions and kinetic model chosen.

Further analysis of the LOGIC concept without limitations of the experimental setup was performed by an adiabatic 1D-reactor model in combination with an equilibrium flash condenser. The analysis showed that at 50 bar and fixed residence time in the catalyst zone a catalyst inlet temperature of 230-250°C combined with a condenser temperature below 70°C ensures optimal productivity and heat exchange areas. Moreover, analysis of the heat flow showed that operation without external heating is possible by heat exchange between gas from the condenser and catalyst section.

Most important design parameter is found to be the conversion per pass over the catalyst. Increasing dimensions of the catalyst section will increase conversion per pass. With increasing conversion per pass, heat exchanger and condenser area are reduced because of lower recycle ratio. Therefore, increasing the size of the catalyst section will decrease the size of the heat exchange and condenser section. Consequently, overall reactor dimensions can be optimized by finding the most optimal sum of dimensions of the catalyst section and the heat transfer area required.

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6.7. Supporting Information

6.7.1. List of symbols

Table 6.S1 | List of symbols in the chapter

Symbol	Unit	Meaning	Ref.
A	m ²	Area	
A _{tubes}	m ² m ⁻¹ _{condenser}	Tube heat transfer area	
C _p	J mol ⁻¹ K ⁻¹	Area	sec. A.3.1
D _r	m ² s ⁻¹	Radial dispersion coefficient	sec. 6.7.3
D _{eff}	m ² s ⁻¹	Effective diffusion coefficient	sec. A.3.3
D _m	m ² s ⁻¹	Molecular coefficient	sec. A.3.3
d	m	Diameter	
h	J mol ⁻¹	Enthalpy	
K	–	Equilibrium constant	
Mw	kg mol ⁻¹	Area	
N _c	–	Number of components	
P	Pa	Pressure	
Pe	–	Peclet number	
r	m	Radius	
r _i	mol kg ⁻¹ s ⁻¹	reaction rate	
R	J mol ⁻¹ K ⁻¹	Gas constant	
Sc	–	Schmidt number	
T	K	Temperature	
U	J mol ⁻¹	Internal energy	
Q	W	Heat flow	
v _s	–	Superficial velocity	
V _m	m ³ mol ⁻¹	Superficial velocity	
w	–	Mass fraction	
x	–	Liquid mole fraction	
y	–	Gas mole fraction	
Y	–	Fit factors	
Z	–	Compressibility factor	
Greek Symbols			
α	W K ⁻¹ m ⁻²	Heat transfer coefficient	
Δ _r H	J mol ⁻¹	Reaction heat	

(table continues.)

Table 6.S1 | Continued.

Symbol	Unit	Meaning	Ref.
ΔP	Pa	Pressure drop	
ε	–	Bed voidage	
μ	Pa s	Viscosity	sec.A.3.2
ν	–	Stoichiometric coefficient	
λ	W m ⁻¹ K ⁻¹	Thermal conductivity	sec. 6.7.3
η	–	Effectiveness factor	
ρ	kg m ⁻³	Density	sec. A.4
ϕ_m	kg s ⁻¹	Mass flow	
ϕ_N	mol s ⁻¹	Mole flow	
ϕ_V	m ³ s ⁻¹	Volume flow	
Φ	–	Fugacity coefficient	
Φ_M	–	Thiele modulus	
χ	–	Vapour fraction	
Subscripts			
cat	–	Catalyst	
cw	–	Cooling water	
eq	–	Equilibrium	
g	–	Gas	
i	–	Component i	
l	–	Liquid	
m	–	Mass	
N	–	Mole	
r	–	Reactor	
v	–	vapour	
w	–	Water	

6.7.2. Reactor and setup

Reactor

In Figure 6.S1 as close up of the condenser section of the LOGIC reactor can be seen. In this figure, the location of the condenser inlet thermocouple ($T_{\text{cond,in}}$, TI-5) can be seen in more detail. In Table 6.S2 the exact dimensions of the catalyst and condenser section as used in the modelling are shown.

Detailed setup flowsheet

In Figure 6.S2 the extended flow sheet of the LOGIC reactor setup can be seen. Feed gas is fed from the buffer vessel (E-1) to the reactor (E-2). The pressure is controlled by a pressure control valve (PCV-1). Condensate is removed from the reactor by opening of valve (V-203) and can be directed to sample vials by multi position valve (MPV-1). V-203 is automatically closed as soon as gas breakthrough occurs by the use of conductivity sensor.

The temperature of the catalyst section is controlled by an electric oven (E-3). The condenser temperature is regulated by water flow and temperature. The water temperature is controlled using a water bath (E-6). The water flow is measured by a flow indicator (FI-1) and can be controlled by a needle valve (V-15) over a bypass. Because of the high pressure drop over the condenser an extra pump is added (E-7) including a pulsation damping vessel (E-8). To prevent evaporation of water, the system is pressurized using a pressure control valve (PCV-2).

The flow inside the reactor can be set by a fan (E-4) which is controlled by a power supply (X-5). The magnetic coupling (to ensure gas-tight propulsion of the fan) is water cooled (E-5) to prevent loss of magnetic field at high oven temperature. The flow in the reactor is determined indirectly by the use of differential pressure measurement (dP-1) over the catalyst section.

Gas samples can be taken from the reactor before (V-201) and after (V-202) the catalyst section. The gas is directly fed into a gas chromatograph (E-10). The lines to the GC can be purged using nitrogen. Selection of gas samples port or nitrogen purge is done by a multi position valve (MPV-2). Catalyst activation can be performed by using low pressure nitrogen and hydrogen connected upstream of valve V-14. Venting of gas can be done slow, using V-7 combined with needle valve V-8 or fast using valve V-9.

Figure 6.S1 | LOGIC Reactor condenser close-up

Table 6.S2 | Reactor dimensions

	Catalyst	Condenser	
Outer diameter	48	n.a.	mm
Inner diameter	24	46	mm
Length	16 (steel spheres)	35	mm
	56 (catalyst)		mm
Tube diameter	n.a	4	mm
Number of tube rows	n.a	9	-
Diameter ring 1	n.a	17	mm
Diameter ring 2	n.a	28	mm
Diameter ring 3	n.a	39	mm

Figure 6.S2 | Detailed Process Flow Diagram of the LOGIC setup.

6.7.3. Reactor model

Thiele modulus

The Thiele modulus concept is used to include intra-particle transport resistances. The method used is discussed by Lommerts et al. [205]. The reaction rate of methanol and water are linearized to pseudo first order reaction rate equations (see eq.(4), Table 6.S3), which can be applied in the standard Thiele modulus approach for first order reactions. Note that the equilibrium constant (eq.(3), Table 6.S3) is a pseudo equilibrium constant because it is dependent of temperature, pressure and composition. The equilibrium composition in equation (3) is found by the equilibrium constants of Graaf and Winkelman [144]. The equilibrium composition is found by solving the extent of reaction to equilibrium using the fmincon solver in Matlab.

Table 6.S3 | Thiele modulus equations

Thiele Modulus	
$r_{CH_3OH} = r_{CO} + r_{CO_2}$	(1)
$r_{H_2O} = r_{CO_2} + r_{RWGS}$	(2)
$K_{ps,i} = \frac{y_{eq,i}}{y_{eq,H_2}}$	(3)
$k_{ps,i} = \frac{r_i(1 - \varepsilon)\rho_{cat}}{(y_{H_2} - y_i/K_{ps,i})\rho}$	(4)
$\phi_{M,i} = \frac{d_p}{6} \sqrt{\frac{k_{ps,i}(K_{ps,i} + 1)}{D_{eff,i}K_{ps,i}}}$	(5)
$\eta_i = \frac{(3\phi_{M,i}) \coth(3\phi_{M,i}) - 1}{3\phi_{M,i}^2}$	(6)

Dispersion Coefficient

The radial dispersion coefficient is calculated by the recommended equation in the review by Delgado [207]. Equation (3) in Table 6.S4 is valid for $Sc < 550$ and $Pe_m < 1600$, in which Pe_m is the inert particle Peclet number defined by equation (1). The shape of the particle is taken into account by τ , which is 1.93 for cylindrical particles. D_m is the gas phase molecular diffusion coefficient as determined in section A.3.3.

Table 6.S4 | Radial dispersion coefficient equations

Dispersion coefficient	
$Pe_m = \frac{d_p v_s}{D_m}$	(1)
$Sc = \frac{\mu}{\rho D_m}$	(2)
$\frac{1}{Pe_r} = \frac{1}{\tau Pe_m} + \frac{1}{12} - \left(\frac{Sc}{1500} \right)^{4.8} (\tau Pe_m)^{3.83 - 1.3 \log_{10}(Sc)}$	(3)
$D_r = \frac{d_p v_s}{Pe_r \varepsilon_p}$	(4)

Thermal Conductivity

The thermal conductivity of the catalyst bed is calculated according to the correlations as described in the VDI Heat Atlas [208]. The thermal conductivity is a combination of primary parameters (porosity, thermal conductivity of fluid and particle) and secondary parameters (pressure, radiation). The relation (see equation (1) in Table 6.S5) including both primary and secondary parameters is taken, because the system is operated at high pressure and temperature.

The overall relation for thermal conductivity across a stagnant medium in a fixed bed is given in equation 6.S1, where k_{bed} is found by the equations in Table 6.S5. The constants used can be found in Table 6.S6 and the fluid conductivity is determined by the equations given in section A.3.2. The particle conduction is taken into account by k_p , influence of radiation is given by k_{rad} and the pressure dependency by k_g . The conductivity of one core cell is given by k_c , which is converted into the overall bed conductivity k_{bed} for a stagnant medium.

$$\lambda_{bed} = k_{bed} \lambda_g \quad (6.S1)$$

Finally this stagnant bed conductivity can be converted to an effective overall radial thermal conductivity by equation 6.S2. This equation includes the effect of flow as determined Yagi and Kunii [209].

$$\lambda_r = \lambda_g \left(\frac{\lambda_{bed}}{\lambda_g} + 0.1 d_t C_{p_g} \left(\frac{\phi_m}{A_r \lambda_g} \right) \right) \quad (6.S2)$$

Table 6.S5 | Equations to determine overall bed thermal conductivity [208].

Thermal conductivity	
$k_{bed} = \left(1 - \sqrt{1 - \epsilon_b}\right) \epsilon_b \left[(\epsilon_b - 1 + k_G^{-1})^{-1} + k_{rad} \right] + \sqrt{1 - \epsilon_b} [\varphi k_p + (1 - \varphi) k_c]$	
with	
$\frac{k_c N}{2} = \frac{B(k_p + k_{rad} - 1)}{N^2 k_G k_p} \ln \frac{k_p + k_{rad}}{B[k_G + (1 - k_G)(k_p + k_{rad})]} + \frac{B + 1}{2B} \left[\frac{k_{rad}}{k_G} - B \left(1 + \frac{1 - k_G}{k_G} k_{rad} \right) \right] - \frac{B - 1}{N k_G}$	(2)
$N = \frac{1}{k_G} \left(1 + \frac{k_{rad} - B k_G}{k_p} \right) - B \left(\frac{1}{k_G} - 1 \right) \left(1 + \frac{k_{rad}}{k_p} \right)$	(3)
$B = C_f \left[\frac{1 - \epsilon_b}{\epsilon_b} \right]^{10/9}$	(4)
$k_{rad} = \frac{\lambda_{rad}}{\lambda_g} = \frac{4\sigma}{(2/\varepsilon) - 1} T^3 \frac{d_t}{\lambda_g} \quad , \quad k_p = \frac{\lambda_p}{\lambda_g}$	(5) , (6)
$k_G = [1 + (l/d_t)]^{-1}$	(7)
$l = 2 \left(\frac{2 - \gamma}{\gamma} \right) \sqrt{\frac{2\pi RT}{MW_{H_2} P} \frac{\lambda_g}{(2C_{p_{H_2}} - RMW_{H_2}^{-1})}}$	(8)
$\log \left(\frac{1}{\gamma} - 1 \right) = 0.6 - \left(\frac{1000}{T} + 1 \right) C^{-1}$	(9)

Table 6.S6 | Parameters used in calculating the overall bed thermal conductivity per catalyst bed section [208].

Variable	Stainless steel balls part	Catalyst part
C	50	50
C_f	1.25	2.50
ϵ_b	0.369	0.4
λ_p	17	0.3 [222]
ε	0.08	0.03
φ	0.0013	0.0253

Flash calculation validation

Validation of the flash calculation and the mSRK equation of state is shown for low temperature in Figure 6.9. In Figure 6.S3 the phase equilibria for methanol-water is shown for 473 and 523 K. The phase equilibria for methanol-hydrogen are shown in Figure 6.S4. It can be concluded that the calculated phase equilibria are in good agreement with the experimental data.

Figure 6.S3 | VLE diagram of methanol - water for 473K and 523K. Symbols are experimental data by Gmehling et al. [219] and lines the SRK EoS predication with parameters of van Bennekom et al.[201].

Figure 6.S4 | VLE diagram of methanol - hydrogen at 373.15K. Symbols are experimental data by Brunner et al. [223] and lines the SRK EoS predication with parameters of van Bennekom et al.[201].

Gas Flow

As discussed in the main text the internal superficial gas velocity is determined by the Stokes-Ergun composite equation for pressure drop over a packed bed. The equations by Pope et al. [212] to determine the pressure drop by the Stokes-Ergun composite solution are given in Table 6.S7 where n and m are 5.

Table 6.S7 | Stokes, Ergun and composite equations for pressure drop over a packed bed. [212]

Packed bed friction factor	$F_f = \frac{\Delta p d_p}{L \rho v_s^2} \frac{\epsilon_b^3}{1 - \epsilon_b}$	(1)
Stokes friction factor	$F_f = \frac{24 \mu_g \epsilon_b}{\rho d_p v_s}$	(2)
Ergun friction factor	$F_f = \frac{150}{Re_b} + 1.75$	(3)
Composite friction factor	$F_f = f_{p_{Stokes}} + \frac{1}{\left(\frac{1}{f_{p_T}}^n + \frac{1}{f_{p_{Ergun}}}^n \right)^{1/n}}$	(4a)
Upper limit Reynolds	$f_{p_T} = f_{p_{Ergun}} \left(\frac{Re_b}{Re_{b,U}} \right)^m$	(4b)
	$Re_{b,U} = 22$	(4c)
Packed bed Reynolds Number	$Re_b = \frac{\rho d_p v_s}{\mu_g (1 - \epsilon_b)}$	(5)

The inlet composition of the catalyst section is determined by the combination of the fresh feed and the recycle gas flow, see Table 6.S8 equation 1 & 2. In the model an PID-type of control loop ensures a constant pressure by changing the feed gas flow rate of the model (Table 6.S8 eq.9). The conversion factor is optimized manually. The following constants are used with t_r being the residence time inside the reactor: $K_p = 15 + 70/t_r$, $K_I = 0.8$, $K_D = 0.1 \times 10^{-2} + 1/t_r$.

The cooling water flow of the condenser is calculated using the same type of PID controller. The reactor pressure as variable is replaced by the condenser outlet temperature and the feed mass flow with the cooling water flow. The constant used are as follows: the conversion constant is 1×10^{-8} and the $K_p = 0.1$, $K_I = 0.8$, $K_D = 0.1 \times 10^{-2}$.

6.7.4. Experimental data

An overview of experimental conditions is given in the Tables 6.S9 to 6.S10.

Table 6.S8 | Mixing point equations

Mixing Point		
	$\phi_m = \phi_{m_{recycle}} + \phi_{m_{feed}}$	(1)
	$w_i = \frac{\phi_{m_{recycle}} w_{recycle_i} + \phi_{m_{feed}} w_{feed_i}}{\phi_m}$	(2)
	$V_m * \frac{n_{total}}{V_{reactor}} - 1 = 0$	(3)
	$V_m = \frac{ZRT}{P_{range}(t)}$	(4)
PID type of controller		
P	$u_1 = K_P y(t)$	(5)
I	$u_2 = K_I \int y(t) dt$	(6)
D	$u_3 = 1000 K_D \frac{dy(t)}{dt}$	(7)
	$y(t) = P_{setpoint} - P_{range}(t)$	(8)
	$\phi_{m_{feed}} = (u_1(t_{end}) + u_2(t_{end}) + u_3(t_{end})) \cdot 1 \cdot 10^{-7}$	(9)

Table 6.S9 | Experimental data of the variation of $T_{cat,out}$. All the temperatures are given in (°C). MBC = Mass Balance Closure and OC = Oven Current @ 230V.

