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Modelling in methanol synthesis

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Abstract: Methanol is very commonly used as a feedstock in the chemical industries. It is also used as fuel and as a solvent. The catalysts are used and widely studied in this field. Nowadays, one of the main interests is the use of CO₂ as a feedstock in methanol synthesis. Even though methanol has been produced commercially since 1923, the reaction mechanism and kinetics are still an open question. This report presents a short literature review of methanol synthesis and its kinetics and modelling. The simulator is developed based on the mass balances and kinetic models from the literature. The simulator is used to evaluate the steady-state and dynamic behaviour of the process. For the selected model, the information about the importance of model parameters are studied through sensitivity analysis.

Keywords: Methanol synthesis, modelling, sensitivity analysis

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1 INTRODUCTION

This report is written during the CO2UTIL research project titled “Towards utilization of CO₂ as a green and versatile commodity chemical: Clean synthesis of Methanol and Dimethyl Carbonate”. The project studies the use of CO₂ in dry reforming to synthesis gas, as well as methanol and dimethylcarbonate (DMC) synthesis processes, with the aim of developing a sustainable production process for the synthesis of methanol and DMC. The possibilities of management and optimization of individual processes as well as the whole production chain are evaluated through modelling and simulation. The data for the modelling are provided through the laboratory experiments. The project is funded by the KETJU (Sustainable Production and Products) Research Programme of the Academy of Finland. It is carried out in co-operation between the Department of Process and Environmental Engineering at the University of Oulu, the Process Chemistry Centre at Åbo Akademi University, and the Institute of Molecular Chemistry at CNRS-University of Bourgogne, Dijon, France.

Methanol is very commonly used as a feedstock in the chemical industries. It is also used as fuel and as a solvent. [Løvik 2001] Commercially it is produced from synthesis gas (CO/CO₂/H₂) under high pressure and temperature. The used catalyst is mainly the copper/zinc based oxide catalyst. [Yang 2008] Methanol is used when producing for example formaldehyde, acetic acid and methyl tertiary butyl ether (MTBE). As a fuel, methanol is used for example in indy cars and in fuel cells. [Løvik 2001]

The commercial methanol synthesis was implemented in 1923 by BASF in Germany. This process was known as the “high-pressure” process. The operation point in this process was 250 - 350 bar and 320 - 450 °C. [Gallucci 2007] The catalyst used in this process was based on chromate. In the 1960s, the so called “low-pressure” process replaced the old one. The ability to produce sulfur free synthesis gas made it possible to use the more active Cu-based catalysts. The process was operated in the lower pressure and temperature, 60 - 80 bar and 250 - 280°C. [Lange 2001] Two low-pressure processes dominate the markets nowadays: ICI- and Lurgi-processes. [Løvik 2001]

The alternative feedstock instead of the synthesis gas has been studied. Biomass, wood or garbage (via partial oxidation) [Gallucci 2007] and CO₂ [Skrzypek 1995] can be used in the methanol production. Especially, the use of CO₂ as a feedstock in methanol synthesis has drawn a lot of attention, and it is widely studied, for example [Skrzypek 1995, Vanden Bussche and Froment 1996, Løvik 2001]. One reason is the strict regulations of CO₂ emissions stated in the Kyoto agreement [Løvik 2001]. The research has focused mainly on the search for the most suitable catalyst as the performance of the process is highly dependent on the used catalyst.

In this report, a short literature review of methanol synthesis and its kinetics and modelling is presented. The simulators for the process are developed based on the models from the literature. The simulators are used to evaluate the dynamic behaviour of the process even though the mutual agreement about the reaction mechanism has not been established and thus the reliability of the results can not be evaluated. The evaluation of

the results will be carried out later when the applicability of the models found from the literature will be studied with the process data. Also, data-based methods, such as neural networks, are used to model the reaction kinetics when the data are available.

2 PROCESS DESCRIPTION

The process chain for producing methanol is rather simple including the following phases [Tijm et al. 2001]:

- production of synthesis gas,
- conversion of synthesis gas to methanol and
- distillation of the reactor effluent to obtain the required product specifications.

Synthesis gas is a mixture of CO, CO₂ and H₂ produced from various sources through steam reforming, partial oxidation, CO₂ reforming or autothermal reforming [Løvik 2001]. In methanol synthesis, either CO or CO₂ or both hydrogenates to methanol. The reactions are [Klier 1982]



Also the water gas shift reaction may occur [Skrzypek 1995]. The water gas shift reaction is



The production of methanol is strongly influenced by thermodynamics. The thermodynamic equilibrium limits the process to a low conversion and thus the recycling of the outlet is required if a high conversion is desired. The overall reaction is also strongly exothermic and thus a significant cooling is required. The recycling and the cooling are the main causes of the investment costs. The methanol synthesis reactors have been designed based on three principles: the high cooling demand, the low pressure drop and the favorable economy of scale. [Lange 2001]

The production of methanol from synthesis gas may take place under the low or high pressure. The high pressure process operates typically at 200 atm and 350°C while the low pressure process operates at 50 - 100 atm and 220 - 250°C. The low pressure process has such economical and operational benefits that almost all the methanol plants built after year 1967 operate at the low pressure. [Klier 1982]