Nr.	$T_{cat,in}$	$T_{cat,out}$	T_{oven}	$T_{cond,in}$	$T_{cond,out}$	$T_{cw,in}$	$T_{cw,out}$	$\phi_{V,cw}$ (mL/min)	Prod. (mmol/g _{cat} h)	ΔP (Pa)	OC (A)	MBC (%)
1	149.1	182.7	258.0	148.7	99.9	60.6	93.8	113	6.0	7.2	1.4	97.8
2	157.0	192.3	275.0	151.4	100.5	59.9	93.8	108	10.4	5.9	1.5	94.0
3	165.4	201.1	298.0	158.4	100.2	60.2	89.3	137	14.5	5.9	1.7	98.7
4	175.3	210.3	318.0	163.8	100.3	60.9	81.5	203	17.4	4.5	1.8	97.2
5	183.2	220.6	335.0	167.7	100.3	60.9	77.3	237	17.5	5.4	1.8	95.8
6	194.4	226.2	356.1	176.4	101.1	49.1	82.7	146	16.3	5.4	2.0	99.7
7	196.3	229.2	366.3	175.3	100.6	56.1	75.0	244	14.8	3.0	2.1	95.9

Table 6.S10 | Experimental data of the variation of v_s . All the temperatures are given in (°C). MBC = Mass Balance Closure and OC = Oven Current @ 230V.

Nr.	$T_{cat,in}$	$T_{cat,out}$	T_{oven}	$T_{cond,in}$	$T_{cond,out}$	$T_{cw,in}$	$T_{cw,out}$	$\phi_{V,cw}$ (mL/min)	Prod. (mmol/g _{cat} h)	ΔP (Pa)	OC (A)	MBC (%)
27	193.9	204.4	317.9	159.2	99.5	60.1	88.1	132	15.4	0.4	1.6	93.9
28	181.3	203.3	311.0	158.7	100.3	60.4	85.8	152	17.1	1.0	1.7	96.3
29	165.4	201.1	298.0	158.4	100.2	60.2	89.3	137	14.5	5.9	1.7	98.7
30	156.8	203.1	290.0	158.7	100.1	60.4	88.7	146	12.3	10.5	1.7	98.7
31	147.0	201.6	280.1	157.9	99.8	60.3	88.5	152	9.2	17.0	1.7	91.7
32	137.6	203.1	270.1	159.1	100.0	61.0	87.7	173	5.8	28.5	1.7	93.4
33	132.3	203.3	270.0	160.8	100.3	61.3	90.5	170	4.5	41.1	1.9	91.9
34	127.3	200.4	272.0	162.9	100.5	61.5	92.0	184	3.6	59.5	2.0	-

Table 6.S11 | Exp. data of the variation of $T_{cond,out}$ at constant T_{oven} . All the temperatures are given in (°C). MBC = Mass Balance Closure and OC = Oven Current @ 230V.

Nr.	$T_{cat,in}$	$T_{cat,out}$	T_{oven}	$T_{cond,in}$	$T_{cond,out}$	$T_{cw,in}$	$T_{cw,out}$	$\phi_{V,cw}$ (mL/min)	Prod. (mmol/ g_{cat} h)	ΔP (Pa)	OC (A)	MBC (%)
8	159.3	194.3	297.9	148.5	84.0	46.8	60.9	280	16.3	4.1	1.8	97.2
9	161.2	194.4	298.1	150.4	86.8	52.5	64.3	261	16.8	4.9	1.8	99.2
10	162.8	191.4	298.0	151.5	87.6	48.9	67.7	221	16.1	4.3	1.7	96.4
11	160.5	197.6	298.0	153.4	89.7	49.0	67.7	262	16.4	4.6	1.8	96.1
12	161.6	197.8	298.1	156.2	94.7	61.6	69.7	326	15.6	8.2	1.6	95.3
13	160.6	198.2	298.0	154.9	91.9	52.5	71.9	215	15.4	5.3	1.7	96.8
14	165.9	197.3	298.0	156.0	96.2	61.2	76.1	250	15.8	7.3	1.7	100.1
15	165.7	203.0	297.0	156.7	97.8	60.6	78.6	205	15.8	4.5	1.6	95.9
16	166.8	202.4	297.0	158.5	98.3	61.2	82.1	189	14.5	6.1	1.7	96.3
17	165.4	201.1	298.0	158.4	100.2	60.2	89.3	137	14.5	5.9	1.7	98.7
18	166.1	201.2	298.0	159.3	101.7	60.3	90.8	134	13.9	5.7	1.7	95.2
19	168.6	201.1	300.9	162.2	104.3	60.2	95.0	117	13.6	5.2	1.7	97.9
20	169.4	201.5	298.0	161.9	105.8	60.1	97.9	111	12.9	5.5	1.7	98.7
21	169.1	205.0	295.0	163.1	108.3	47.4	106.4	69	11.8	5.7	1.6	97.5

Table 6.S12 | Exp. data of the variation of $T_{cond,out}$. All the temperatures are given in (°C). MBC = Mass Balance Closure and OC = Oven Current @ 230V.

Nr.	$T_{cat,in}$	$T_{cat,out}$	T_{oven}	$T_{cond,in}$	$T_{cond,out}$	$T_{cw,in}$	$T_{cw,out}$	$\phi_{V,cw}$ (mL/min)	Prod. (mmol/ g_{cat} h)	ΔP (Pa)	OC (A)	MBC (%)
22	170.5	204.8	321.9	157.1	87.8	48.4	62.3	309	22.3	3.3	1.9	98.2
23	170.5	205.1	317.0	157.7	90.2	52.4	64.4	343	20.6	4.4	1.8	96.8
24	169.7	203.3	317.1	157.0	92.6	56.1	67.1	364	19.6	5.1	1.8	95.7
25	170.2	204.2	312.0	156.4	94.3	61.0	70.3	364	18.3	3.8	1.7	94.9
26	168.2	201.9	306.0	157.2	95.9	61.0	73.8	260	17.5	4.5	1.8	97.6

EVALUATION AND OUTLOOK

IV

7

Wind power to Methanol

Abstract

A 100MW wind power to methanol process has been evaluated to determine the capital requirement and power to methanol efficiency. Power available for electrolysis determines the amount of hydrogen produced. The stoichiometric amount, for the methanol synthesis, of CO₂ is produced using direct air capture. Capital cost for all process steps is estimated using short-cut equipment sizing and economics.

Power to methanol efficiency was determined to be around 50%. The cost of methanol is around 300€ ton⁻¹ excluding and 800€ ton⁻¹ including wind turbine capital cost. Excluding 300M€ investment cost for 100MW of wind turbines, total plant capital cost is around 200M€. About 45% of the capital cost is reserved for electrolyzers, 50% for the CO₂ air capture installation, and 5% for the methanol synthesis system.

The conceptual design and evaluation shows that renewable methanol from CO₂ from air, water and renewable electricity is becoming a realistic option at reasonable costs of 750-800 € ton⁻¹.

In the evaluation below, elements from this thesis are combined into a conceptual design and evaluation of a process for renewable methanol production from CO_2 from air and H_2O , using renewable electricity as energy input.

The dutch government is planning several wind parks on the coast of the Netherlands with total installed power of around 10GW [224]. The (planned) locations of the wind parks have an installed power around 1.5GW per location. As design basis for this study we assume that 100MW (6.7%) of this 1.5GW is available to produce methanol for 8000 hours per year.

7.1. Blackbox evaluation

Prior to a more detailed process evaluation, a blackbox calculation is performed on the feedstock prices for methanol production. Using the prices for CO_2 and H_2 the price of methanol can be calculated. Note that this first calculation only includes feedstock prices and includes no other OpEx nor CapEx costs. The results of the blackbox calculation of the methanol product price, as a function of CO_2 and H_2 prices, is shown in Figure 7.1. To show the economical operation window, the methanol sales price (375 €/ton, [225]) is shown by the dashed line. As renewable methanol might be sold by a premium price, the price of renewable methanol is assumed at 550 €/ton.

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Prices for fossil hydrogen range from 1,500 €/ton for coal gasification and autothermal reforming of natural to 2,000 €/ton for steam methane reforming [226]. However, to produce hydrogen in a renewable and anthropogenic carbon-free way, hydrogen should be produced by electrolysis of water or from biomass resources. According to literature [226], prices of biomass produced hydrogen are in the same range as for fossil based resources. For example, hydrogen produced by biomass gasification (1,700-2,100 €/ton), bio-photolysis by algae (2,100 €/ton) or by fermentation (2,600 €/ton) [226]. Hydrogen produced by electrolysis is somewhat more expensive, as estimates range from 4,000 to 10,000 €/ton. [226]

Starting from wind energy, biomass schemes are excluded and only electrolysis of water for hydrogen production is used in this evaluation. Consequently, the price of hydrogen is strongly correlated to the electricity price. Therefore, the effect of the electricity price is shown as the second x-axis in Figure 7.1, assuming an electrolysis efficiency of 70%. Running a profitable operation of methanol production while using water electrolysis is, currently, very challenging. At current electricity prices of 0.07-0.10 € kWh⁻¹ [227], the cost of produced hydrogen is too high to produce methanol at a competitive price compared to fossil fuel based methanol. At an electricity price of 0.03-0.05 € kWh⁻¹, the cost of CO_2 should be between 50-100

Figure 7.1 | Cost of methanol as a function of the feedstock cost. Apart from feedstock cost, no other OpEx or CapEx cost included. Efficiency of electrolysis is assumed 70% for electricity requirement. Dashed lines show methanol sales price (375 €/ton, [225]) and renewable methanol premium price (550 €/ton).

€ ton⁻¹. In all cases, the capital and operational expenditures should be low to sell the methanol at a competitive price.

The cost of CO₂ produced by air capture, ranges from 100 to 1000 € ton⁻¹ in literature [228, 229]. Recently, a detailed paper of the system by Keith et al. [36] showed already costs in the range of 93-232 \$ ton⁻¹ of CO₂. A price of 200 € ton⁻¹CO₂ combined with (very) cheap hydrogen would thus potentially lead to a profitable production of methanol. Using CO₂ from a post-combustion capture source would improve the range of profitable operation even further. This cost of CO₂ from a post-combustion capture is estimated in the range of 30-60 € ton⁻¹ [230, 231]. In this study CO₂ is produced by air capture.

It can be concluded that, at this moment, the production of hydrogen by electrolysis is the main cost driver. Lower cost hydrogen, produced during periods of excess production of electricity, or available from biomass resources will improve the business case. With ongoing development on hydrogen production technologies, direct air capture and increasing availability of low-cost renewable electricity, the production of methanol from air, water and renewable electricity is more and more competitive.

7.2. Process evaluation

In the proposed process methanol is produced from CO_2 captured from air and H_2 produced by water electrolysis using renewable electricity. The design basis is 100MW of electric input and operating 8000 hours per year. The schematic flow diagram of the process is shown in Figure 7.2. First, it is determined how much hydrogen can be produced by the electricity. Next, the required stoichiometric amount of CO_2 for the methanol reaction is determined. The separations in the process are assumed to be 100% efficient. Co-adsorbed water during air capture can be used in the electrolyser and the co-produced water during methanol synthesis is recycled. The required amount of extra water – or excess of water – is shown by the magnitude of stream 13.

The main heat consuming steps in the process are the desorption of CO_2 (Q_{CO_2} in Fig. 7.2) and the reboiler of the distillation column (Q_{reb} in Fig. 7.2). When operating the electrolyser at elevated temperature, the heat produced during the production of hydrogen (Q_{H_2} in Fig. 7.2) can directly be integrated with the heat consuming steps in the process. If the heat demand exceeds heat production by electrolysis, further heat integration can be done by using the cooler and condenser heat. However, the temperature level of these heat duties is too low for direct heat integration. In that case heat pumps are required to upgrade the temperature level of these heat sources, at the cost of spending electric energy.

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The feed compressor of CO_2 and H_2 for the methanol reactor, the air fans and – if required – the heat pumps consume electric energy, at the expense of electricity available for hydrogen production. Therefore, the mass and energy balances are solved iteratively to make sure the total electric energy demand sums up to 100MW.

7.2.1. Electrolysis

For electrolysis of water three main technologies are available today; alkaline electrolysis, proton exchange membrane (PEM) electrolysis and Solid Oxide electrolysis. An overview of the technologies is given in Table 7.1. In alkaline electrolysis the electrodes are immersed in a liquid electrolyte separated by a diaphragm. Normally, the electrolyte is a KOH-solution and OH^- ions are passing through the diaphragm, releasing hydrogen at the cathode and oxygen and water at the anode. Alkaline electrolyzers are already available at MW scale systems [232].

With proton exchange membrane electrolysis protons are passing through a membrane. At the cathode, two protons are combined to hydrogen and at the anode

Figure 7.2 | Schematic process flow diagram, including electrolysis section, air capture section and methanol synthesis.

Table 7.1 | Electrolysis technologies. [232–236]

	Alkaline	PEM	Solid Oxide	Unit
Temperature	60-90	50-80	600-1000	°C
Pressure	1.05 - 30	10-200	1-25	bar
Energy consumption	4.2-6.6	4.2-6.6	3.7-3.9	kWh m _{H₂} ⁻³
Max. Capacity	5.3	1.1	n.a	MW
Capital cost	800-1500	900-2200	>2000	€ kW ⁻¹
TRL	9	5-7	3-5	-

oxygen and protons are produced. Because of the corrosive acidic conditions noble metals are required for the electrodes, increasing capital cost of the electrolyser [232].

Solid oxide electrolyzers operate at 700-900°C, resulting in a lower energy requirement for hydrogen production, because of thermal activation. Therefore, with good heat integration, these electrolyzers are expected to be more efficient than alkaline and PEM electrolyzers. Currently, solid oxide electrolyzers are in the development phase and not commercially available yet [232].

Because of the significant lower capital cost and the mature state of alkaline electrolysis technology, alkaline electrolyzers are used in this evaluation. The operating conditions for electrolysis, as presented in Table 7.2, are 120°C and 30 bar. By operating the electrolysis at higher temperature opportunities for heat integration in the process are increased. Especially, heat integration for the energy required for desorption of CO₂ would reduce energy requirement of the overall process. Operating at 30 bar lowers the compression energy of hydrogen for the methanol synthesis as compression of liquid water is less energy consuming compared to gas compression.

7.2.2. CO₂ Air capture

The air capture installation is sized on the stoichiometric amount of CO₂ required for methanol synthesis, based on the amount of hydrogen produced. The sorbent working capacities for CO₂ and water adsorption are determined from the isotherm values. For CO₂ the Toth isotherm as presented in section 2.3.1 is used. For the water capacity the Guggenheim, Anderson, de Boer isotherm is fitted on experimental data by Veneman [85], see Figure 7.S1.

The conditions for air capture are shown in Table 7.2. The average temperature

in the Netherlands is 15°C with a relative humidity (RH) of 75%. While the relative humidity is more or less constant around the year, the temperature has more variation. Therefore, cases at lower (5°C) and higher (25°C) temperature are defined. As concluded, in chapter 4 the desorption temperature should be higher than 100°C and the pressure is 500mbar for the base case. The effect of desorption pressure is investigated by calculating cases at 100 and 1000mbar.

Using the stoichiometric time approach as presented by Yu et al. [60] the time for adsorption and desorption can be coupled to the gas and solid efficiency. The gas efficiency shows the amount of CO₂ removed from the air passing through the adsorbent bed. At 100% efficiency all the CO₂ in the air is removed. The solid efficiency shows the approach of the working capacity to the equilibrium working capacity. At 100% both the adsorption and desorption equilibrium capacities are reached, resulting in a maximum working capacity.

The total sorbent mass is found by the required amount of CO₂ and the effective working capacity. The number of adsorbent beds is found by the total sorbent mass required and the mass per adsorbent bed. An adsorbent bed is assumed to have a 5m diameter and 0.03m length. The length of the sorbent bed is found by optimization of energy requirement using experimental values in the work by Yu et al. [60]. In the Supporting Information, section 7.5, detailed equations for the calculations performed are given.

7.2.3. Methanol section

The methanol reactor is scaled to the adiabatic reactor model in section 6.5. The conditions of 240°C at the catalyst inlet, 60°C at the condenser outlet and 50 bara are chosen, see Table 7.2. By normalizing the calculated heat flow and heat exchanger area to mass of methanol produced, the numbers can be used to estimate sizes for an upscaled reactor.

The distillation column has been sized by the short-cut Fenske-Underwood method [238] to determine the minimum reflux and theoretical number of stages. The reflux ratio is assumed to be 1.2 times the minimum reflux ratio and the number of stages is determined by the graphical Erbar-Maddox approach. Column diameter is determined by the vapour flow and the column height is found by the number of stages and the height of one stage [239].

All the assumptions taken for the process evaluation are presented in Table 7.2. In the Supporting Information, section 7.5, more details about the calculations performed are given. Moreover, the equations for the cost estimation of equipment is presented.

Table 7.2 | Overview of assumptions for process evaluation.