The methanol synthesis may be performed in two-phase or three-phase reactors. Two-phase reactors can be categorized in two classes based on the mechanism of the cooling. In multiple catalyst bed reactors, the catalyst is divided into several sections and the cooling is performed between the sections. The sizes of the catalyst beds are designed so that the reactions reach the equilibrium. The cooling may be arranged with heat exchangers or by the injection of cold synthesis gas. In single bed designs, heat is continuously removed through a media such as water. In three-phase processes, methanol is removed from the reactor with the liquid phase through which the heat is also regulated. An example of the single bed design is a Lurgi process which is presented in Figure 2. The three-phase processes aim to avoid the problem of the low conversion. [Tijm et al. 2001]

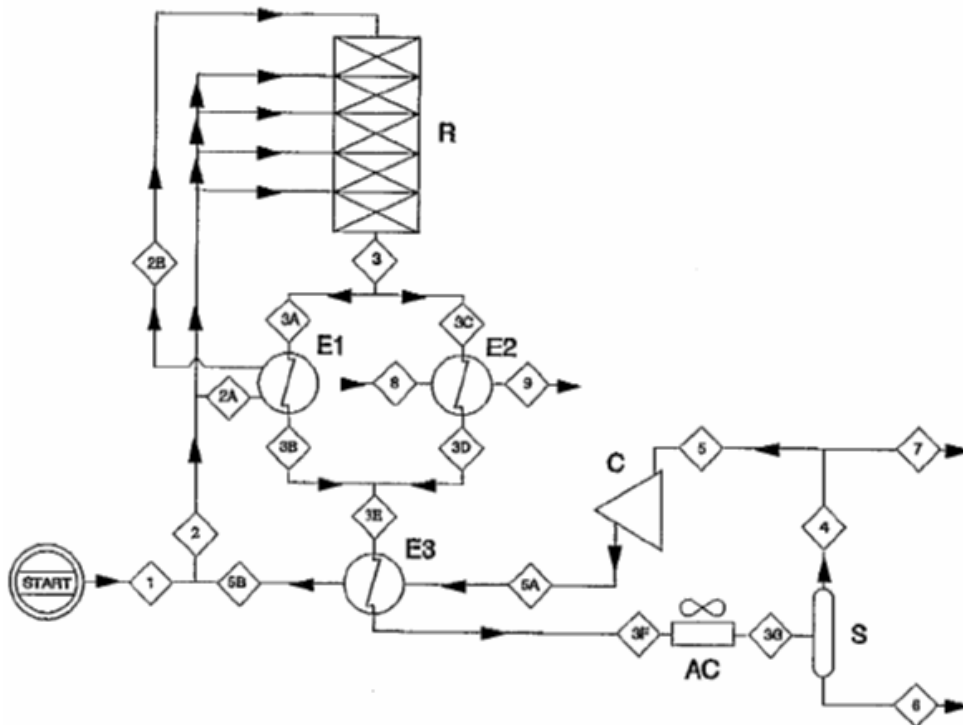


Fig. 8. Process flow diagram of the two-phase methanol synthesis loop: R, reactor; E, heat exchanger; AC, air cooler; S, separator; C, recycle compressor.

Figure 1. The multiple catalyst bed design. [Graaf and Beenackers 1996]

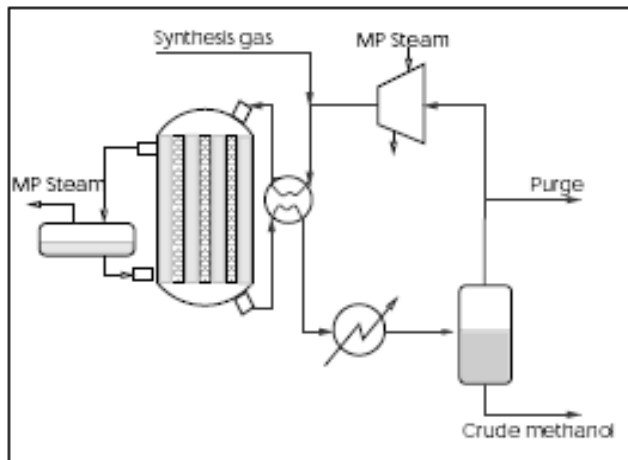


Figure 2. The single catalyst bed design, the Lurgi process. [Løvik 2001]

3 CATALYSTS IN METHANOL SYNTHESIS

In this section, a short review of the used catalysts in methanol synthesis is presented. First, the basics about the catalytic processes are given followed by a review about the commercially used Cu-based catalysts. The rest of the section is dedicated to studies aiming to find more suitable catalysts for methanol synthesis from CO₂.

3.1 Catalyst basics

Catalysts increase the reaction rates of the chemical reactions but are not consumed in the reactions. They lower the energy required for the initiation of the reactions and thus make the reactions easier to occur. Catalysts do not have influence on the position of the equilibrium and do not enable the reactions that are forbidden by the thermodynamics. Typically more than one chemical reaction occurs in chemical reactors. Catalysts may influence only the desired reaction and thus increase the selectivity of the process. This improves the utilization of the feedstock materials. [Richardson 1989]

Heterogeneous catalyzed reactions occur on the gas/solid or liquid/solid interface. Thus the actual chemical reactions are preceded by the diffusion and adsorption of the reacting substances to the surface and into the pores of the catalysts and followed by the desorption and diffusion of the products to the bulk phase. The diffusion of the substances can be divided into the external and internal diffusion. In the external diffusion, the reacting substances are transported to the surface of the catalyst. In the internal diffusion, the reacting substances are transported into the pores of the catalyst where the adsorption takes place as the substances attach to the active sites of the catalyst. The chemical reaction takes place in the active sites. After the reaction, the products detach through the desorption and then diffuse to the bulk phase through the internal and external diffusion. [Richardson 1989]