Overall			Electrolysis			
E _{input}	100	MW	T _{elec.}	120	°C	
Oper. hours	8000	h/y	P _{elec.}	30	bar	
C _{wind turbines}	3000 [237]	€/kW	E _{req.}	5.0	kWh m _{H₂} ⁻³	
			η _{elec.}	0.65	-	
			C _{elec.}	1000 [232]	€/kW	
Methanol synthesis [Chap.6]			Distillation			
P _{MeOH}	50	bar	T _{feed}	80	°C	
T _{cat,in}	240	°C	x _{distillate}	0.999	-	
T _{cond,out}	60	°C	x _{bottom}	0.001	-	
F _{Prod}	40	mol/kg _{cat} /h	l _t	0.5	m	
F _{Q,cond}	5.5 × 10 ⁶	W/kg _{MeOH}	d _{wt}	5	mm	
F _{A,cond}	640	m ² /kg _{MeOH}				
F _{A,hex}	700	m ² /kg _{MeOH}				
C _{catalyst}	15	€/kg				
CO ₂ air capture						
	1: Base Case	2A: Low T _{ads}	2B: High T _{ads}	3A: Low P _{des}	3B: high P _{des}	Unit
T _{ads}	15	5	25	15	15	°C
RH _{ads}			75			%
t _{ads}			2700			s
v _{air}			0.3			m s ⁻¹
P _{des}	500	500	500	100	1,000	mbar
T _{des}			115			°C
t _{des}			900			s
η _g & η _{s,CO₂}			0.55 [60]			-
η _{s,H₂O}			0.75			-
L _{bed}			0.03 [60]			m
D _{bed}			5			m
C _{sorbent}			30			€/kg

7.3. Results and discussion

7.3.1. Base case

First, the detailed results of the base case are discussed, followed by a sensitivity analysis on the effect of the adsorption temperature and the desorption pressure. The base case will produce 65kton of methanol yearly, with 100MW of electric energy input this results in a Power to Methanol efficiency of 51%, as shown in Table 7.3.

In the base case, 87MW is available for electrolysis resulting in 28MW of heat production at an electrolysis efficiency of 65%. Since electrolysis is operated at elevated temperature, the heat produced can directly be integrated with the CO₂ capture system. However, 44MW of heat is required for the desorption of CO₂ for the base case. Therefore 16MW of heat has to be integrated with lower temperature heat sources (e.g the cooler and condenser) using heat pumps. It is clear that by reducing the heat demand of the capture process the overall efficiency of the power to methanol process can be increased.

The heat requirement for CO₂ desorption is shown in more detail in Figure 7.3. The energy required for sensible heat of the sorbent takes about 45% of the total heat. Recovery of the sensible heat in fixed bed operation is difficult. At maximum, a cold bed finished adsorption and a hot bed finished desorption can be levelled in temperature, reducing the sensible heat by 50% at maximum heat exchange efficiency. This would reduce the heat pump duty by around 3.5 MW electric, boosting process efficiency. In literature [240] a heat integration concept between fixed beds using heat pump technology was shown to reduce energy requirement. Further recovery of the sensible heat of the sorbent, could be performed by circulating the sorbent between separate adsorption and desorption reactors. This would enable counter-current heat exchange between sorbent leaving and entering the desorption reactor, increasing the maximum amount of heat exchanged. Moreover, this would save the sensible heat of the reactor, reducing energy requirement by 2.5MW (5.7%). Application of full heat exchange combined with a circulating system would take away the need of a heat pump.

Another method of reducing sorbent sensible heat requirement is increasing the solid efficiency. Currently, only 55% percent of the equilibrium working capacity is used. Increasing solid efficiency by increasing the adsorption time, would reduce gas efficiency due to reduced uptake rates when the sorbent bed approaches equilibrium. A method to increase solid efficiency while maintaining gas efficiency would be reduction of the air velocity with increasing bed loading. However, this

dynamic operation of the adsorption bed requires more detailed modelling and optimization of the capture process.

Further reduction of heat required for desorption can be done by reducing the amount of water co-adsorbed. Weather conditions can change and pre-conditioning of air is too costly, as a few thousand cubic meter of air are processed per second. Therefore, the amount of water adsorbed cannot be optimized. To reduce the water working capacity, the amount of water desorbed should be reduced. By increasing the relative humidity during desorption less water is desorbed. Using steam would increase relative humidity, however as shown in chapter 4 this does not result in a nett reduction of energy requirement.

Furthermore, by changing the absolute pressure the maximum relative humidity in the reactor is influenced. As relative humidity is the ratio between the partial pressure of water and the saturation pressure, reducing absolute pressure will reduce the maximum relative humidity in the reactor. Therefore, based on water working capacity, the desorption pressure should kept high. However, for CO₂ working capacity, the pressure should be reduced. Therefore, the desorption pressure should be optimized to the ratio of CO₂ and water. The optimal ratio in CO₂ and water working capacity would be around two, as net two hydrogen molecules are required for one CO₂ molecule to produce methanol.

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The total electricity requirement of the process is shown in Figure 7.4. As shown, currently the heat pump is accountable for about 50% of the electricity requirement. Reduction of heat pump duty is already discussed above. The electricity requirement of the air fans can be reduced by either reducing the pressure drop over the adsorbent bed or by increasing the gas efficiency. Because already a very short bed is used, further reduction of pressure drop is unlikely. Changing a bed of sorbent particles for a monolith type of adsorbent material might open up opportunities for further pressure drop reduction. As already pointed out above, increasing gas efficiency might be done by dynamic operation of the air fans. By optimizing the air velocity as a function of the bed loading an increased gas efficiency and optimized pressure drop might be achieved.

The total capital cost for the power to methanol plant is estimated around 200M€, this excludes a investment of 300M€ for 100MW of wind turbines. The capital cost split-up – as shown in Table 7.3 – of the plant is roughly 45% for the electrolyzers, 50% for the CO₂ capture installation and 5% for the methanol section including purification.

The capital cost the CO₂ capture installation is dominated by the sorbent cost, as shown in Figure 7.5. The cost for the sorbent is assumed 30 € kg⁻¹, which is half

Figure 7.3 | Heat consumption for CO₂ desorption. Total heat requirement 44MW or 14GJ/ton.

Figure 7.4 | Electricity consumption in the process apart from the electrolysis. Total electricity consumption is 13MW.

the current – lab scale – price. Further reduction of price can be expected as soon as CO₂ is applied at large scale. The minimum price is expected to be price of polystyrene (around 5 € kg⁻¹). On the other hand, the cost of the sorbent is depreciated over 10 years. Thereby, it is assumed that the sorbent does not significantly degrade over ten years, which is expected to be optimistic. Increasing the working capacity of the sorbent would reduce the required sorbent mass and reduce capital cost. At the same time, sensible heat requirement will be reduced. Therefore, it is important to increase sorbent efficiency and working capacity. By reducing the amount of sorbent mass required, the number of adsorbent beds is reduced. This will reduce the capital costs further, as seen by the capital cost of the fans in Figure 7.5. Per bed one fan is required, consequently reducing the number of beds will reduce cost. It can be concluded that the capital cost of the CO₂ capture installation is mainly a function of the sorbent working capacity and sorbent lifetime.

The cost of the methanol reactor system including purification is given in Figure 7.6. The cost of the system is dominated by the cost of the feed compressors for the methanol reactor. The capital cost of the feed compressors is a function of the required power. Reducing the operating pressure of the methanol reactor will decrease investment cost. However, this will reduce reactor productivity and therefore increase capital cost of the reactor. The cost of the methanol reactor system can therefore be optimized by the ratio in capital cost for the feed compressors and the reactor.

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7.3.2. Adsorption temperature

Comparing the case 1 and 2 in Table 7.3 it is seen that reducing the adsorption temperature increases working capacity. In the discussion above, it was hypothesised that increasing working capacity would increase power to methanol efficiency. In Table 7.3 it is confirmed that the 5°C has the highest efficiency. By increasing the working capacity the desorption heat requirement is reduced, increasing overall efficiency.

As shown in Table 7.3, in the calculations the number of beds is altered, due to the changed working capacity. In reality however, the productivity of the system will be changed as the number of beds is fixed by design. On the other hand, it can be decided to put part of the capture system in standby in the case of increased productivity. In this way, system efficiency will be increased although capital cost might suffer. The number of adsorbent beds range from 1,000 to 2,000. On first sight this seems to be an enormous number of beds. By assuming a total bed height of 0.5m, the total height of the CO₂ capture system is 1000m. However, in order to produce 100MW of electric wind power, at least 10 wind turbines are required

Figure 7.5 | Capital cost for the air capture installation, total capital cost for air capture installation is 95 million euro.

Figure 7.6 | Capital cost for methanol synthesis, including compression and distillation. Total investment cost for the methanol section is 11 million euro.

with a height of more than 150m each. Therefore, easily 200 beds can be incorporated per tower and the complete CO₂ capture system could be fitted in the base towers of the ten wind turbines required to produce 100MW. In other words, each wind turbine can accommodate the required air capture installation for methanol production, in line with its own power generation capacity.

Although, it is seen that the productivity is increased at lower adsorption temperatures, in chapter 2 it is shown that the adsorption kinetics are significantly reduced at low temperature. However, the effect of kinetics on solid and gas efficiency is not included in the current evaluation. As both solid and gas efficiency are negatively influenced by reduced kinetics, the advantage of operating at low adsorption temperature might be decreased when kinetics are included. Therefore, more detailed modelling of the adsorption bed and process is required to optimize the system.

The total fixed capital investment is strongly correlated with the working capacity of the sorbent, as shown in Table 7.3. This a results of the increase in mass of sorbent required with lower working capacity. Moreover, because the number of bed is higher with a low working capacity the capital cost of the air fans is increased. Therefore, capital investment can be optimized by increasing the CO₂ working capacity.

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7.3.3. Desorption pressure

With decreasing desorption pressure the working capacity of CO₂ is increased as shown in Table 7.3. However, also the water working is significantly increased because of the reduced relative humidity at low absolute pressure. Therefore, the effect on power to methanol efficiency and cost of methanol production are not the same compared to changes in lower adsorption temperature.

Due to the increased water working capacity and lower absolute pressure the duty of the vacuum compressor is increased, see Table 7.3. This is a consequence of increased flow and pressure difference over the compressor. Accordingly, the power for electrolysis is reduced resulting in a lower methanol production. The duty of vacuum compressor might be reduced by (partial) condensation of the water upstream of the vacuum compressor reducing the flow through the compressor. The total capital cost of the system is reduced because of the significant reduction in sorbent requirement, due to increase in CO₂ working capacity.

On the other hand, operation of the desorption at atmospheric pressure reduces CO₂ working capacity and increases capital cost. Because of increased sorbent inventory, the energy requirement of desorption is increased increasing the cost per

Table 7.3 | Main performance indicators for the five case defined in Table 7.2.

Parameter	1: Base Case	2A: Low T_{ads}	2B: High T_{ads}	3A: Low P_{des}	3B: high P_{des}	Unit
$E_{Electrolysis}$	87	90	82	82	86	MW
η_{P2M}^1	51	53	49	49	51	%
$\Phi_{m,MeOH}$	65	67	62	62	65	kton y^{-1}
Φ_{m,CO_2}	90	93	85	85	89	kton y^{-1}
T_{ads}	15	5	25	15	15	°C
T_{des}	115	115	115	115	115	°C
P_{des}	500	500	500	100	1000	mbar
$x_{CO_2,des}$	0.16	0.21	0.12	0.13	0.25	–
RH_{des}	25	23	26	5.2	45	%
Δq_{CO_2}	0.56	0.70	0.42	0.71	0.40	mol kg^{-1}
Δq_{H_2O}	2.8	2.6	3	4.9	1.2	mol kg^{-1}
$m_{sorberent}$	454	375	580	340	635	ton
N_{beds}	1428	1184	1824	1072	2000	–
$\Phi_{v,air}$	6316	5222	8064	4727	8829	$m^3 s^{-1}$
Q_{H_2}	28	29	27	27	28	MW
Q_{CO_2}	44	38	52	42	46	MW
E_{Fan}	3.7	3	4.7	2.8	5.1	MW
E_{VSA}	1.6	1.3	2.1	7.3	0.12	MW
$E_{Heat pump}$	6.3	4.2	9.6	6.4	7.2	MW
$C_{Electrolysis}$	87	90	82	82	86	M€
$C_{CO_2 capture}^2$	95	77	121	89	124	M€
$C_{Methanol}^3$	11	11	10	10	11	M€
C_{Total}^4	194	181	216	183	222	M€
$C_{CO_2 capture}^5$	308	254	403	360	353	€ $ton_{CO_2}^{-1}$
C_{Total}	298	268	350	298	344	€ ton_{MeOH}^{-1}
$C_{Total,incl. WT}^6$	758	713	836	785	809	€ ton_{MeOH}^{-1}

¹ Power to methanol efficiency.² Includes capital cost for sorbent, air fans, vacuum compressor and reactor steel.³ Includes capital cost for feed compressors, methanol reactor and distillation.⁴ Excludes 300M€ capital cost for 100MW of wind turbines.⁵ Cost of CO_2 , including capital cost, cost for electric energy (0.1€ kWh⁻¹) and cost steam (25€ ton⁻¹).⁶ Includes 300M€ capital cost for 100MW of wind turbines.

Table 7.4 | Production cost for fossil, biomass and electrolyse based methanol.

		Methanol technology	Carbon source	Capacity (kton/y⁻¹)	Cost (€ ton⁻¹)
Fossil	Blug et al. [241]	Syn gas	Natural gas reforming	1,800	200
	Blug et al. [241]	Syn gas	Coal gasification	1,800	250
Biomass	Carvalho [242]	Syn gas	Forest residu gasification		600
	Balegedde Ramachandra [243]	Syn gas	Reforming of glycerol		500
Electrolysis	Mccord et al. [244]	Direct CO ₂	CO ₂ flue gas capture by calcium carbonate	365	1,400
	Rivera-Tinoco [245]	Direct CO ₂	CO ₂ (input)	16	900
	This work	Direct CO ₂	CO ₂ air capture by solid amines	65	800

ton of methanol. Again, this shows the importance of optimizing working capacity of both CO₂ and water.

7.3.4. Methanol production

The total cost per ton of methanol of around 800 € ton⁻¹ is about 1.5 times the estimated premium price of renewable methanol of 550 € ton⁻¹. This opens opportunities for renewable methanol production, especially with decreasing prices for wind energy and electrolysis [235, 246]. It should be noted that the numbers presented are first estimate capital cost and do not included operational cost such as cost for employees and maintenance. Estimated values for future cost are a reduction of 30% in capital cost for wind turbines [246] in 2030, 500 € kW⁻¹ for electrolysis [235] in 2030 and the cost of air captured CO₂ is expected to go down to 100 € ton_{CO₂}⁻¹ [229]. With these numbers, methanol could be produced competitively for the premium price for renewable methanol.

The production cost for methanol production based on fossil fuels, biomass based and direct conversion of CO₂ by electrolysis based hydrogen are shown in Table 7.4. The production cost of fossil based methanol is in the range of 200-250 € ton⁻¹, based on the feedstock. Biomass or electrolysis based methanol is not able to compete with fossil methanol purely based on production cost. Despite cost reduction for renewable technology, as discussed above, competing with fossil based fuels is extremely difficult. When using fossil fuels, both the energy and carbon source, are recovered from ground at low cost. Switching to electrolysis and CO₂, serious investment have to be made to harvest energy (e.g. wind turbines or solar PV) and recovery of the carbon source by CO₂ capture. With the growth, harvesting and transport of biomass also significant cost are involved, raising the production price of methanol. Moreover, fossil fuel will benefit from the economy of scale, as the plants for fossil fuel based production are significantly larger compared to renewable based plants in Table 7.4.

Keeping in the mind the extra process steps required to produce renewable methanol, a first estimate of 800 € ton⁻¹ is a good starting point. With expected cost reduction for renewable electricity, electrolysis and direct air capture the production of renewable methanol is promising as electricity storage medium and feedstock for the chemical industry.

7.4. Conclusion

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A 100MW wind power to methanol plant has been evaluated based on energy requirement and capital cost. A Power to Methanol efficiency of around 50% has been found. The cost of methanol is around 300€ ton⁻¹ excluding and 800€ ton⁻¹ including wind turbine capital cost. Excluding 300M€ investment cost for 100MW of wind turbines, total plant capital cost is around 200M€. About 45% of the capital cost is reserved for electrolysis, 50% for the CO₂ air capture installation, and 5% for the methanol synthesis system.

Apart from the efficiency of electrolysis, the main parameter to be optimized is the sorbent working capacity for the CO₂ air capture system. Increasing working capacity would reduce both, the heat demand and the capital cost. Both, heat demand for CO₂ desorption and capital cost for CO₂ capture are dominated by the mass of sorbent required in the process. Reducing heat demand for CO₂ would increase process efficiency and reduction in sorbent mass reduces cost per ton of methanol. Moreover, optimizing the co-adsorption of water to the requirement for methanol synthesis can further optimize system efficiency and cost.

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7.5. Supporting Information

In this chapter the process of CO₂ to methanol is evaluated. In the section below detailed equations, for energy requirement, equipment sizes and capital costs are given.

The design basis of the plant is 100MW of electricity as input. By iterative calculation of the amount of power required in the rest of the process, the power for electrolysis can be found. Thereby, the production of H₂ is known by using the electrolysis efficiency (see eq(1), Table 7.S1). For the methanol reaction, stoichiometric reaction is assumed and thereby the required amount of CO₂ and the amount of methanol produced are known.

7.5.1. Hydrogen production

The amount of hydrogen produced is calculated from the power available and power consumption by an alkaline electrolyser, see equation (1) in Table 7.S1. The power available for electrolysis is the design power (100MW) of the plant minus the electricity requirement elsewhere in the plant, e.g. compressors and air fans. The heat produced by electrolysis is determined by the efficiency (see eq. 7.S1.2) minus the sensible heat of the water (see eq. 7.S1.3) fed to the electrolyser. The electric energy required to increase the pressure of the water to the electrolyser pressure is given by equation 7.S1.4.

Table 7.S1 | Equations for Electrolysis

Electrolysis.	
$\phi_{N,H_2} = \frac{E_{\text{electrolysis}} \eta_{\text{electrolysis}}}{\Delta H_{\text{electrolysis}}}$	(7.S1.1)
$Q_{H_2} = P_{\text{electrolysis}} \cdot (1 - \eta_{\text{electrolysis}}) - Q_{H_2O}$	(7.S1.2)
$Q_{H_2O} = \phi_{N,H_2O} c_{p,H_2O} (T_{\text{electrolysis}} - T_{\text{electrolysis,in}})$	(7.S1.3)
$E_{FP,H_2O} = \frac{\phi_{m,\text{water,in}}}{\rho_{H_2O}} \Delta P$	(7.S1.4)

7.5.2. CO₂ capture

The design basis of the CO₂ capture installation is to produce a stoichiometric amount of CO₂ for methanol production to the amount H₂ produced in the electrolyzers. The equilibrium working capacity (eq. 7.S2.3) is determined by adsorption and des-

orption loading according to the Toth isotherm determined in chapter 2, see Table 2.3. The water working capacity is determined by the Guggenheim, Anderson, de Boer (GAB) isotherm, see Table 7.S3. The isotherm is fitted to data by Veneman et al. [85], see Figure 7.S1. The CO₂ concentration during desorption is determined by the ratios of working capacities of water and CO₂, see equation 7.S2.1. However, the working capacity is a function of the concentration during desorption. Therefore, the CO₂ fraction and relative humidity during desorption are solved iteratively.

The required amount of sorbent (eq. 7.S2.4) can be calculated using the CO₂ working capacity and the solid efficiency (i.e. approach to the equilibrium working capacity) as defined in previous work [60]. The calculated amount of sorbent is determined for one cycle, that is the sorbent mass required per desorption step. Because the time for adsorption is three times longer than the desorption time, a total of four cycle operate parallel (eq. 7.S2.7). The number of parallel sorbent beds per cycle is determined by total sorbent mass and the volume per bed (eq. 7.S2.5). The diameter of bed is assumed and the length is determined to minimize the power required for the fans was determined in previous work [60]. The total air flow per cycle is given by equation eq. 7.S2.6.

The heat requirement for desorption of CO₂ is given by the equations 7.S2.8-11. The adsorption heat and the sensible heat for both CO₂ and H₂O are included. Moreover, the sensible over the sorbent, averaged over the desorption time, is included. The sensible heat of reactor is included by estimating the steel mass of the reactor, assuming a reactor length of 0.5m.

The electric energy requirement for the air fans and the vacuum compressor are shown in equations 7.S2.11 and 7.S2.12. The pressure drop over the fixed bed is found by the Ergun equation for an assumed velocity of 0.3 m/s. The total air flow is found by multiplying the bed cross sectional area by the velocity and number of beds. Because, three cycles are in adsorption mode and one in desorption the energy requirement is multiplied by N-1 cycles. The compression energy of the vacuum pump is mainly a function of the pressure difference and the mole flow in the outlet.

Table 7.S2 | Equations for Air capture

Air capture.	
$x_{\text{CO}_2, \text{des}} = \frac{\Delta q_{\text{CO}_2} \eta_{s, \text{CO}_2}}{\Delta q_{\text{CO}_2} \eta_{s, \text{CO}_2} + \Delta q_{\text{H}_2\text{O}} \eta_{s, \text{H}_2\text{O}}}$	(7.S2.1)
$RH_{\text{des}} = \frac{P_{\text{des}} (1 - x_{\text{CO}_2})}{P_{\text{sat}}(T_{\text{des}})}$	(7.S2.2)
$\Delta q_i = q_{i, \text{ads}} - q_{i, \text{des}}$	(7.S2.3)
$m_{\text{sorbent}} = \frac{\phi_{N, \text{CO}_2, \text{out}} t_{\text{des}}}{\Delta q_{\text{CO}_2} \eta_{s, \text{CO}_2}}$	(7.S2.4)
$N_{\text{beds}} = \frac{m_{\text{sorbent}} \rho_{\text{sorbent}}^{-1}}{0.25 \pi D_{\text{bed}}^2 L_{\text{bed}}}$	(7.S2.5)
$\phi_{V, \text{air}} = 0.25 \pi D_{\text{bed}}^2 v_{\text{air}} N_{\text{beds}}$	(7.S2.6)
$N_{\text{parallel cycles}} = \frac{t_{\text{ads}}}{t_{\text{des}}} + 1$	(7.S2.7)
$Q_{\text{reaction}, i} = \phi_{N, i, \text{out}} \Delta_r H_i$	(7.S2.8)
$Q_{\text{sensible}, i} = \phi_{N, i, \text{out}} C_{P, i} (T_{\text{des}} - T_{\text{ads}})$	(7.S2.9)
$Q_{\text{sensible}, \text{sorbent}} = \frac{m_{\text{sorbent}} C_{P, \text{sorbent}} (T_{\text{des}} - T_{\text{ads}})}{t_{\text{des}}}$	(7.S2.10)
$Q_{\text{sensible}, \text{reactor}} = \frac{\pi D_{\text{bed}} L_{\text{reactor}} l_{\text{wt}} \rho_{\text{steel}} C_{P, \text{steel}} (T_{\text{des}} - T_{\text{ads}})}{t_{\text{des}}}$	(7.S2.11)
$E_{\text{Fan}} = \Delta P \phi_{V, \text{air}} (N_{\text{parallel cycles}} - 1)$	(7.S2.12)
$E_{\text{VSA}} = \frac{1}{\eta} \cdot \frac{k}{k-1} \cdot \phi_N R T \cdot \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$	(7.S2.13)
$E_{\text{Heat pump}} = \frac{Q_{\text{CO}_2} + Q_{\text{reb}} - Q_{\text{H}_2}}{\text{COP}}$	(7.S2.14)

Table 7.S3 | Guggenheim, Anderson, de Boer isotherm equations and parameters

Guggenheim, Anderson, de Boer isotherm		
$C_g = C_{g,0} \exp\left(\frac{\Delta H_c}{RT}\right)$		
$K_{ads} = K_0 \exp\left(\frac{\Delta H_k}{RT}\right)$		
$q_{H_2O} = \frac{C_m C_g K_{ads} RH}{(1 - K_{ads} RH) (1 - (1 - C_g) K_{ads} RH)}$		
Parameter	Value	Unit
$C_{g,0}$	99.9976	-
C_m	5.5497	mol kg ⁻¹
ΔH_c	-8685.5	J mol ⁻¹
K_0	0.9171	-
ΔH_k	-820.02	J mol ⁻¹

Figure 7.S1 | Fit of the GAB isotherm on experimental data by Veneman et al.[85]. Various includes data of temperatures in the range of 18-67°C.

7.5.3. Methanol synthesis

The methanol reactor is scaled to the results of the adiabatic reactor model in the previous chapter, see section 6.5. Using the factors scaled to a kilogram of methanol, the heat transfer areas in the internal heat exchanger and the condenser can be calculated. The condenser duty and the mass of catalyst are calculated in a similar way, see Table 7.S4.

Table 7.S4 | Equations for methanol synthesis.

Methanol synthesis	
$A_{\text{Heat exchanger}} = F_{A,\text{hex}} \phi_{m,\text{MeOH}}$	(7.S4.1)
$A_{\text{Condenser}} = F_{A,\text{cond}} \phi_{m,\text{MeOH}}$	(7.S4.2)
$Q_{\text{Condenser}} = F_{Q,\text{cond}} \phi_{m,\text{MeOH}}$	(7.S4.3)
$m_{\text{Catalyst}} = \frac{F_{\text{Prod}}}{\phi_{N,\text{MeOH}}}$	(7.S4.4)

7.5.4. Methanol purification

The methanol distillation column is designed by the short-cut method using the Fenske-Underwood correlations. First, the relative volatility (α , eq. 7.S5.1) is determined at inlet conditions. Next, the minimum reflux ratio is found by the Underwood correlation (eq. 7.S5.2) using the methanol mole fraction in the feed and distillate (x_F/x_D). The minimum number of theoretical stages is found by the Fenske equation (eq. 7.S5.4). The total number of stages N is found by the graphical Erbar-Maddox approach [239]. A tray spacing l_t of 0.5m is assumed to calculate the maximum gas velocity (eq. 7.S5.5) to determine the column diameter (eq. 7.S5.6). Moreover, using the number of stages and the tray spacing the column length is estimated (eq. 7.S5.7).

7.5.5. Cost Calculation

The equations used to estimate the capital cost of the plant are given in Table 7.S6 below. The cost of the fans blowing air over the adsorbent bed is given by equation 7.S6.1. A vane-axial fan constructed out of carbon steel is assumed, where Q is the flow in actual cubic feet per minute (ACFM). To find the total investment cost for the air fans, the capital cost per fan is multiplied by the total number of adsorbent beds.

For the vacuum compressor and the feed compressors of the methanol reactor a reciprocating compressor is assumed. The capital cost is calculated using equation

Table 7.S5 | Equations for methanol distillation [238, 239].

Methanol Distillation	
$\alpha = \frac{P_{\text{sat,MeOH}}}{P_{\text{sat,H}_2\text{O}}}$	(7.S5.1)
$R_{\min} = \frac{\frac{x_D}{x_F} - \alpha \frac{1-x_D}{1-x_F}}{\alpha - 1}$	(7.S5.2)
$R = 1.2R_{\min}$	(7.S5.3)
$N_{\min} = \frac{\ln \left[\left(\frac{x_D}{1-x_D} \right) / \left(\frac{x_B}{1-x_B} \right) \right]}{\ln(\alpha)}$	(7.S5.4)
$v_{\max} = (-0.171l_t^2 + 0.27l_t - 0.047) \left[\frac{\rho_l - \rho_v}{\rho_v} \right]^{0.5}$	(7.S5.5)
$D_c = \sqrt{\frac{4\phi_{\text{m,vapour}}}{\pi\rho_{\text{vapour}}v_{\max}}}$	(7.S5.6)
$L_c = Nl_t$	(7.S5.7)

7.S6.2, where P_c is the consumed power of the compressor in horsepower. The required power is found by equation 7.S2.12.

The cost of the heat exchangers, including coolers, condensers and reboiler, in the process are estimated by a carbon steel shell and tube type of heat exchanger with a fixed head construction. The capital cost is found by equation 7.S6.3, where A is the heat exchange area in square feet. The cost increase by high pressure operation is included by F_p , where is the operating pressure in psig. For calculation of the heat exchange area by heat duty, the logarithmic mean temperature difference and a estimated overall heat transfer coefficient of $100 \text{ W m}^{-2} \text{ K}^{-1}$ are used.

The total cost for the distillation tower is a combination of the cost for the tower (eq. 7.S6.5), for bubble cap trays ($F_{tt}=1.87$, eq. 7.S6.9) and the reboiler and condenser (eq. 7.S6.3). The cost of the tower is a function of the steel mass W (eq. 7.S6.7) in pounds as shown in equation 7.S6.6. Equation 7.S6.8 shows the added cost for platforms and ladders as function of the column diameter and length in feet. The cost of the reboiler and condenser are included by the cost of a shell and tube heat exchanger with a fixed head.

To determine the total amount of fixed capital investment, a Lang factor of 5 is taken [247]. The sum of capital cost is applied by the Lang Factor to find the fixed

capital investment.

Table 7.S6 | Equations for the capital expenditure with cost per equipment (C) in dollar [247].

Capital Expenditure	
$C_{\text{Air Fan}} = \exp(9.5229 - 0.97566 \ln(Q) + 0.08532 \ln(Q)^2)$	(7.S6.1)
$C_{\text{compressors}} = \exp(7.9661 + 0.8 \ln(P_c))$	(7.S6.2)
$C_{\text{Heat exchanger}} = F_p \exp(11.0545 - 0.9228 \ln(A) + 0.09861 \ln(A)^2)$	(7.S6.3)
$F_p = 0.9803 + 0.018 \left(\frac{P}{100} \right) + 0.0017 \left(\frac{P}{100} \right)^2$	(7.S6.4)
$C_{\text{Distillation Tower}} = C_v + C_{PL}$	(7.S6.5)
$C_v = \exp(7.2756 + 0.18255 \ln(W) + 0.02297 \ln(W)^2)$	(7.S6.6)
$W = \pi (D_c + d_{wt}) (L_c + 0.8D_c) d_{wt} \rho_{\text{steel}}$	(7.S6.7)
$C_{PL} = 300.9 D_c^{0.63316} + L_c^{0.80161}$	(7.S6.8)
$C_{\text{trays}} = N_t F_{tt} 468 \exp(0.1739 D_c);$	(7.S6.9)

7.5.6. Results

7

In Table 7.S7 the detailed results of the process evaluation are given for the cases defined in Table 7.2. In Table 7.S8 the full overview of capital cost involved is given.

Table 7.S7 | Overview of the key performance indicators and energy flows.

Parameter	1: Base Case	2A: Low T_{ads}	2B: High T_{ads}	3A: Low P_{des}	3B: high P_{des}	Unit
$E_{\text{Electrolysis}}$	87	90	82	82	86	MW
η_{P2M}^1	51	53	49	49	51	%
$\Phi_{\text{m,MeOH}}$	65	67	62	62	65	kton y ⁻¹
$\Phi_{\text{m,CO}_2}$	90	93	85	85	89	kton y ⁻¹
$\Phi_{\text{m,H}_2\text{O}}^2$	113	67	184	173	38	kton y ⁻¹
$\Phi_{\text{m,O}_2}$	97.6	101	92.4	92.2	96.7	kton y ⁻¹
T_{ads}	15	5	25	15	15	°C
T_{des}	115	115	115	115	115	°C
P_{des}	500	500	500	100	1000	mbar

(Table continues.)

Table 7.S7 | Continued.

Parameter	1: Base Case	2A: Low T_{ads}	2B: High T_{ads}	3A: Low P_{des}	3B: high P_{des}	Unit
$x_{\text{CO}_2,\text{des}}$	0.16	0.21	0.12	0.13	0.25	–
RH_{des}	25	23	26	5.2	45	%
Δq_{CO_2}	0.56	0.70	0.42	0.71	0.40	mol kg^{-1}
$\Delta q_{\text{H}_2\text{O}}$	2.8	2.6	3	4.9	1.2	mol kg^{-1}
m_{sorbent}	454	375	580	340	635	ton
N_{beds}	1428	1184	1824	1072	2000	–
$\Phi_{\text{v,air}}$	6316	5222	8064	4727	8829	$\text{m}^3 \text{s}^{-1}$
Q_{H_2}	28	29	27	27	28	MW
Q_{CO_2}	44	38	52	42	46	MW
$Q_{\text{MeOH,cond}}$	12	13	12	12	12	MW
$Q_{\text{Reb.}}$	3.4	3.5	3.2	3.2	3.4	MW
$Q_{\text{CO}_2,\text{cool}}$	25	19	33	32	15	MW
$Q_{\text{H}_2,\text{cool}}$	0.5	0.52	0.47	0.47	0.49	MW
E_{Fan}	3.7	3	4.7	2.8	5.1	MW
E_{VSA}	1.6	1.3	2.1	7.3	0.12	MW
$E_{\text{FC,CO}_2}$	1.5	1.5	1.4	1.4	1.4	MW
$E_{\text{FC,H}_2}$	0.39	0.4	0.37	0.37	0.39	MW
$E_{\text{FP,H}_2\text{O}}$	0.015	0.015	0.014	0.014	0.015	MW
$E_{\text{Heat pump}}$	6.3	4.2	9.6	6.4	7.2	MW

¹Power to methanol efficiency.

²Excess water.

Table 7.S8 | Overview of the capital cost.