The structure of the catalyst is important concerning its usability. The shape and size influence the fluid flow through the catalyst bed and the mechanical strength ensures the long enough lifetime. High activity and selectivity are ensured if the catalyst has the correct chemical components and a high enough surface area. The stable operation of the catalyst may be achieved by the addition of components. The catalysts have typically three components: the support, active components and promoters. The active sites are responsible for the chemical reactions. The support is the basis of the catalyst over which the active components are placed. It must provide a high enough surface area for the active components to be evenly distributed to avoid undesired sintering. It is desired that the support does not have the catalytic activity. Promoters are substances that either enhance or inhibit the catalytic activity. Only a small amount of promoters is typically added to catalysts to obtain the desired activity, selectivity and stability properties. [Richardson 1989]

The preparation of the catalysts is essential because the operation of the catalytic processes depends on the properties of the catalyst. Catalyst preparation procedure is

typically obtained through time-consuming empirical studies. May be the most widely used methods for preparing heterogeneous catalysts are the impregnation and precipitation. In the impregnation method, the support of the catalyst is fabricated to small cylindrical shapes, such as pellets, rings or spheres. The support material is then exposed to a solution with an appropriate compound, which provides the active phase or a compound that is easily converted into the active phase. Precipitated catalysts are prepared by the rapid mixing of the concentrated solutions of metal salts leading to precipitates in a high surface area form. The precipitation step is followed by filtering and washing, where unwanted soluble salts are removed. Then the precipitate is dried and heated to convert the suitable oxides for the active phase. [Twigg 1981]

The decrease in the activity of catalysts is called the deactivation. The deactivation is associated with the reduction in the number of active sites on the catalyst surface. The reasons for the deactivation are mechanical, thermal or chemical. The poisoning of catalysts is due to the adsorption of impurities on the catalyst surface, which blocks the access to the active sites. [Butt et al. 1987] Fouling of catalysts is caused by an unfavorable interaction of catalyst with the reactants or products [Petersen 1987]. Fouling is very common cause of deactivation. The third mechanism of the deactivation is sintering, which is associated with supported metal catalysts. The loss of the active sites is due to the sintering process, where the active metal particles agglomerate to form bigger particles in expense of the number of the active sites. [Wanke et al. 1987]

3.2 Used catalysts

The hydrogenation of carbon monoxide and carbon dioxide favors higher alcohols over methanol as products and dimethylether may also form in methanol synthesis. Thus an efficient and selective catalyst is required to produce methanol. Nowadays, there are catalysts allowing the production of almost pure methanol from synthesis gas under the low pressure (< 100 atm). These catalysts contain copper and a mixture of oxides such as ZnO - Al₂O₃ or ZnO – Cr₂O₃. Other oxides have also been used. [Klier 1982]

The mechanism of the methanol synthesis is still an open question. Studies have been carried out in order to find the underlying mechanism, for example Fujitani et al. (1997) and Ostrovskii (2002). The mechanism is not discussed in this report.

The effect of the catalyst preparation is essential concerning the usability of the catalyst as has been mentioned earlier. The preparation of the catalyst for the methanol synthesis has been studied and it has been found out that among the number of substances also the preparation methods and the conditions (pressure and temperature) have a great influence to the catalyst performance (Li and Inui 1995, Ma et al. 1998, Wu et al. 1998, Fujita et al. 2001).

3.2.1 Cu/ZnO-Al₂O₃ catalysts

The first catalyst used for the methanol production from the synthesis gas was ZnO-Cr₂O₃. It was commercialized by BASF and used in the high pressure and high

temperature synthesis. The improvements in the purification of the methanol synthesis feed (especially removal of sulphur) led to a major improvement in catalysts as the use of Cu-ZnO catalyst was enabled. The Cu/ZnO catalyst has a high activity and the synthesis can be operated at the lower pressure and temperature. Nowadays, the Cu/ZnO-Al₂O₃ catalyst is almost exclusively used in industry. [Klier 1982]

The Cu/ZnO-Al₂O₃ catalyst is widely studied in the literature. Also, studies with Cr₂O₃-based catalysts can be found (for example Bradford et al. 2003) Kinetic models of methanol synthesis (Section 4) are based on the experiments performed with commercial Cu/ZnO-Al₂O₃ catalysts. The mechanism of the adsorption of substances on the catalyst has been studied and a series of articles is written about it [Słoczyński et al. 1991a, 1991b and 1991c]. The Cu/ZnO-Al₂O₃ catalyst is very active for CO-rich feed but loses some activity with CO₂-rich feed [Yang 2006]. However, the utilization of CO₂ is very topical due to the environmental regulations and thus many studies have been carried out in order to find a catalyst that is active with CO₂-rich feed. For this task, Cu-based catalysts with metallic additives have been studied.