Parameter	1: Base Case	2A: Low T_{ads}	2B: High T_{ads}	3A: Low P_{des}	3B: high P_{des}	Unit
$C_{\text{Electrolysis}}$	87	90	82	82	86	M€
C_{Sorbent}	68	56	87	51	95	M€
$C_{\text{Air Fans}}$	19	16	25	15	27	M€
C_{VC}^3	6.7	5.6	8.2	23	0.8	M€
$C_{\text{Reactor steel}}$	0.6	0.5	0.8	0.5	0.9	M€
$C_{\text{CO}_2 \text{ capture}}$	95	77	121	89	124	M€
$C_{\text{CO}_2 \text{ capture}}^4$	308	254	403	360	353	€ ton $^{-1}_{\text{CO}_2}$
$C_{\text{FC CO}_2}^5$	6.2	6.3	5.9	5.9	6.1	M€
$C_{\text{FC H}_2}$	2.2	2.2	2.1	2.1	2.1	M€
C_{Reactor}	1.9	1.9	1.8	1.8	1.9	M€
$C_{\text{Distillation}}$	0.5	0.5	0.4	0.4	0.5	M€
C_{Methanol}	11	11	10	10	11	M€
C_{coolers}	2.0	1.5	2.6	2.5	1.3	M€
C_{Total}	194	181	216	183	222	M€
C_{Total}	298	268	350	298	344	€ ton $^{-1}_{\text{MeOH}}$
$C_{\text{Total, incl WT}}^6$	494	481	516	483	522	M€
$C_{\text{Total, incl WT}}$	758	713	836	785	809	€ ton $^{-1}_{\text{MeOH}}$

³VC = Vacuum compressor⁴Cost of CO₂, including capital cost, cost for electric energy (0.1€ kWh⁻¹) and cost steam (25€ ton⁻¹.)⁵FC = Feed compressor⁶Including capital cost of Wind Turbines

8

Outlook and recommendations

In this thesis the storage of renewable electricity into methanol is studied. Technology for the production of CO₂ from air is developed and a novel reactor for the conversion of CO₂ to methanol is designed, constructed and tested. In Chapter 1 it was shown that electricity storage in chemicals is required for long term and large scale storage (i.e. seasonal storage). Methanol is a good chemical storage medium because it is liquid at ambient conditions and a versatile product.

In Chapter 2 transport phenomena for the adsorption of CO₂ on solid amine sorbent were studied. An experimental method to measure intrinsic kinetics of adsorption was developed. It was found that a rate based isotherm equation is necessary for consistent prediction of both, adsorption rate and equilibrium loading. For air capture of CO₂ it can be concluded that the uptake rate of adsorption of CO₂ is strongly inhibited by diffusional resistances inside the sorbent particle.

The desorption of CO₂, studied in Chapter 3, showed that – when using an inert purge flow – the desorption rate is strongly influenced by the equilibrium between the gas and adsorbed phase. Because of the strong dependency of the isotherm on temperature, heat transfer is an import design parameter for a desorption reactor. The production of pure CO₂ from air was shown in Chapter 4. It was found that the energy requirement for desorption is strongly dependent on the working capacity of CO₂ and the amount of water co-adsorbing. Moreover, it was shown that a steam purge does not reduce energy requirement for desorption, although CO₂ working capacity was increased.

A novel reactor concept for the conversion of CO₂ to methanol was introduced in Chapter 5. Using two temperature zones in the reactor, ensures optimal catalyst temperature and full CO₂ conversion by in situ condensation of products. Moreover, proof of concept for operation under natural convection conditions was shown. The concept was analysed in more detail by modelling and experimental work in Chapter 6. It was shown by simulations that autothermal operation of the reactor is possible by internal heat exchange. The conversion per pass over the catalyst bed is identified as the most important design parameter for the reactor. Increasing residence time in the catalyst zone will increase conversion per pass – unless equilibrium is reached – and reduce the area required for heat exchange and the condenser because of lower recycle ratios.

The complete process of electricity to methanol was evaluated in chapter 7. The conceptual design and evaluation shows that renewable Methanol from CO₂ from air, water and renewable electricity is becoming a realistic option at reasonable costs of 750-800 € ton⁻¹.

8.1. Recommendations

In Chapters 4 and 7 it was shown that the energy and capital cost of CO₂ capture is strongly correlated to the CO₂ and H₂O working capacity. Compared to the base conditions in Chapter 7, a 25% decrease in CO₂ working capacity increases CO₂ by 30%, whereas a 25% increase reduces cost by 18%. While the adsorption of CO₂ on Lewatit VP OC 1065 in dry conditions is well known, the exact adsorption mechanism under humid conditions is not clear. In the work of Veneman et al. [85] a higher CO₂ capacity was seen with increasing relative humidity in the gas. In Figure 4.6, after an initial increase in CO₂ capacity at low relative humidity no further enhancement was seen at high relative humidity. Further investigation of this phenomena is important, because it might enhance CO₂ capacity and thereby reduce cost.

As discussed above, on one hand the co-adsorption of H₂O enhances the CO₂ working capacity, reducing energy requirement. On the other hand, the desorption of water raises an energy penalty for desorption. Therefore, a more detailed description of the H₂O isotherm can help to identify the sweet spot of the ratio between H₂O and CO₂ working capacities. Especially, the prediction of water capacities under desorption conditions is not well described and open for improvement.

Another major factor determining the effective working capacity is the solid efficiency, i.e. how close the actual working capacity is approaching the maximal equilibrium working capacity. In Chapter 7 a solid efficiency of 55% was used, as shown by the stoichiometric time approach by Yu et al. [60]. However, an constant air velocity was used in the evaluation by Yu. Controlling the air velocity by the loading of the sorbent – or by the outlet gas concentration – will enhance both solid and gas efficiency, while preventing excessive cost for air/solid contacting. Optimization of this operation strategy can be performed by dynamic modelling of the adsorption reactor.

The LOGIC reactor has been analysed under forced convective conditions in Chapter 6. However, ideally this reactor is operated under natural convection conditions to remove the requirement for moving parts inside the reactor. Operating under natural convection is shown to be successful in Chapter 5. Optimizing and designing such a natural convection reactor requires more knowledge about the prediction of the flow rate by natural convection in a system with chemical conversion and condensation. Therefore, (experimental) evaluation of natural convection flow in model systems and developing prediction methods for natural convection flow are important. Moreover, the influence of heat exchange on natural convection – as already touched upon in Chapter 6.5.3 – might even be more im-

portant for development of the LOGIC concept.

The control philosophy of the LOGIC reactor is another point requiring attention. Once the reactor including heat exchange is designed and built, only the condenser temperature can be changed during operation of the reactor. At constant condenser outlet temperature, the catalyst inlet temperature will be determined by the amount of heat exchanged. The catalyst outlet temperature will follow by the amount of reaction heat released. Moreover, when operating under natural convection conditions, the flow rate will be determined by the temperature difference between the catalyst and condenser section. To conclude, the condenser temperature can be controlled, while the flow rate and catalyst temperature follow by impulse and heat balances in the reactor.

In Chapter 6 it was seen that the predicted reactor productivity was strongly dependent on the kinetic model selected. Although, little variation between kinetic models was seen for predictions of single-pass fixed bed experiments in Appendix C. A difference between the two studies was the residence time in the catalyst, which was significantly higher in the LOGIC reactor. Therefore, further (experimental) studying of methanol kinetics is advised to improve model predictions of the LOGIC reactor and methanol reactor models in general. Especially, the prediction of initial reaction rates require more attention.

8.2. Outlook

8

In thesis we evaluated a process for the production of renewable methanol from air captured CO_2 and H_2O and renewable electricity. Currently it is not economically viable to produce renewable methanol using direct air capture and electrolysis. According to literature [229, 235, 246] cost for wind power, electrolysis and air capture are expected to reduce, improving process economics for renewable methanol. However, it is not expected that the renewable process will outperform the fossil based process in the near future. For renewable based processes, expensive harvesting of energy and carbon cannot compete with the large scale, low costs fossil fuels based alternatives.

Governmental legislation on emissions and ambitions for a climate-neutral future do open up opportunities for renewable based processes. The new Renewable Energy Directive II (RED II) of the European Union requires 14% of renewable energy, including methanol, to be used in the transport sector by 2030. In total 66 countries have put targets and mandates for the implementation of biofuels, some as high as 27% [248].

Moreover, general climate targets of the European Commission foresee a climate-neutral European Union in 2050 [249]. However, the chemical industry still requires a carbon source for the production of chemicals such as plastics. Next to biomass, renewable methanol – or indirectly CO_2 – is an excellent feedstock for the chemical industry. Processes for the production of olefins from methanol are already commercially available and by conversion of methanol to syngas, practically any chemical is within reach.

In the latest report of the Internal Panel on Climate Change [23] the need for negative emission technology to keep within the 1.5 degree scenario was shown. This shows the importance of development of direct air capture technology, especially for a country (partially) below the sea level as the Netherlands. Exceeding the 1.5 degree scenario will lead to further increase in sea levels.

It can be concluded that, although the proposed process of CO_2 and H_2O conversion to methanol using renewable electricity is not economically profitable today, it might be an important process for tomorrow.

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Appendices

A

Material properties and
prediction methods

A

A.1. Lewatit properties

Table A.1 | Lewatit VP OC 1065 properties.

Symbol	Value	Unit	Meaning	Reference
r_{pore}	12.5	nm	Pore radius	[55]
A_{pore}	50	m g^{-2}	Surface area	[55]
V_{pore}	0.27	cm g^{-3}	Pore volume	[55]
ε	0.23	$\text{m}^3 \text{m}^{-3}$	Particle voidage	[55]
τ	2.3	m m^{-1}	Pore tortuosity	[184]
d_p	520	μm	number average particle diameter	[55]
ρ_s	880	kg m^{-3}	Sorbent density	[184]
ρ_b	539	kg m^{-3}	Sorbent bulk density	App. B
λ_s	0.43	$\text{W m}^{-1} \text{K}^{-1}$	Sorbent thermal conductivity	App. B
$C_{p,s}$	1.58	$\text{kJ kg}^{-1} \text{K}^{-1}$	Sorbent heat capacity	[62]
$\Delta_r H$	75	kJ mol^{-1}	Reaction heat CO_2	[62]
$\Delta_{\text{ads}} H$	41	kJ mol^{-1}	Adsorption heat H_2O	[85]

A.2. Methanol catalyst

Table A.2 | Methanol catalyst properties.

Symbol	Value	Unit	Meaning	Reference
d_{particle}	5	mm	Pore radius	[159]
r_{pore}	10	nm	Pore radius	
ε_{bed}	0.4	–	Catalyst bed voidage	[159]
ε/τ	0.123	nm	Ratio porosity and tortuosity	
ρ_{cat}	1300	kg m^{-3}	Catalyst density	

A.3. Fluid Properties

A

Table A.3 | Fluid properties

Property	Unit	CO ₂	CO ₂	H ₂	CH ₃ OH	H ₂ O	Ref.
$h_0(298K)$ ¹	J mol ⁻¹	-393,500	-110,540	0	-201,160	-241,820	[214]
MW ²	kg mol ⁻¹	0.044	0.028	0.002	0.032	0.018	
V_{diff} ³	cm ³	26.9	18.9	29.9	7.07	12.7	[250]
P_c ⁴	MPa	7.374	3.494	1.293	8.097	22.064	[201]
T_c ⁵	K	304.12	132.85	32.98	512.64	647.14	[201]
ω ⁶	–	0.225	0.045	-0.217	0.565	0.344	[201]
p_f ⁷	–	0	0	0	0.2359	0.1277	[201]

¹ Standard enthalpy of formation

² Mol weight

³ Diffusion volume

⁴ Critical Pressure

⁵ Critical Temperature

⁶ Acentric factor, equation of state

⁷ Polarity factor, equation of state

A

A.3.1. Heat capacity

The mixed heat capacity is calculated as follows:

$$C_p = \sum_{i=1}^{N_c} \frac{C_{p,i}(T)w_i}{M_{w_i}} \quad (\text{A.1})$$

The gas heat capacity is given by equation A.2 with the constants in Table A.4 [215].

$$C_{p,i}^G = A + BT + CT^2 + DT^3 + ET^4 \quad (\text{A.2})$$

The liquid heat capacity is given by equation A.3 with the constants in Table A.5 [214].

$$C_{p,i}^L = R \left(\frac{A}{\tau} + B + C\tau + D\tau^2 + E\tau^3 + F\tau^4 \right), \tau = 1 - \frac{T}{T_c} \quad (\text{A.3})$$

Table A.4 | Constants for gas heat capacity [J mol^{-1}]. [215]

Compound	A	B	C	D	E
CO ₂	27.437	0.042315	-1.9555e-05	3.9968e-09	-2.9872e-13
CO	29.556	-0.0065807	2.013e-05	-1.2227e-08	2.2617e-12
H ₂	25.399	0.02017	-3.8549e-05	3.188e-08	-8.7585e-12
CH ₃ OH	40.046	-0.038287	0.00024529	-2.1679e-07	5.9909e-11
H ₂ O	33.933	-0.0084186	2.9906e-05	-1.7825e-08	3.6934e-12

Table A.5 | Constants for liquid heat capacity [J mol^{-1}]. [214]

Compound	A	B	C	D	E	F
CO ₂	0.500361	8.830377	-3.868837	10.32459	0.675891	1.845183
CO	0.434226	6.85227	-7.82624	25.69357	-39.2193	31.50626
H ₂	0.412752	1.939203	-0.676502	2.161263	-9.684044	14.4102
CH ₃ OH	0.612632	13.19554	-5.20887	-45.76212	91.19027	-44.45618
H ₂ O	0.25598	12.54595	-31.40896	97.7665	-145.4236	87.0185

A.3.2. Viscosity and Thermal conductivity

A

The gas phase mixed viscosity is calculated according to the mixing rules described by Wilke et al. [189, 216], see equation A.4.

$$\mu_g = \sum_{i=1}^{N_c} \frac{x_i \mu_i}{\sum_{j=1}^{N_c} x_j \Phi_{ij}} \quad (\text{A.4})$$

The mixed gas phase thermal conductivity is calculated similar to the mixed viscosity [217], as shown in equation A.5

$$\lambda_g = \sum_{i=1}^{N_c} \frac{x_i \lambda_i}{\sum_{j=1}^{N_c} x_j \Phi_{ij}} \quad (\text{A.5})$$

The Φ_{ij} is given in equation A.6 and is identical for both the mixed viscosity and mixed thermal conductivity.

$$\Phi_{ij} = \frac{\left(1 + \left(\frac{\mu_i}{\mu_j} \right)^{0.5} \left(\frac{M_{wj}}{M_{wi}} \right)^{0.25} \right)^2}{\sqrt{8} \left(1 + \frac{M_{wj}}{M_{wi}} \right)^{0.5}} \quad (\text{A.6})$$

In which μ is the viscosity at 200 °C and 50 bara of the pure component. For both properties the pure components are taken from the NIST database [218], see table A.6.

Table A.6 | Constants used for the calculation of the mixed gas phase viscosity and thermal conductivity [218].

	μ (Pa s)	λ (W m ⁻¹ K ⁻¹)
CO ₂	2.3365×10^{-5}	0.0329
CO	2.5212×10^{-5}	0.0382
H ₂	1.2277×10^{-5}	0.2700
CH ₃ OH	1.6400×10^{-5}	0.0386
H ₂ O	1.5710×10^{-5}	0.0400

A

A.3.3. Diffusion coefficients

The binary molecular diffusion coefficients are estimated by the method of Fuller, Schettler and Giddings [250, 251]. The molecular diffusion volume (V_{dif}) can be found in Table A.3.

$$D_{i,j} = \frac{1.013 \cdot 10^{-2} T^{1.75} ((Mw_i + Mw_j) / (Mw_i Mw_j))^{0.5}}{P \left((V_{\text{dif},i})^{1/3} (V_{\text{dif},j})^{1/3} \right)^2} \quad (\text{A.7})$$

The diffusion coefficient of component i in the mixture is found by [251]:

$$D_{i,m} = \left(\sum_{j,j \neq i}^{N_c} \frac{y_j}{D_{i,j}} \right)^{-1} \quad (\text{A.8})$$

The Knudsen diffusion coefficient, inside the catalyst pore, can be found by [187]:

$$D_{k,i} = \frac{2r_{\text{pore}}}{3} \sqrt{\frac{8RT}{\pi Mw}} \quad (\text{A.9})$$

The effective diffusion coefficient for diffusion inside the catalyst pore is found by [187]:

$$D_{i,\text{eff}} = \left(\frac{1}{D_{k,i}} + \frac{1}{D_{i,m}} \right)^{-1} \varepsilon / \tau \quad (\text{A.10})$$

A.4. Soave-Redlich-Kwong Equation of State

In the section below, the modified Soave-Redlich-Kwong equation of state is discussed [201]. The fluid density and enthalpy are determined with the use of the equation of state.

A.4.1. Fugacity

For pure substance the original SRK EoS is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (\text{A.11})$$

which can be written in the cubic form:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (\text{A.12})$$

in this equation A and B are defined as:

$$A = \frac{aP}{R^2T^2}, \quad B = \frac{bP}{RT} \quad (\text{A.13})$$

When working with mixtures, the parameters a and b are a function of the composition, as shown in equation A.14. The binary interaction parameters (k_{ij}) can be found in Table A.7 [201].

$$a = \sum_i^{N_c} \sum_j^{N_c} y_i y_j \sqrt{a_i a_j} (1 - k_{ij}), \quad b = \sum_i^{N_c} y_i b_i \quad (\text{A.14})$$

The pure component a_i and b_i are a function of the critical temperature (T_c), critical pressure (P_c), the acentric factor (ω_i) and a polarity correction parameter ($p_{f,i}$), see Table A.3 [201].

$$a_i = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}^2} \alpha_i, \quad b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (\text{A.15})$$

$$\alpha_i = 1 + m_i \left(1 - \sqrt{\frac{T}{T_c}} \right) - p_{f,i} \left(1 - \frac{T}{T_c} \right) \left(0.7 - \frac{T}{T_c} \right) \quad (\text{A.16})$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \quad (\text{A.17})$$

A

Now Z can be found by the solving equation A.11, the smallest solution for Z is the liquid phase value and the largest solution is the gas phase value. Next the fugacity coefficient can be found by:

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left[\frac{2 \sum_j^{N_c} y_j a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left(1 + \frac{B}{Z} \right) \quad (\text{A.18})$$

Table A.7 | mSRK equation of state interaction parameters [201].

k_{ij}	CO ₂	CO	H ₂	CH ₃ OH	H ₂ O
CO ₂	0	0.1164	0.1164	0.10	0.30
CO	0.1164	0	-0.0007	-0.37	-0.474
H ₂	0.1164	-0.0007	0	-0.125	-0.745
CH ₃ OH	0.10	-0.37	-0.125	0	-0.075
H ₂ O	0.30	-0.474	-0.745	-0.075	0

A.4.2. Enthalpy

The enthalpy of a for a certain composition y at pressure P and temperature T can be found by:

$$h(P, T, y) = \sum_i^{N_c} (h^{\text{id}}(T)y_i) + h_{\text{SRK}}(P, T, y) \quad (\text{A.19})$$

The ideal heat capacity for a pure compound at certain temperature is found by equation A.20, the standard enthalpy h_0 is found in Table A.3.

$$h^{\text{id}}(T) = h_0(298K) + \int_{298K}^T C_p \partial T \quad (\text{A.20})$$

The SRK-correction on the enthalpy can be found in the equation below [211].

$$h_{\text{SRK}}(P, T, y) = \left(\frac{P}{BRT} \right) \left(\frac{AR^2T^2}{P} - T \frac{\partial a}{\partial T} \right) \ln \left(\frac{Z}{Z+B} \right) + RT(Z - 1) \quad (\text{A.21})$$

$$\frac{\partial a}{\partial T} = -\frac{1}{\sqrt{T}} \sum_i^{N_c} \sum_j^{N_c} y_i y_j (1 - k_{ij}) \frac{1}{2\sqrt{a_i a_j}} \left(a_i \frac{a_j m_j}{\sqrt{\alpha_j T_{c,j}}} + a_j \frac{a_i m_i}{\sqrt{\alpha_i T_{c,i}}} \right) \quad (\text{A.22})$$

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B

Thermal conductivity of Lewatit VP OC 1065

Abstract

The thermal conductivity of Lewatit VP OC 1065 is determined by investigating temperature gradients within a fixed bed of particles, heated from the cylindrical wall and bottom area. From these experiments the effective thermal conductivity through the sorbent/air bulk can be determined. By use of the Zehner and Schlönder [188] equation the measured effective thermal conductivity is translated into the solid thermal conductivity. An average value of $0.43 \text{ W m}^{-1} \text{ K}^{-1}$ was found for the solid thermal conductivity of Lewatit VP OC 1065.

This appendix is based on the Supporting Information of the following publication:

M.J. Bos, T. Kreuger, S.R.A. Kersten, D.W.F. Brilman, *Study on heat and mass transfer limitations and intrinsic kinetics for CO₂ adsorption in solid amine sorbent*, Accepted for publication in **Chemical Engineering Journal**, doi: 10.1016/j.cej.2018.11.072

B

In this appendix more details are given about the experiments and interpretation to determine the solid thermal conductivity of Lewatit VP OC 1065. The thermal conductivity of the sorbent is determined by investigating temperature gradients within a sorbent volume. From these experiments the effective thermal conductivity through the sorbent bulk can be determined. Using literature equations the sorbent particle thermal conductivity can be determined.

B.1. Theory

Within the sorbent bed heat is transferred by conduction. The effective thermal conduction of the sorbent bed is unknown, but is a function of two parameters; 1) the thermal conduction of the sorbent bulk, which is unknown and 2) the change in effective conduction due to the fact that the bed is composed of particles instead of a continuous sorbent bulk.

The effect of particles instead of continuous bulk can be incorporated in numerous ways. The effective thermal conduction is usually derived by lumping several heat transfer mechanisms together into a single value.[252] A typical thermal conductivity model takes into account a selection of the following types of heat transfer:

- Thermal conductivity of a packed bed saturated with a stagnant fluid, consisting of
 - Conduction within the solid particle
 - Conduction through the contact area between particles
 - Conduction through the stagnant gas phase
 - Radiation between solid surfaces
- Enhanced thermal conductivity by a moving fluid
- Enhanced thermal conductivity by moving both fluid and solid.

The developed models each have an expression for their respective selection of heat transfer types. The effective thermal conductivity of a porous sorbent in stagnant gas is lower than the conductivity of a continuous sorbent volume as long as the thermal conductivity of the solid is higher than the fluid. A moving fluid enhances effective thermal conductivity.

B.2. Experimental

B.2.1. Experimental setup

The experimental setup is presented in figure B.1. A double walled 1200 mL glass vessel was heated using a closed loop of glycerol-water thermostated by a Julabo F32-HD circular heater. The fluid was circulated between the volume enclosed by the vessel walls and the heater. Thermocouples were inserted throughout the reactor lid, in figure B.1 the position of the thermocouples are represented by blue dots. The temperature of the surroundings is also measured.

B

B.2.2. Experimental procedure

Sorbent was dried at 50°C for 48 hours under N₂ to eliminate water and CO₂ adsorbed and was transferred to the vessel directly after drying was completed. The vessel lid was sealed to attenuate further contact between sorbent and environment, minimizing sorption effects during heat transfer experiments. To ensure a homogeneous sorbent temperature the reactor is kept at a temperature of 20°C for 18 hours before measurements commence.

At the start of a typical measurement the circular heater is set to the experimental temperature and the data logging is started. Experimental temperatures were varied between 30 to 50 °C. The hot fluid transfers heat to the sorbent volume. Since the location of thermocouples is known exactly, precise data on temperature gradients within the sorbent over time is obtained.

B.3. Calculation method

In this section the calculation method is discussed. A model is constructed that uses the heating curve of the internal vessel walls and vessel bottom to model the temperature gradients within the sorbent volume. Modelled temperature increase at the location of several thermocouples will be compared to experimental data. Model data is fit to experimental data by varying λ_{eff} .

B.3.1. Assumptions and simplifications made

For this calculation several assumptions are made:

1. The sorbent volume is considered a homogeneous mass.
2. The gas still present in the vessel is stationary. Therefore no free convective

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Figure B.1 | Experimental setup used to determine λ_{eff} . Blue dots indicate the location of the thermal couples. The red arrows indicate heat flows.

Figure B.2 | Simplification used in the model to describe the experimental setup. Numbers denote the boundaries as described in Table B.1

term is taken into account in the calculation of λ_{eff} .

3. The sorbent temperature at the vessel wall and bottom are equal to the inner wall and bottom temperature, respectively.
4. The liquid temperature does not vary over the wall length.
5. Sorption effects may be ignored completely due to pretreatment in an oven.

The reactor vessel is cylindrical, meaning an internal axis of symmetry is present. This axis of symmetry is used to reduce the system from a three-dimensional cylinder to a two-dimensional area. This area encloses the central cylinder axis, bottom of the vessel, wall of the vessel and top of the vessel. The simplification is presented in Figures B.2.

B.3.2. Model equations

In this section the model equations will be derived. Starting from a heat balance taking into account only conductive heat transport:

$$\rho_s C_{p,s} \frac{\partial T}{\partial t} - \nabla \cdot [\lambda_{\text{eff}} \nabla T] = 0 \quad (\text{B.1})$$

Since the problem has the shape of a cylinder it is beneficial to use cylindrical coordinates:

$$\rho_s C_{p,s} \frac{\partial T}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left[\lambda_{\text{eff}} r \frac{\partial T}{\partial r} \right] - \frac{1}{r^2} \frac{\partial}{\partial \theta} \left[\lambda_{\text{eff}} \frac{\partial T}{\partial \theta} \right] - \frac{\partial}{\partial z} \left[\lambda_{\text{eff}} \frac{\partial T}{\partial z} \right] = 0 \quad (\text{B.2})$$

Since the problem has an internal axis of symmetry $\frac{\partial}{\partial \theta} = 0$ and may be removed:

$$\rho_s C_{p,s} \frac{\partial T}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left[\lambda_{\text{eff}} r \frac{\partial T}{\partial r} \right] - \frac{\partial}{\partial z} \left[\lambda_{\text{eff}} \frac{\partial T}{\partial z} \right] = 0 \quad (\text{B.3})$$

Multiplying by r :

$$r \rho_s C_{p,s} \frac{\partial T}{\partial t} - \frac{\partial}{\partial r} \left[\lambda_{\text{eff}} r \frac{\partial T}{\partial r} \right] - \frac{\partial}{\partial z} \left[r \lambda_{\text{eff}} \frac{\partial T}{\partial z} \right] = 0 \quad (\text{B.4})$$

Since MATLAB uses a cartesian coordinate system, r is substituted by y and the problem is translated into a format suitable for MATLAB:

$$y \rho_s C_{p,s} \frac{\partial T}{\partial t} - \nabla \cdot [y \lambda_{\text{eff}} \nabla T] = 0 \quad (\text{B.5})$$

B.3.3. Boundary conditions

Assumption 1 dictates the boundary conditions of edge 2 and 3. The central axis (edge 1) condition follows from symmetry, dictating that no energy is transported through this edge. Edge 4 is not controlled by the heater, therefore an flux $\vec{J}_{top}A_{top}$ is present here. This parameter is also fitted during the solving process, by comparing model and experimental steady state temperatures. Initial conditions are known, since an uniform bed temperature is achieved before measurements commence.

Table B.1 | Boundary conditions used in λ_{eff} model

No.	Boundary	Equation	Comment
1	Center axis	$\frac{dT}{dr} = 0$	Symmetry conditions
2	Vessel bottom	$T = T_{water,bot}$	From exp. data
3	Vessel wall	$T = T_{water,wall}$	From exp. data
4	Vessel top	$\rho_s C_{p,s} \frac{dT}{dt} = J_{top} A_{top}$	Heat leak, solved parameter

B.3.4. Results effective thermal conductivity

One results of a fit of the model is shown in Figure B.3. All the found effective thermal conductivity of the bulk can be seen in Table B.2.

B.4. Bed void fraction

The bed void fraction can be determined by dividing the sorbent bed density by the sorbent density. Therefore, first the sorbent bed density is determined. For this reason, Lewatit VP OC 1065 has been dried under N_2 for 48h. The density has been measured by weighing a known volume of the sorbent, see results Figure B.4. The density has been calculated at $533 \pm 3 \text{ kg m}^{-3}$.

The error in mass δM arising from balance accuracy is 0.1 gram. The error in volume, arising from vessel accuracy δV is 0.002 L. The error in ρ_s is found by error propagation to be 3 kg m^{-3} .

$$\delta \rho_s = \rho_s \sqrt{\left(\frac{\delta M}{M}\right)^2 + \left(\frac{\delta V}{V}\right)^2} \quad (\text{B.6})$$

Using the solid density of 880 kg m^{-3} from literature [184] and the bed density of

Figure B.3 | Example of model fit

Figure B.4 | Mass as function of volume

533 kg m⁻³ a bed voidage of 0.39 is found by equation B.7.

$$\varepsilon_{bed} = 1 - \frac{\rho_{bed}}{\rho_s} \quad (\text{B.7})$$

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B.5. Solid thermal conductivity

With the equation B.8 by Zehner and Schlünder [188] the measured effective thermal conductivity can be translated into the solid thermal conductivity. The results are shown in Table B.2. As shown there is a small influence of temperature in the thermal conductivity. However, since the measured value are averages over the whole temperature range no trend in temperature can be determined. For now, the average value of 0.43 W m⁻¹ K⁻¹ will be used in the calculations in the main text.

$$\frac{\lambda_e^g}{\lambda_f} = (1 - \sqrt{1 - \epsilon}) + \frac{2\sqrt{1 - \epsilon}}{1 - \kappa^{-1}B} \cdot \left[\frac{(1 - \kappa^{-1})B}{(1 - \kappa^{-1}B)^2} \ln\left(\frac{1}{\kappa^{-1}B}\right) - \frac{B + 1}{2} - \frac{B - 1}{1 - \kappa^{-1}B} \right] \quad (\text{B.8})$$

with

$$B = 1.25 \left(\frac{1 - \epsilon}{\epsilon} \right)^{\frac{10}{9}} \quad (\text{B.9})$$

Table B.2 | Overview of found k_{eff} and k_{solid}

T_{cold} (°C)	T_{hot} (°C)	k_{eff} (W m ⁻¹ K ⁻¹)	k_{solid} (W m ⁻¹ K ⁻¹)
20	30	0.120	0.409
20	40	0.121	0.419
20	40	0.121	0.419
20	40	0.123	0.438
20	50	0.126	0.458

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Kinetics of methanol synthesis

Abstract

The kinetics of methanol synthesis have been studied. The widely used kinetic models of Graaf et al. and Bussche and Froment have been refitted on a new experimental data set containing 234 experiments. A new kinetic model is proposed to incorporate recent physical evidence in literature and to reduce over-parametrisation of rate equations for methanol synthesis. The kinetic parameters are fitted by the chi-squared method. Statistical analysis by the 5-fold Cross-Validation method showed that the proposed 6-parameter kinetic model has the best predictive power to experimental data.

C.1. Introduction

Methanol kinetics have been widely studied in literature and already shortly discussed in the Chapter 1.5.3. However, consensus about reaction pathways is not reached. Bozzano and Manenti [157] gave an overview of kinetic models in literature. The most widely used models are the kinetic rate equations of Graaf et al. [143, 159] and Bussche and Froment [149]. In the current work, the kinetic models of Graaf et al. and Bussche and Froment are reassessed using a new experimental data set containing 234 experiments. Moreover, effort is taken to reduce the number of fitting parameters in the rate equations by critical analysis of cross correlations and by developing a new kinetic model for methanol synthesis. By reducing the number of parameters, the robustness of the rate equations is increased and the predictive value of the model is improved.

C.2. Theoretical section

In the section below the models discussed are given. Partial pressures are replaced by fugacities, as calculated by the mSRK equation of state as presented by van Bennekom et al. [201]. For the chemical equilibrium constants, the reassessed relationships from Graaf and Winkelman [144] are used.

C.2.1. Graaf et al.

The original model of Graaf et al. [143, 159] includes three rate equations, one for CO hydrogenation (eq. C.1), one for CO₂ hydrogenation (eq. C.2) and one for the RWGS reaction (eq. C.3). The model of Graaf uses two adsorption sites, one site for CO and CO₂ (eq. C.4) and another side for H₂ and H₂O (eq. C.5).

$$r_{CO} = k_{CO} K_{CO} \left(f_{CO} f_{H_2}^{\frac{3}{2}} - \frac{1}{K p_{CO}^{\circ}(T)} \frac{f_{CH_3OH}}{f_{H_2}^{\frac{1}{2}}} \right) \Theta_{G_A} \Theta_{G_B} \quad (C.1)$$

$$r_{CO_2} = k_{CO_2} K_{CO_2} \left(f_{CO_2} f_{H_2}^{\frac{3}{2}} - \frac{1}{K p_{CO_2}^{\circ}(T)} \frac{f_{CH_3OH} f_{H_2O}}{f_{H_2}^{\frac{3}{2}}} \right) \Theta_{G_A} \Theta_{G_B} \quad (C.2)$$

$$r_{RWGS} = k_{RWGS} K_{CO_2} \left(f_{CO_2} f_{H_2} - \frac{1}{K p_{RWGS}^{\circ}(T)} f_{H_2O} f_{CO} \right) \Theta_{G_A} \Theta_{G_B} \quad (C.3)$$

$$\Theta_{G_A} = (1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})^{-1} \quad (C.4)$$

$$\Theta_{G_B} = \left(f_{H_2}^{\frac{1}{2}} + \frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}} f_{H_2O} \right)^{-1} \quad (C.5)$$

C.2.2. Bussche and Froment

Bussche and Froment [149] pointed out, that Graaf et al. by assuming three reaction equations, predict the intermediate surface concentrations of formyldehyde and methoxy species two times. Therefore, they proposed a kinetic model without a separate reaction rate equation for CO hydrogenation. Consequently, according to this model, CO can only be converted to methanol by the water gas shift reaction followed by CO₂ hydrogenation. Moreover, only one active surface adsorption site for CO₂ hydrogenation and heterolytic decomposition of H₂ is assumed. The kinetic rate equations of Bussche and Froment are given in equations (C.6) to (C.8).

$$r_{CO_2} = k_{CO_2}f_{CO_2}f_{H_2} \left(1 - \frac{1}{Kp_{CO_2}^\circ(T)} \frac{f_{H_2O}f_{CH_3OH}}{f_{H_2}^3f_{CO_2}} \right) \Theta_{BF^3} \quad (C.6)$$

$$r_{RWGS} = k_{RWGS}f_{CO_2} \left(1 - \frac{1}{Kp_{RWGS}^\circ(T)} \frac{f_{H_2O}f_{CO}}{f_{CO_2}f_{H_2}} \right) \Theta_{BF} \quad (C.7)$$

$$\Theta_{BF} = \left(1 + \frac{K_{H_2O}}{K_8K_9K_{H_2}} \frac{f_{H_2O}}{f_{H_2}} + K_{H_2}f_{H_2}^{\frac{1}{2}} + K_{H_2O}f_{H_2O} \right)^{-1} \quad (C.8)$$

C.2.3. Proposed model

A new kinetic model for methanol synthesis is proposed, to incorporate recent physical insights and experimental evidence presented in literature and to reduce over-parametrisation of reaction rate equations. The basis of the proposed model is the model of Bussche and Froment [149]. Instead of assuming one adsorption site, three active surface sites are introduced [151]. The sites included are an oxidized surface site active in CO-hydrogenation ($\odot$), a reduced surface site active in CO₂ hydrogenation ($*$) and an adsorption site for heterolytic decomposition of hydrogen ($\otimes$). The model is a Langmuir-Hinshelwood type model. The rate determining step (RDS) for the RWGS is assumed to be the dissociation of CO₂ on the

Table C.1 | Elementary reaction steps for the proposed kinetic model. $\odot$ = oxidized site for CO hydrogenation, $*$ = reduced site for CO_2 hydrogenation, $\otimes$ = hydrogen adsorption site.