Saito et al (1996) presented that Cu/ZnO-based catalysts perform well with CO-rich feed but lose their activity with the increased amount of CO₂ in the feed. They noticed that the activity loss is due to water, which is produced along with methanol in CO₂ hydrogenation. Also, Novak et al. (1991) obtained results proving that water is responsible for the activity loss of the CuO/ZnO-Al₂O₃ catalyst. Wu et al. (2001) used different feed compositions to prove the detrimental effect of water to the Cu/ZnO catalysts. They found that the methanol yield decreases and water yield increases with the increasing amount of CO₂ in the feed. They concluded that the presence of water accelerates the deactivation of the Cu/ZnO-based catalysts. However, Wu et al. (2001) supposed that silica added to a Cu/ZnO-based catalyst could inhibit the detrimental effect of water thus allowing the methanol synthesis from the CO₂-rich feed with the Cu/ZnO-based catalysts. Thermal sintering, sulphur and chloride poisoning, carbon deposition and physical damage may decrease the activity of the Cu-based catalysts in processes with methanol according to Twigg and Spencer (2003). Quinn et al. (2004) present that in three-phase methanol synthesis there may be arsine in the feed. They found that arsine is a strong deactivator of the Cu/ZnO-Al₂O₃ catalyst.

A new method for the low-pressure methanol synthesis has been proposed [Yang et al. 2006, Yang et al. 2008, Zhang et al. 2008]. It utilizes Cu/ZnO catalysts with alcohol promoters. Reubroycharoen et al. (2004) and Yang et al. (2008) used a Cu/ZnO-Al₂O₃ catalyst and Zhang et al. (2008) used a Cu/ZnO catalyst. In these studies, ethanol, propanol and butanol have been studied as possible alcohol promoters. This new method was operated at the temperature of 443 K and at the pressure of 3.0 MPa. The low reaction temperature led to the high CO conversion (50 - 80 %) [Yang et al. 2008].

Other than Zn oxides have been tested with Cu-based catalysts. For example, Huang et al. (2004) studied the influence of Zn, Cr and Co oxide additives to Cu-based catalysts. They noticed significant improvements in the catalyst activities for the water gas shift reaction and methanol synthesis when Cr₂O₃ was added to a Cu catalyst. No significant activity

changes were observed with CoO addition. Also, SiO₂ and its influence to the activity of the Cu-based catalysts have been studied (Fisher et al. 1997, Choi et al. 2001). Choi et al. (2001) noticed that the addition of SiO₂ increased the catalytic activity for the methanol synthesis from CO₂.

3.2.2 Catalysts with Zirconium

Zirconium has been recognized as an interesting support material to Cu-based catalysts, since it has been shown to improve the activity of catalysts for methanol synthesis from both CO and CO₂ [Fisher et al. 1997, Fisher et al. 1998, Jung et al. 2002, Yang et al. 2006, Pokrovski et al. 2006]. Jung et al. (2002) studied the use of the Cu/ZrO₂ catalyst for methanol synthesis. They found that the activity of the catalyst is strongly dependent on the phase of the ZrO₂. This has been reported also by Liu et al. (2005), who studied the Cu-based catalysts with the nanocrystalline Zr addition. Yang et al. (2006) compared a Cu/ZnO catalyst supported by Zr to the pure Cu/ZnO catalyst. They presented that the Cu/ZnO with the Zr support showed the high activity and selectivity towards CO and CO₂, especially CO₂. A ZrO₂ doped Cu/ZnO catalyst showed also the high stability in a long period test. Yang et al. (2006) noticed that the conversion and selectivity were higher with the Zr supported catalyst.

Słoczyński et al. (2004) compared the use Cu, Ag and Au in the catalysts for methanol synthesis. The studied catalysts were of M/(3ZnO·ZrO₂) form, where M is Cu, Ag or Au. They found out that the catalyst with Cu showed the highest activity in methanol synthesis. They concluded that the synergy between Cu and the support is apparent and advantageous for methanol synthesis.

Fisher et al. (1997) studied Cu/SiO₂ catalyst with Zr addition. They experimented with the catalyst with different Zr loadings and noticed that the increase in the Zr loading increased the rate of methanol synthesis. The effect was found out to be more significant for CO hydrogenation than for CO₂ hydrogenation. They also noticed that the maximum selectivity to methanol is obtained with intermediate Zr loadings. Fisher and Bell (1998) compared Cu/SiO₂ and Cu/ZrO₂/SiO₂ in the hydrogenation of CO. They also studied the mechanism of the CO hydrogenation on the applied catalysts. They found that the rate of methanol synthesis is enhanced with the catalyst with Zr. Schilke et al. (1999) studied the same catalysts but also examined the catalysts with Ti addition. They found that the addition of Ti has a similar influence than the addition of Zr.

Zhang Y. et al. (2006) experimented with Cu/γ-Al₂O₃ and 12Cu10Zr/γ-Al₂O₃ catalysts. They studied the influence of the reaction temperature, space velocity and the molar ratio of H₂/CO₂ to methanol synthesis. They noticed that the presence of Zr in the catalyst improves the catalytic performance. They also noticed that the low temperature, high space velocity and the proper molar ratio of H₂/CO₂ are advantageous for methanol synthesis. Pokrovski et al. (2006) studied the influence of the Ce addition to the Zr oxide. They prepared and tested Cu/Ce_xZr_{1-x}O₂ catalysts with varying Ce content. They noticed that the addition of Ce increased the activity of the catalyst for methanol synthesis

through the CO₂ hydrogenation. They also defined the optimal amount of Ce to be added to the catalyst.

Słoczyński et al. (2003) and Słoczyński et al. (2006) have studied the effect of metal oxide additives on Cu/ZnO/ZrO₂ catalyst. The studied additives were Ga, B, In, Gd, Y, Mg and Mn. They noticed that the oxide additives have a great influence in the catalyst activity. The highest methanol yield was obtained with the addition of Ga while the addition of In lead to a severe activity loss. Also, Toyir et al. (2001) have reported the applicability of Ga as an effective catalyst. They reported on the experiments with an active and selective Cu/ZnO/Ga₂O₃ catalyst for the methanol synthesis through the CO₂ hydrogenation. Liu et al. (2005) studied Cu-based catalysts with oxide additives. However, they focused on the addition of nanocrystalline Zr and its advantageous effects on the catalyst activity.

Saito et al. (1996) have noticed the promoting action of Ga oxide to the catalyst for methanol synthesis from CO₂. They experimented with Ga, Al, Zr and Cr oxide additives. Based on their experiments they prepared two multicomponent catalysts (Cu/ZnO/ZrO₂/Al₂O₃ and Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃) and noticed that the activities of the catalysts were higher than the activities of the traditional Cu-based catalysts. In Saito et al. (1997) and Wu et al. (1998), optimal preparation conditions for multicomponent catalysts were defined. Saito et al. (1996) and Saito et al. (1997) reported that the developed multicomponent catalysts are highly effective and stable for methanol synthesis from CO₂. A similar multicomponent catalyst has been developed also by Omata et al. (2004). They prepared Cu/Zn/Al/Cr/B/Zr/Ga catalysts with different amounts of substances and measured their activities. A neural network was trained to predict the activity based on the amounts of substances. The network model was then used to find the optimal composition of the catalyst (Omata et al. 2004).

3.2.3 Pd-based catalysts

At the high temperature, a Cu/ZnO catalyst deactivates quickly in methanol synthesis [Zhang Q. et al. 2006]. Supported Pd catalysts have been studied and showed to be more stable [Zhang Q. et al. 2006]. Kim et al. (2003) studied the influence of preparation methods to Pd-ZnO catalysts. They found the best catalyst structure and proposed methods for obtaining such a structure. Tsubaki and Fujimoto (2003) studied the effect of different oxide additives to supported Pd catalyst. In their experiments, Pd supported by CeO₂ showed the high activity and long lifetime for methanol synthesis from CO₂. They also noticed that La₂O₃ and TiO₂ showed similar results. Zhang Q. (2006) used a Pd supported Cr/ZnO catalyst on their experiments. The addition of Pd improved the activity and selectivity of the catalyst for methanol synthesis from syngas. Shen et al. (2005) developed a Cu-based Ce supported catalyst and compared it with a Pd-based Ce supported catalyst. The results showed that the Cu-based catalyst performed as well as the Pd-based catalyst.

Fujitani et al. (1995) developed a Pd/Ga₂O₃ catalyst which activity is comparable to the classical Cu/ZnO catalyst. Ga₂O₃ has a positive effect to the supported Pd catalyst

(Bonivardi et al. 2000). They experimented with a Pd/SiO₂ catalyst with Ga addition with good results. Chiavassa et al. (2008) studied a Ga promoted Pd/SiO₂ catalyst and the influence of the reaction products to its activity. They presented that CO and H₂O has detrimental effects on the activity and selectivity of the applied catalyst.

3.2.4 Other catalysts

Maack et al. (2003) studied methanol synthesis from CO. They prepared a Cu-based catalyst with the addition of potassium. Maack et al. (2003) noticed that potassium acts as a promoter for the methanol production and that the prepared catalyst was selective for methanol. They found out that CO₂ had a negligible effect on the performance of the catalyst with the applied pressure regime.

Shao et al. (1995) studied Pt-bases catalysts. They prepared two catalysts, one with Pt, W and SiO₃ and the other with Pt, Cr and SiO₃, and found them very active and selective for the methanol synthesis from CO₂. However, the use of noble metals as a catalyst is not commercially feasible.

4 KINETICS

The thorough literature review of reported kinetic studies for methanol synthesis is presented in this section. Many of the developed kinetic models with used operating conditions are also presented. The experimental constants for models in this section are collected in Appendix 1. Some authors have not presented the numerical values for those constants.

Even though methanol synthesis has been a commercial process since 1923, the reaction mechanism and kinetics are still an open question (Rozovskii et al. 2003). However, the prevailing view is that methanol is produced primarily through CO₂ hydrogenation (Skrzypek et al. 1995, Coteron and Hayhurst 1994, Vanden Bussche and Froment 1996, Šetinc et al. 1999, Wu et al. 2001). Šetinc et al. (1999) states that the role of CO is to remove absorbed oxygen from the catalyst surface, which results in a reaction between CO₂ and H₂. Many authors have examined the reaction kinetics of methanol synthesis. The studies vary in reaction conditions (temperature and pressure), feedstock and used catalysts. Some models are derived for the synthesis from CO and H₂ while some others take CO₂ into the consideration as a feed. Thus, there exists a variety of kinetic equations with different levels of detail. The basic form of the kinetic equations may also vary due to the assumptions about the limiting conditions. Some authors consider that thermodynamics limit the reaction rate while some others base their equations on mass transfer limitations. Furthermore, the laboratory scale studies often ignore the limitations.