Reaction	Elementary reaction step	Equilibrium constant
CO ₂ hydrogenation		
1	$\text{H}_2(\text{g}) + 2\otimes \rightleftharpoons 2\text{H}\otimes$	K_{H_2}
2	$\text{CO}_2(\text{g}) + \text{O} * + * \rightleftharpoons \text{CO}_3 **$	K_2
3	$\text{CO}_3 ** + \text{H}\otimes \rightleftharpoons \text{HCO}_3 ** + \otimes$	K_3
4	$\text{HCO}_3 ** + * \rightleftharpoons \text{HCO}_2 ** + \text{O}*$	K_4
5	$\text{HCO}_2 ** + \text{H}\otimes \rightleftharpoons \text{H}_2\text{CO}_2 ** + \otimes$	k_{5a} (RDS)
6	$\text{H}_2\text{CO}_2 ** \rightleftharpoons \text{H}_2\text{CO} * + \text{O}*$	K_{5b}
7	$\text{H}_2\text{CO} * + \text{H}\otimes \rightleftharpoons \text{H}_3\text{CO} * + \otimes$	K_6
8	$\text{H}_3\text{CO} * + \text{H}\otimes \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) + * + \otimes$	K_7
Water formation		
9	$\text{O} * + \text{H}\otimes \rightleftharpoons \text{OH} * + \otimes$	K_8
10	$\text{OH} * + \text{H}\otimes \rightleftharpoons \text{H}_2\text{O} * + \otimes$	K_9
11	$\text{H}_2\text{O} * \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$	K_{10}
RWGS reaction		
12	$\text{CO}_2(\text{g}) + * \rightleftharpoons \text{CO}_2*$	K_{11}
13	$\text{CO}_2 * + \odot \rightleftharpoons \text{CO} \odot + \text{O}*$	k_{12} (RDS)
14	$\text{CO} \odot \rightleftharpoons \text{CO}(\text{g}) + \odot$	K_{13}

catalyst surface [158]. For the other reactions the RDS is given in Table C.1, next to all elementary reaction steps.

Targeting a statistically sound model, an effort is made to reduce the amount of fitted parameters as much as possible. This resulted in two models: the first model includes 8 parameters and is physically sound. However, on fitting the kinetic data some parameters were found to be highly cross-correlated, see Table C.3. It was found that K_{H_2} is strongly cross correlated with $\frac{K_{\text{H}_2\text{O}}}{K_9}$ and $K_{\text{CH}_3\text{OH}}$. Therefore, the 8-parameter model was further reduced to an 6-parameter model, as further discussed below.

The kinetic rate equation is based on the elementary pathways as shown in Table C.1. Below, the derived rate equations are given.

$$r_{\text{CO}_2} = k_{\text{CO}_2} K_{\text{H}_2} f_{\text{CO}_2} f_{\text{H}_2} \left(1 - \frac{1}{K p_{\text{CO}_2}^o(T)} \frac{f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}}}{f_{\text{H}_2}^3 f_{\text{CO}_2}} \right) \theta^{*2} \theta^{\otimes} \quad (\text{C.9})$$

where $k_{CO_2} = k_{5a}^+ c_{*,t}^2 c_{\odot,t} K_2 K_3 K_4$.

$$r_{RWGS} = k_{RWGS} f_{CO_2} \left(1 - \frac{1}{K p_{RWGS}^\circ(T)} \frac{f_{CO} f_{H_2O}}{f_{CO_2} f_{H_2}} \right) \theta^* \theta^\odot \quad (C.10)$$

where $k_{RWGS} = k_{12}^+ c_{*,t} c_{\odot,t} K_{11}$.

According to catalyst surface measurements [253] the hydroxyl, methoxy and formate groups are most abundant on the surface. Therefore, all other surface species are assumed to be zero at surface and the following balance for the surface occupation is derived:

$$c_{*,t} = c_* + c_{OH*} + c_{H_3CO*} + c_{HCO_2**} \quad (C.11)$$

Methoxy groups are assumed to adsorb on the reduced active centers, because Kandemir et al. [253] pointed out that formate and methoxy compete for the same sites. The concentration of formate species (c_{HCO_2**}) is omitted from the surface concentration balance and included in the overall rate constant because it was seen that this factor was constant based on statistics. When the balance of equation (C.11) is solved for the fraction of free reduced active sites (θ^*), equation (C.12) is found. The same balance is made and solved for the hydrogen site (eq. (C.13) and for the oxidized active centers (eq. C.14). No surface species associated with the oxidized sites were found in literature, therefore the fraction of free oxidized sites is equal to unity.

$$\theta^* = \left(1 + \frac{f_{H_2O} K_{H_2O}}{\sqrt{f_{H_2} K_{H_2}} K_9} + \frac{f_{CH_3OH} K_{CH_3OH}}{\sqrt{f_{H_2} K_{H_2}}} \right)^{-1} \quad (C.12)$$

$$\theta^\odot = \left(1 + \sqrt{f_{H_2} K_{H_2}} \right)^{-1} \quad (C.13)$$

$$\theta^\odot = 1 \quad (C.14)$$

The above model (eq. C.9-C.14) contains 8 *fitting parameters* when the adsorption isotherms of K_{H_2O}/K_9 and K_{CH_3OH} are taken constant. The amount of parameters can be further reduced by the assumption that the hydrogen active sites are always occupied [143]. This assumption will hold in any system where hydrogen is available in excess. Assuming the adsorption constants are linearly dependent on each other, the hydrogen adsorption isotherm can be lumped under the k_{CO_2} and

k_{RWGS} . Following, a kinetic model with 6 *fitting parameters* (eq. C.15-C.17) is proposed:

$$r_{CO_2} = k_{CO_2} f_{CO_2} f_{H_2}^{\frac{3}{2}} \left(1 - \frac{1}{K p_{CO_2}^\circ(T)} \frac{f_{CH_3OH} f_{H_2O}}{f_{H_2}^3 f_{CO_2}} \right) \theta^{*2} \quad (C.15)$$

where k_{CO_2} is a lumped fitting parameter representing $k_{5a}^+ c_{*,t}^2 c_{O,t} K_{H_2}^{\frac{3}{2}} K_2 K_3 K_4 K_{CH_3OH}^{-2}$.

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$$r_{RWGS} = k_{RWGS} f_{CO_2} f_{H_2}^{\frac{1}{2}} \left(1 - \frac{1}{K p_{RWGS}^\circ(T)} \frac{f_{CO} f_{H_2O}}{f_{CO_2} f_{H_2}} \right) \theta^* \quad (C.16)$$

where $k_{RWGS} = k_{12}^+ c_{*,t} c_{O,t} K_{11} K_{H_2}^{\frac{1}{2}} K_{CH_3OH}^{-1}$ and with:

$$\theta^* = \left(f_{H_2}^{\frac{1}{2}} k_{H_2} + f_{H_2O} k_{H_2O/9} + f_{CH_3OH} \right)^{-1} \quad (C.17)$$

In the above equations f_i is in bar and r_i is in mol/kg_{cat}s. k_{CO_2} and k_{RWGS} are both described using the Arrhenius equation (eq. C.22). k_{H_2} and $k_{H_2O/9}$ are constants. In the results section the two models are distinguished by their number of parameters ($N_p = 6$ or 8).

C.3. Experimental section

The experimental data of this work is divided into three groups. The experimental data set consists of 140 CSTR-type experiments by Seidel et al. [151], 91 experiments with data of this work, using a PFR-type set-up. The set of experiments of this work can be split-up in two different sets. The first set is measured at National Institute of Chemistry of Slovenia, containing 80 experiments. The other set, containing 11 experiments is measured at the University of Twente. The total experimental set covers conditions in the following ranges: 453 to 573 K, 20 to 70 bar and 2,000 to 10,000 GHSV. Conditions in the LOGIC reactor range from 423 to 573K and 20,000 to 150,000 GHSV at 50 bar.

C.3.1. Setup Kemijski inštitut

The first of data is produced with the use of the set-up of the National Institute of Chemistry of Slovenia, Kemijski inštitut. The experimental set-up and methods for this data can be found in literature [254, 255]. Experiments are performed in the range from 483 K to 533 K, 20 and 50 bara and 2000 to 10000 GHSV. Dimensions for

Figure C.1 | Experimental setup for the kinetic experiments. The insert shows the positioning of the catalyst bed and thermocouples inside the reactor.

this reactor are $6.35 \cdot 10^{-3}$ m in diameter and $3.16 \cdot 10^{-2}$ m in length. The amount of catalyst varies per reactor and can be found in the Supporting Information per experimental point.

C.3.2. Setup University of Twente

The experiments at the University of Twente are performed in the fixed bed setup shown in Figure C.1. Premixed gas (MG) is supplied from a gas bottle and preheated before it enters the isothermal catalyst bed. Product vapors are condensed and collected in a small reservoir (E-6, Fig. C.1), while non-condensable gases leave the system by the gas flow meter (GM-1, Fig. C.1). The process flow diagram is discussed in more detail below.

The top section of the flow scheme includes the feed gas preparation. The flow of each individual gas feed is regulated by a mass flow controller (MFC-1 to MFC-5) (Brooks Instruments, 5850TR). All gaseous feed stream are mixed in a central tube located in the pre-heater block (E-1) controlled by an Eurotherm 2132 PID controller. A pressure sensor (PI-1) (GE Oil & Gas, Unik PTX-7517-3257) measures the inlet pressure.

The Cu/ZnO/Al₂O₃ methanol catalyst (Johnson Matthey, CP-488) is crushed and loaded into a 67 centimeters long quartz tube (E-4) with 3 mm internal diameter. The insert in figure C.1 shows the layout of the quartz tube and the positioning of the thermocouples. The catalyst bed is about 0.28 m long and contains about 1.54 grams of catalyst. Two centimeters of quartz wool keeps the catalyst in position and ensures equal gas distribution. The quartz tube is placed in a metal tube (Inconel 600) (E-3). The metal tube is enclosed by two heaters in an isolation shell [E-2].

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Gas analysis

Vapor products are condensed in the shell and tube condenser (E-5) with water as coolant. Liquid products are collected in a small reservoir (E-6) and can be removed from the setup by opening V-13. The temperature (TI-3) and pressure (PI-2) after the reactor are monitored. A back pressure controller (BPC) regulates the pressure in the reactor. Pressure sensor PI-3 and PI-4 indicate the pressure directly after the BPC and before the gas meter, respectively. Needle valve V-15 is adjusted so a pressure around 0.3 barg is created to transport the product gases to the GC (E-7). When no gas samples are taken the product gases leave the setup by the gas meter (GM) (Ritter, TG0.5-1.4571-PVC). Temperature sensor TI-4 is used to correct the gas flow for temperature. Gas composition was determined using gas chromatography (Varian 450-RGA). The GC is equipped with three channels. Channel 1 analyses hydrogen using TCD detection on a Hayesep Q column (Agilent CP1305) and a Molsieve 5A column (Agilent CP1306) using N₂ as carrier gas. Channel 2 detects permanent gases using TCD detection on a Hayesep Q column (Varian CP1308), Hayesep N column (Varian CP1307) and a Molsieve 13X column (Varian CP1309) using helium as carrier gas. Channel 3 detect hydrocarbons using FID detection using a CP-Sil 5CB column (Varian CP1310) and a Select Al₂O₃/MAPD column (Varian CP7433) using helium as carrier gas. The reactor is directly connected to the GC and the tubing between the GC and setup is flushed using N₂ between gas samples.

Liquid analysis

The liquid product was analyzed in a HPLC (Agilent Technologies 1200 Series) using RID detection and GROM Resin H+ IEX column equipped with a pre-column. The injected volume was 10 μL, the temperature 65°C and the mobile phase 5 mM H₂SO₄ at 0.6 mL min⁻¹. Calibration curves were obtained by injecting mixtures of known composition (Sigma Aldrich HPLC grade Methanol and milliQ ultrapure water) in the range of interest.

Experimental procedure

First the cooling water is switched on and the mix gas MFC is set to the desired gas flow. The system is pressurized using the feed gas, after which it will flush the system. Heaters are switched on and the system is stabilized for at least 30 minutes after reaching the set point conditions. At the start of the experiment liquid is drained from the collection vessel. At the end of an experiment the weight of the total collected liquid is measured on an analytical balance (Mettler AE 160). The conversion of CO₂ is determined by the gas composition and the total outlet gas flow. Selectivity is determined by the gas composition of CO assuming methanol and CO being the only carbon containing products, next to CO₂. Experiments are performed between 451 K and 523 K, at a pressure of 20 to 50 bara and at a constant flow of 3000 GHSV.

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C.4. Parameter estimation and statistical method

For analysis of experimental data and fitting of the kinetic models a reactor model is constructed. The reactor model (eq. C.18) consists of an isothermal plug flow pseudo-homogeneous model [206]. The presence of external and internal mass transfer limitations are checked using respectively the Mears' and Weisz-Prater criteria [256]. The criteria were met for all of the experimental conditions. Thereby, it can be concluded that there are no significant mass transport limitations present during the experiments. Heat effects are neglected, since the diameter of the quartz tube is small (3mm)

$$\frac{\phi_m}{A_r} \frac{dw_i}{dx} = M_{wi} \sum_{j=1}^3 v_{i,j} (1 - \epsilon_b) \rho_{cat} r_j \quad (\text{C.18})$$

For a fair comparison, also the kinetic parameters for the Graaf et al. and Bussche and Froment kinetic models are refitted to the entire data set. The Arrhenius equations for adsorption constants and kinetic rate equations are rewritten in its logarithmic form (eq. (C.19) and (C.20)) to improve numerical sensitivity. All constants are back calculated to the original Arrhenius form (eq. (C.21) and (C.22)).

$$\ln(K_i) = a_i - b_i T^{-1} \quad (\text{C.19})$$

$$\ln(k_i) = a_i - b_i T^{-1} \quad (\text{C.20})$$

$$K_i = A_i \exp\left(\frac{B_i}{RT}\right) = \exp\left(\frac{\Delta S^\circ_{ads}}{R}\right) \exp\left(\frac{-\Delta H^\circ_{ads}}{RT}\right) \quad (C.21)$$

$$k_i = A_i \exp\left(\frac{B_i}{RT}\right) = A \exp\left(\frac{-E_A}{RT}\right) \quad (C.22)$$

where $A_i = \exp(a_i)$ and $B_i = -b_i R$.

C

A physically sound fit of kinetic parameters must follow these rules [143, 149, 257]:

- Rule 1: $k > 0$ and $K > 0$, imposed by logarithmic Arrhenius form
- Rule 2: $E_A > 0$ or $b_i > 0$, imposed by bounds
- Rule 3: $-\Delta H^\circ_{ads} > 0$ or $b_i < 0$, imposed by bounds
- Rule 4: $0 < -\Delta S^\circ_{ads} < S^\circ_{gas}$, checked afterwards

The parameter estimation is done by using the χ^2 (chi-Square) fitting method. The quantity of χ^2 is a sum of six component residual squared errors summed over N measurements and normalized on the unit standard deviation, as shown in equation (C.23). The global minimum in χ^2 is found by using the Global Optimization Toolbox of MATLAB®. GlobalSearch is initiated with the fmincon solver and the Sequential Quadratic Programming (SQP) algorithm. The bounds for the fitted parameters are set to follow the rules presented above to produce physically correct solutions.

$$\chi^2 = \sum_{j=1}^N \sum_{i=1}^{N_c} \left(\frac{w_i - \hat{w}_i}{\sigma_{w_i}} \right)^2_j \quad (C.23)$$

The σ_{w_i} from equation (C.23) is calculated for each experiment. It is composed of the standard deviation of the calibration curve of the GC plus the standard deviation of at least three GC measurements per experiment. The standard deviation of the measured flows and feed compositions are also taken into account. For the experiments of Seidel it is assumed that each component has a standard deviation of 0.002 in mole fraction. All experimental values can be found in the Supporting Information and in the article of Seidel [151].