There have been early attempts to model the reaction kinetics for the high-pressure methanol synthesis with the ZnO/Cr₂O₃ catalyst. The equation proposed by Natta is a good example of the work done in the early days [Vanden Bussche and Froment 1996]. Natta considered only CO hydrogenation and proposed the kinetic equation [Vanden Bussche and Froment 1996]

$$r_{CH_3OH} = \frac{f_{CO} f_{H_2}^2 - f_{CH_3OH} / K_2^*}{\left(A + B f_{CO} + C f_{H_2} + D f_{CH_3OH} \right)^3}, \quad (4)$$

in which f_i denotes the fugacity of component i and A, B, C and D are estimated constants. [Vanden Bussche and Froment 1996]

A typical assumption was that solely the hydrogenation of CO occurred in the synthesis. Later, it was noticed that also CO₂ must be considered as a feed and that it also contributes to the reaction kinetics. Bakemeier et al. included the presence of CO₂ in the kinetic equation with a Langmuir-type isotherm. They studied also the catalytic process with ZnO/Cr₂O₃ catalyst and ended up with the kinetic equation [Vanden Bussche and Froment 1996]

$$r_{CH_3OH} = \frac{A e^{-E/RT} \left[p_{CO}^m p_{H_2}^n \left(1 - \left(p_{CH_3OH} / p_{CO} p_{H_2}^2 K_2^* \right) \right) \right]}{1 + D e^{-F/RT} p_{CO_2} / p_{H_2}}. \quad (5)$$

The newer models are derived for the low-pressure synthesis over the Cu-based catalysts as their use was enabled through process improvements. The first published kinetic equation is from Leonov et al. [Vanden Bussche and Froment 1996]:

$$r_{CH_3OH} = k \left(\frac{P_{CO}^{0.5} P_{H_2}}{P_{CH_3OH}^{0.66}} - \frac{P_{CH_3OH}^{0.34}}{P_{CO}^{0.5} P_{H_2} K_2^*} \right). \quad (6)$$

Leonov et al. (1970) still assumed that methanol is produced only from CO and neglected CO₂. Since then several authors have studied the kinetics of methanol synthesis. Klier et al. (1982) considered methanol synthesis primarily through CO hydrogenation but also included CO₂ in the kinetic equation. They noticed that the reaction rate reaches a maximum value with a certain p_{CO}/p_{CO₂} ratio. The kinetic model proposed by Klier et al. (1982) is

$$r_1 = k_1 \left(1 + \frac{1}{K_{redox}^{eq}} \frac{P_{CO}}{P_{CO_2}} \right)^{-3} \frac{K_{CO} K_{H_2}^2 (p_{CO} p_{H_2}^2 - p_{CH_3OH} / K_1^{eq})}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2})} \quad (7)$$

$$r_2 = k_2 \left(p_{CO_2} - \frac{1}{K_2^{eq}} \frac{P_{CH_3OH} P_{H_2O}}{P_{H_2}^3} \right).$$

The operating conditions in the study of Klier et al. (1982) are presented in the Table 1.

Table 1. The experimental conditions used by Klier et al. (1982).

Catalyst	Reactions	Feed [mol %]	T [K]	P [bar]	Type of reactor
CuO-ZnO	(1) CO + 2H ₂ ⇌ CH ₃ OH	CO: 0-30	498-	75	tubular
30-70 metal	(2) CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	CO ₂ : 0-30 H ₂ : 70	523		integral fixed bed
atomic percent	(3) A _{red} + CO ₂ ⇌ A _{ox} + CO				

Villa et al. noticed that also the water gas shift reaction must be considered. They assumed that methanol is produced only through CO hydrogenation. Villa et al. proposed the kinetic model [Vanden Bussche and Froment 1996]

$$r_{CH_3OH} = \frac{f_{CO} f_{H_2}^2 - f_{CH_3OH} / K_2^*}{(A + B f_{CO} + C f_{H_2} + G f_{CO_2})^3} \quad (8)$$

$$r_{RWGS} = \frac{f_{CO_2} f_{H_2} - f_{CO} f_{H_2O} K_3^*}{M^2}.$$

Graaf et al. (1988a) and Graaf et al. (1990) derived a kinetic model considering both CO and CO₂ hydrogenation and the water gas shift reaction. They used the kinetic equations of elementary steps of each reaction and ended up with 48 possible reaction schemes. Through statistical discrimination they selected the equations for their kinetic model. The kinetic model derived by Graaf et al. (1988a) and Graaf et al. (1990) is

$$\begin{aligned}
 r_{CH_3OH} &= \frac{k_1 K_{CO} (c_{CO} c_{H_2}^{3/2} - c_{CH_3OH} / c_{H_2}^{1/2} K_1^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})} \\
 r_{H_2O} &= \frac{k_2 K_{CO_2} (c_{CO_2} c_{H_2} - c_{H_2O} c_{CO} / K_2^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})} \\
 r_{CH_3OH}^* &= \frac{k_3 K_{CO_2} (c_{CO_2} c_{H_2}^{3/2} - c_{CH_3OH} c_{H_2O} / c_{H_2}^{3/2} K_3^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) (c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O})}
 \end{aligned} \tag{9}$$

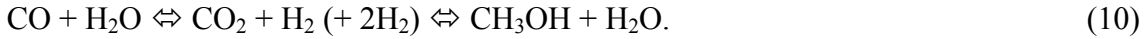
The operating conditions used in the study by Graaf et al. (1988a) and Graaf et al. (1990) are presented in Table 2. The original kinetic equation for two-phase methanol synthesis is derived in Graaf et al. (1988a). Later, the authors noticed that mass transport limitations influence the values of the model parameters. In Graaf et al (1990), the authors modelled the mass transport limitations and recalculated the values of the parameters. The mass transport limitations have also been modelled by Skrzypek et al. (1985). Skrzypek et al. (1985) developed a rather complex dusty gas diffusion model. Later, Lommerts et al. (2000) compared different kinds of diffusion models of varying complexity. They concluded that the internal mass transport can be adequately modelled with simple models.