To statistically determine a good fit with uncertainty boundaries the 5-fold Cross-Validation (CV) method is used [258]. The method states that a data set can be divided into five random folds (groups). Five unique training sets can be made when one of the five folds is taken out. The training set (consisting of four folds) is used for fitting the model and the test set (consisting of one fold) is used for validation.

The purpose of this method is to determine the predictive ability of a model outside the original training set.

Per training set the mean squared error (MSE) for all experimental data points can be calculated as shown in equation (C.25). The mean of the five test MSE's gives an indication of the prediction outside the training set (eq. (C.24)), the lower $CV_{(5)}$ the better the predictive capabilities of the model. Once the parameter set with lowest $CV_{(5)}$ is found, the MSE (defined as MSE_{best}) is calculated over the total experimental data set. Using these two definitions, the predictive capabilities ($CV_{(5)}$) and the ability to fit a known data set (MSE_{best}) for each kinetic model is shown. A kinetic model is preferable better in predicting, rather than fitting a known data set extremely well. When the model is good in predicting, the model can be used to predict conversion and selectivity's outside the original experimental conditions.

$$CV_{(5)} = \frac{1}{5} \sum_{i=1}^5 MSE_i \quad (C.24)$$

with

$$MSE_i = \frac{1}{N_{exp}} \frac{1}{N_c} \sum_{j=1}^N \sum_{i=1}^{N_c} (w_i - \hat{w}_i)_j^2 \quad (C.25)$$

The standard deviation of each fitted parameter is calculated as the standard deviation over parameters found by the five training sets, see equation (C.26). In this equation p_i is the fitted parameter of the MSE_{best} fit. The higher $\sigma_{p,avg}$, the more the parameters are changing between training sets. Therefore, the lower the found standard deviation is the more reliable the fit is.

$$\sigma_{p,avg} = \frac{1}{N_p} \sum_{i=1}^{N_p} \frac{\sigma_{p_i}}{|p_i|} \quad (C.26)$$

Another number indicating the goodness of model prediction is shown in equation C.27. This relation indicates what percentage of predicted model points is within one experimental standard deviation. The higher $\hat{w}_{pred}$ the better the prediction capabilities of the model are.

$$\hat{w}_{pred} = \frac{1}{N} \frac{1}{N_c} \sum_{i=1}^N \sum_{i=1}^{N_c} (w_i - \sigma_{w_i}) < \hat{w}_i < (w_i + \sigma_{w_i}) \quad (C.27)$$

Table C.2 | Comparison between the fitted kinetic models based on the mean squared error (MSE) and the R^2 . Also the original model R^2 on this data set is shown and the number of parameters (N_p). All of the parameters of each model are refitted.

Model	$CV_{(5)}$ ($\cdot 10^{-5}$)	MSE_{best} ($\cdot 10^{-5}$)	R^2	R^2 original	$\sigma_{p,avg}$ (%)	$\hat{w}_{pred}$ (%)	N_p
Graaf et al.	1.58	1.36	0.995	0.904	54	52.4	12
Bussche and Froment	3.57	2.52	0.991	0.977	34	52.7	9
This work	3.40	2.85	0.990	-	14	47.8	8
This work	1.89	1.80	0.994	-	8.8	59.4	6

Table C.3 | Cross-correlation matrix between the constants of the eight parameter kinetic model.

	k_{CO_2} a	k_{RWGS} a	k_{CO_2} b	k_{RWGS} b	K_{H_2} a	K_{H_2} b	$\frac{K_{H_2O}}{K_9}$	K_{CH_3OH}
k_{CO_2} a	1.00	-0.47	0.69	-0.49	0.02	0.08	0.02	0.08
k_{RWGS} a		1.00	-0.53	0.99	0.33	0.31	0.36	0.24
k_{CO_2} b			1.00	-0.45	-0.37	-0.66	-0.40	-0.55
k_{RWGS} b				1.00	0.25	0.18	0.27	0.12
K_{H_2} a					1.00	0.64	1.00	0.89
K_{H_2} b						1.00	0.68	0.90
$\frac{K_{H_2O}}{K_9}$							1.00	0.91
K_{CH_3OH}								1.00

Table C.4 | Fitted values of the six parameter model as proposed in this work. Given in the form of equation (C.20). The number of significant figures shown, are needed to keep the same quality of the original fit. The shown error is the standard deviation over the five fits as produced with the cross-validation method (eq. C.26).

Parameter	Estimated value
$\ln(k_{CO_2})$	a 35.19 ± 0.7 $k_{CO_2} = 1.918 \cdot 10^{15} \exp\left(\frac{-166,000}{RT}\right)$ b $19,970 \pm 250$
$\ln(k_{RWGS})$	a 40.44 ± 3.7 $k_{RWGS} = 3.655 \cdot 10^{17} \exp\left(\frac{-191,400}{RT}\right)$ b $23,020 \pm 1,900$
k_{H_2}	1.063 ± 0.17
$k_{H_2O/9}$	81.09 ± 13

C.5. Results

The result of the analysis performed can be found in Table C.2. It can be seen that Graaf has the lowest $CV_{(5)}$ and therefore is the best predicting model. The 6-parameter model presented in this work, has only a slightly worse predictive capability compared to the Graaf et al. model. However, looking at the variation of the parameters values between the five training sets ($\sigma_{p,avg}$), it is seen that the value is much larger for Graaf et al. compared to the 6-parameter model. Moreover, the 6-parameter model predicts a large percentage of the points within one experimental standard deviation ($\hat{w}_{pred}$). This shows that the predictive capability of the 6-parameter model and the Graaf model are almost equal, while the 6-parameter has only half of the fit parameters.

The original set of parameters for the model of Graaf et al. does not predict the current data set well. This can be attributed to the fact that, the study of Graaf et al. is almost three decades old and meanwhile catalysts improved in activity. For the Bussche and Froment model, it is seen that for all fit indicators the performance is worse compared to the Graaf et al. and the 6-parameter model. Although, the Bussche and Froment model is not a bad model, other models outperform it by a small margin.

The covariance of the parameters for the 8 parameter model are shown in Table C.3, in the form of the cross-correlation matrix. As can be seen the K_{H_2} adsorption enthalpy is cross-correlated to the adsorption isotherms of $K_{H_2O/9}$ and k_{CH_3OH} . Therefore the adsorption isotherm (K_{H_2}) cannot be fitted independently using the experimental current dataset. Experiments without excess of hydrogen present are required to be able to fit K_{H_2} independently. What can be fitted is the linear relation between the H_2 adsorption isotherm and the kinetic rate constants, which is reflected in the lower cross-correlation parameter of the pre-exponential constants.

Concluding the above, the 8-parameter model parameters cannot be fitted independently and this supports our assumption for the six parameter model, where K_{H_2} was not fitted independently. Based on the good predictive properties ($CV_{(5)}$), the low variance $\sigma_{p,avg}$ and the best prediction of experiments ($\hat{w}_{pred}$) the 6-parameter model is shown to be a good model. However, the work described in this appendix is still in progress and might be subject to changes.

The fitted parameters for the 6 parameter model are shown in Table C.4, for the other models the parameters can be found in the Supporting Information. The relatively large activation energies are a result of the lumping procedure of the adsorption isotherms. Consequently, the pre-exponential factor is compensated for this

effect. The errors shown are the standard deviations of the parameters as defined in equation C.26. The error is quite large in the pre-exponential factor of the RWGS rate constant, although this is within the error margin of the experiments.

C.6. Conclusion

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In this study the kinetic models for methanol synthesis of Graaf et al. and Bussche and Froment are compared to a newly developed model. It was found that 12-parameter Graaf et al. model is predicting the data set the best. The Bussche and Froment model is predicting slightly worse, especially outside the original data set. The new kinetic model uses the Bussche and Froment model as a basis, incorporating recent literature findings for surface species. The 6-parameter based model can predict the trends in the experimental data with almost equal performance to the Graaf et al. model, while having half of the fitting parameters. Moreover, it is a good predicting model, as is confirmed with the cross-validation method.

Therefore, the newly proposed 6-parameter model will be used for steady state calculations of methanol synthesis. The model is given in equations C.15 to C.17 and the fitted parameters can be found in Table C.4.

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C.7. Supporting Information

Table C.S1 | List of symbols.

Parameter	Unit	Meaning
A,B		Arrhenius constants
a,b		Logarithmic Arrhenius constants
A_r	m ²	Area of the fixed bed reactor
f	bar	Fugacity
ΔG	J mol ⁻¹	Gibbs free energy
ΔH_r	kJ mol ⁻¹	Heat of reaction
$Kp_j^\circ(T)$		Temperature dependent equilibrium constant
k_j		Reaction rate constant
K_i		Adsorption constant
M_{w_i}	kg mol ⁻¹	Molecular weight
N		Number of experiments
N_c		Number of components
N_p		Number of parameters
R	J mol ⁻¹ K ⁻¹	Ideal gas constant
r_j	mol/kg _{cat} s	Reaction rate
T	K	Temperature
w_i		Weight fraction
$\hat{w}_i$		Predicted weight fraction
ϵ_b		Fixed bed porosity
$\frac{\gamma^*}{\gamma_0}$		Relative surface contact free energy
Θ^i		Fraction of free surface centers
$\nu_{i,j}$		Stoichiometric reaction rate constant
ρ	kg m ⁻³	Density
ϕ		Total amount of relative reduced surface centers
ϕ_m	kg s ⁻¹	Mass flow
ϕ_V°	mL min ⁻¹	Standard volume flow

C.8. Estimated parameters

Table C.S2 | Graaf et al. fitted parameters.

Parameter		Original	Fitted		Fitted
k_{CO}	A	$2.69 \cdot 10^7$	$5.887 \cdot 10^5$	a	13.29 ± 6.9
	B	-109900	-101900	b	12260 ± 1500
k_{CO_2}	A	436	2414	a	7.789 ± 4.4
	B	-65200	-59840	b	7197 ± 2200
k_{RWGS}	A	$7.31 \cdot 10^8$	$1.369 \cdot 10^{10}$	a	23.34 ± 5.1
	B	-123400	-116900	b	14060 ± 2500
K_{CO}	A	$7.99 \cdot 10^{-7}$	$7.562 \cdot 10^{-8}$	a	-16.40 ± 6.1
	B	58100	62210	b	-7482 ± 2000
K_{CO_2}	A	$1.02 \cdot 10^{-7}$	$9.638 \cdot 10^{-7}$	a	-13.85 ± 3.7
	B	67400	56980	b	-6854 ± 2000
$\frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}}$	A	$4.13 \cdot 10^{-11}$	$2.021 \cdot 10^{-8}$	a	-17.72 ± 4.9
	B	104500	94080	b	-11320 ± 2400

Table C.S3 | Bussche and Froment fitted parameters.

Parameter		Original	Fitted		Fitted
k_{CO_2}	A	1.07	1.840	a	0.6100 ± 0.91
	B	36696	32380	b	-3895 ± 290
k_{RWGS}	A	$1.22 \cdot 10^{10}$	$6.7370 \cdot 10^9$	a	22.63 ± 1.4
	B	-94765	-100900	b	12130 ± 570
$\sqrt{K_{H_2}}$	A	0.499	0.2042	a	-1.589 ± 1.5
	B	17197	18650	b	-2244 ± 660
K_{H_2O}	A	$6.62 \cdot 10^{-11}$	$1.426 \cdot 10^{-10}$	a	-22.67 ± 1.9
	B	124119	121100	b	-14570 ± 740
$\frac{K_{H_2O}}{K_8 K_9 K_{H_2}}$	A	3453.38	3742		3742 ± 120

Table C.S4 | Fitted values of the eight parameter model of this work.

Parameter		Fitted		Fitted
k_{CO_2}	A	$3.938 \cdot 10^{23}$	a	54.33 ± 4.5
	B	-177500	b	21350 ± 1800
k_{RWGS}	A	$5.410 \cdot 10^{20}$	a	47.74 ± 2.6
	B	-188700	b	22690 ± 1300
K_{H_2}	A	0.1069	a	-2.236 ± 0.98
	B	6845	b	-823.2 ± 120
$\frac{K_{H_2O}}{K_9}$		177500		177500 ± 11000
K_{CH_3OH}		7948		7948 ± 1800

Table C.S5 | Fitted values of the six parameter model as proposed in this work.

Parameter		Fitted		Fitted
k_{CO_2}	A	$1.918 \cdot 10^{15}$	a	35.19 ± 0.7
	B	-166,000	b	$19,970 \pm 250$
k_{RWGS}	A	$3.655 \cdot 10^{17}$	a	40.44 ± 3.7
	B	-191,400	b	$23,020 \pm 1,900$
k_{H_2}		1.063		1.063 ± 0.17
$k_{H_2O/9}$		81.09		81.09 ± 13

List of publications

9. **M.J. Bos**, S.R.A. Kersten, D.W.F. Brilman, *Wind power to methanol*, In preparation.
8. R.T. Driessen, J.J.Q van der Linden, S.R.A. Kersten, **M.J. Bos**, D.W.F. Brilman, *Characterization of mass transfer in a shallow fluidized bed for adsorption processes: modelling and supporting experiments*, In preparation.
7. **M.J. Bos**, Y. Slotboom, S.R.A. Kersten, D.W.F. Brilman, *Characterization of a condensing CO₂ to methanol reactor*, Submitted to peer reviewed journal.
6. **M.J. Bos**, S. Pietersen, D.W.F. Brilman, *Production of high purity CO₂ from air using solid amine sorbents.*, Accepted for publication in **Chemical Engineering Science: X**, doi:10.1016/j.cesx.2019.100020
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Selected other publications

8. Oral presentation at GHGT-14 (Conference), Melbourne (Australia), *High Purity CO₂ production from air using solid amine sorbent*, 2018
7. Oral presentation at NPS-15 (Conference), Enschede (Netherlands), *Intrinsic kinetics of CO₂ adsorption on solid amine sorbent*, 2018
6. Poster presentation at ISCRE 25 (Conference), Florence (Italy), *Intrinsic kinetics of CO₂ capture on solid amine sorbent*, 2018
5. Oral presentation at Chains 2017 (Conference), Veldhoven (Netherlands), *CO₂ to methanol – The LOGIC process*, 2017
4. Oral presentation at 4th International Workshop CO₂: CCU/CCR and P2X (Workshop), Dusseldorf (Germany), *CO₂: closing the loop*, 2017
3. Poster presentation at 4th Conference on Carbon Dioxide as Feedstock for Fuels, Chemistry and Polymers (Conference), Essen (Germany), *CO₂ to methanol: The LOGIC process and CO₂ capture with supported amine adsorbents*, 2015
2. Oral presentation at NPS-14 (Conference), Utrecht (Netherlands), *CO₂ to methanol – The LOGIC process*, 2014
1. Poster presentation at ISCRE 23 (Conference), Bangkok (Thailand), *A novel condensation reactor for efficient CO₂ to Methanol conversion*, 2014

About the author

Martin Bos was born on 26 March 1989 in Oosterhesselen and grew up in Lochem, the Netherlands. After graduating high school at Baudartius College in Zutphen, he started studying Chemical Engineering at the University of Twente in 2007. For his Bachelor Thesis (2010) he studied heat exchange for super critical water gasification of biomass. At the end of his bachelor studies he joined the study tour Gung He to China.

After his bachelor, he started a master in Chemical Engineering with a specialization in Process Engineering at the University of Twente. In 2011 he joined the engineering contractor Tebodin (currently Bilfinger Tebodin) for an internship on the processing of unconventional gas resources. After this internship he continued to work at Tebodin as a Process Engineer (0.2fte). Parallel to this position, he finished his master's courses and started his master graduation project on CO₂ to methanol conversion under supervision of dr. ir. D.W.F. Brilman.

After obtaining his masters degree (2013), he continued with a PhD-project under supervision of dr.ir. D.W.F. Brilman and prof.dr. S.R.A. Kersten in the Sustainable Process Technology group at the University of Twente. The topic of research was technology development for CO₂ air capture and – small scale – conversion of CO₂ to methanol. Both subjects were studied by a combination of experimental and modelling efforts. The work of his PhD is presented in this thesis. Next to his PhD-position, he was appointed Lecturer in Chemical Engineering in the Sustainable Process Technology group in 2015. His teaching efforts included courses in transport phenomena, reaction engineering and process design projects.

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