Graaf et al. (1986) studied also the chemical equilibria in methanol synthesis. They identified the equations for the equilibrium constants by assuming the ideal gas behaviour and compensating the non-ideality with Soave-Redlich-Kwong equation of state. The equations for the chemical equilibria derived by Graaf et al. (1986) have been used in other studies as well, for example by Vanden Bussche and Froment (1996). Also, Skrzypek et al. (1990) used the equations presented by Graaf et al. (1986) while they examined the dependence between the initial feed composition, temperature and pressure on the equilibrium concentrations of the components. They noticed that the temperature and pressure have a considerable influence to equilibrium conversions. The increasing temperature decreases the conversion of the main reaction (the production of methanol) while the increasing pressure has the opposite effect.

Table 2. The operating conditions used by Graaf et al. (1988a).

Catalyst	Reactions	Feed [mol %]	T [K]	P [bar]	Type of reactor
CuO-ZnO- Al ₂ O ₃ Haldor Topsøe Mk 101	(1) CO + 2H ₂ ⇌ CH ₃ OH	CO: 0-22	483-	15-50	gradientless spinning basket
	(2) CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	CO ₂ : 2,1- 26,1	518		
(3) CO ₂ + H ₂ ⇌ CO + H ₂ O	H ₂ : 67,4-90				

Graaf et al. (1988b) studied the kinetics of the three-phase methanol synthesis. They noticed that the same form of the kinetic equation as developed for two-phase methanol synthesis also holds for the three-phase synthesis. They identified the parameters for the three-phase system and noticed that in three-phase synthesis the CO₂ hydrogenation dominates while the CO hydrogenation dominates in two-phase synthesis. However, according to Vanden Bussche and Froment (1996), the equation proposed by Graaf et al. (1988a) and Graaf et al. (1990) has some disagreement concerning the intermediate species of the overall reaction. Vanden Bussche and Froment (1996) assumed that CO₂ is the main source of carbon in methanol synthesis. They derived the kinetic equation based on the reaction mechanism given by



Vanden Bussche and Froment (1996) made observations about the intermediate species but neglected them from their kinetic model. The kinetic model proposed by Vanden Bussche and Froment (1996) is

$$r_{\text{CH}_3\text{OH}} = \frac{k p_{\text{CO}_2} p_{\text{H}_2} \left(1 - p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}} / K_1^{\text{eq}} p_{\text{CO}_2} p_{\text{H}_2}^3\right)}{\left(1 + K_{\text{WH}} p_{\text{H}_2\text{O}} / p_{\text{H}_2} + \sqrt{K_{\text{H}_2} p_{\text{H}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}\right)^3} \quad (11)$$

$$r_{\text{RWGSR}} = \frac{k_2 p_{\text{CO}_2} \left[1 - K_3^{\text{eq}} \left(p_{\text{H}_2\text{O}} p_{\text{CO}} / p_{\text{CO}_2} p_{\text{H}_2}\right)\right]}{\left(1 + K_{\text{WH}} p_{\text{H}_2\text{O}} / p_{\text{H}_2} + \sqrt{K_{\text{H}_2} p_{\text{H}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}\right)}$$

The operating conditions used by Vanden Bussche and Froment (1996) are presented in Table 3.

Table 3. The operating conditions used by Vanden Bussche and Froment (1996).

Catalyst	Reactions	Feed [mol %]	T [K]	P [bar]	Type of reactor
Cu/ZnO/ Al ₂ O ₃	(1) CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	CO: 0-30 CO ₂ : 0-30	453- 553	15- 51	tubular
	(2) CO ₂ + H ₂ ⇌ CO + H ₂ O	H ₂ : 70 pCO ₂ /pCO: 0-4,1			

The equilibrium constants K_1^{eq} and K_3^{eq} are thermodynamically determined and the values are taken from Graaf et al. (1986).

Von Wedel et al. (1988) developed a power law rate equation for methanol synthesis. They used catalyst based on Cu/ZnO and synthesis gas in their study. They concentrated to model methanol synthesis in vapor phase. The kinetic equation von Wedel et al. (1988) developed is

$$r_{CH_3OH} = kc_{H_2}^{0,4}c_{CO}^{0,18} - k_{-1}c_{CH_3OH}^{0,13} \quad (12)$$

The operating conditions used in the study by von Wedel et al. (1988) are presented in Table 4.

Table 4. The operating conditions used by van Wedel et al. (1988).

Catalyst	Reaction	Feed [mol %]	T [K]	P [bar]	Type of reactor
BASF S3-85 < 60µm	(1) $CO + 2H_2 \rightleftharpoons CH_3OH$	CO: 17-50 CO ₂ : 1-5 H ₂ : 31-65	493-523	20-60	gradientless autoclave

Ledakowicz et al (1992) studied methanol synthesis in a bubble column slurry reactor. They used two commercial catalysts suspended in two different inert liquids; paraffin oil (BMT-15) and molten wax (Vestowax SH 105). Kinetic equation developed in their study is

$$r_{CH_3OH} = k \left[\left(c_{H_2}^2 c_{CO} \right) - \left(\frac{c_{CH_3OH}}{K_c} \right) \right] \quad (13)$$

The operation conditions used by Ledakowicz et al. (1992) are presented in the Table 5.

Table 5. The operating conditions used by Ledakowicz et al. (1992).

Catalyst	Reaction	Feed [mol %]	T [K]	P [bar]	Type of reactor
BASF S3-85 and BT-d < 63µm	(1) $CO + 2H_2 \rightleftharpoons CH_3OH$	CO: 17-50 CO ₂ : 1-5 H ₂ : 30-65	490- 533	20- 60	stirred autoclave and bubble column slurry reactor

Skrzypek et al. (1991) presented Langmuir-Hinshelwood-type kinetic equation for low-pressure methanol synthesis. They used a Polish commercial catalyst, CuO (60 % wt)-ZnO (30%)-Al₂O₃ (7,5%) in their study. They found that methanol synthesis favors CO₂

in spite of CO as a carbon source. Thus they based their kinetic model on reactions (2) and (3). For evidence, Skrzypek et al. (1991) performed a couple of simple experiments. When they used the feed consisting only CO₂ and H₂ methanol formed with no difficulties. Also, the selectivity of synthesis was very high. If the feed flow included CO and H₂ without CO₂ and H₂O (steam was completely removed from the feed), methanol was not formed. Methanol synthesis initiated as soon as water was introduced in the feed. This is due to the water gas shift reaction, where CO and H₂O produce CO₂, which further reacts with H₂ to produce methanol. Skrzypek et al. (1991) proposed the kinetic model

$$r_1 = k_1 K_{H_2}^2 K_{CO_2} \left[\frac{P_{H_2}^2 P_{CO_2} - \frac{P_{CH_3OH} P_{H_2O}}{K_1^{eq} P_{H_2}}}{\left(1 + K_{H_2} P_{H_2} + K_{CO_2} P_{CO_2} + K_{CH_3OH} P_{CH_3OH} + K_{H_2O} P_{H_2O} + K_{CO} P_{CO}\right)^3} \right] \quad (14)$$

$$r_2 = k_2 K_{H_2} K_{CO_2} \left[\frac{P_{H_2} P_{CO_2} - \frac{P_{CO} P_{H_2O}}{K_1^{eq} P_{H_2O}}}{\left(1 + K_{H_2} P_{H_2} + K_{CO_2} P_{CO_2} + K_{CH_3OH} P_{CH_3OH} + K_{H_2O} P_{H_2O} + K_{CO} P_{CO}\right)^2} \right]$$

The operating conditions used by Skrzypek et al. (1991) are presented in the Table 6.

Table 6. The operating conditions used by Skrzypek et al. (1991).

Catalyst	Reaction	Feed [mol %]	T [K]	P [bar]	Type of reactor
CuO-ZnO-Al ₂ O ₃ commercial	(1) CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	CO: 0- 20	460- 550	30- 90	integral fixed bed
Blasiak's catalyst CuO: 62, ZnO: 30 and Al ₂ O ₃ : 7 w%	(2) CO ₂ + H ₂ ⇌ CO + H ₂ O	CO ₂ : 5- 35 H ₂ : 10- 80			(and also differential)

Skrzypek and his group have a lot of reported studies in the area of methanol synthesis. They have reported the kinetic and mechanistic studies but also reported studies about catalysts. About the kinetic and mechanistic studies can be read for example from [Skrzypek et al. 1985, Skrzypek et al. 1990, Skrzypek et al. 1991]. Nowadays, the research seems to concentrate in finding the effective catalysts for methanol synthesis from CO₂ and H₂ [Słoczyński et al. 2003, Słoczyński et al. 2004, Słoczyński et al. 2006].

Coteron and Hayhurst (1994) studied the methanol synthesis with varying CO₂ concentration while keeping H₂/CO ratio constant in the feed flow. They used amorphous catalysts of composition Cu₇₀Zr₃₀ and Cu₇₀Zn₃₀ (subscripts indicates atom percent) when studying the kinetics of the methanol synthesis. For the catalyst with Zr, the rate of

methanol synthesis increased with the increasing CO₂ content in the feed. A slight decrease in the rate of synthesis was observed with the CO₂ content higher than 10 mol %. For the Cu/Zn catalyst, the decrease in the rate of synthesis was observed when the CO₂ content exceeded 2 mol %. The kinetic equations derived by Coteron and Hayhurst (1994) are as follows: synthesis of methanol from H₂ and CO

$$r_M = \frac{k_{f_1} K_{CO} K_H^2 K_{CH} P_{CO} P_{H_2}^2}{1 + K_{CO} P_{CO} + K_{CO} K_H^{3/2} K_{CH} P_{CO} P_{H_2}^{3/2}} \quad (15)$$

and synthesis of methanol from H₂, CO and CO₂

$$r_M = \frac{k_{f_2} K_{CO_2} K_H K_{HCO_2} P_{CO_2} P_{H_2}}{1 + K_{CO_2} P_{CO_2} + K_{CO_2} K_H^{1/2} K_{HCO_2} P_{CO_2} P_{H_2}^{1/2} + \frac{K_{CO_2} P_{CO_2}}{K_{CO} P_{CO}}} \quad (16)$$

According to the model by Coteron and Hayhurst (1994), methanol is produced through CO₂ hydrogenation and the role of CO is the removal of oxygen absorbed on the catalyst surface. Operation conditions used in this study are presented in Table 7.

Table 7. The operating conditions used by Coteron and Hayhurst (1994).

Catalyst	Reaction	Feed [mol %]	T [K]	P [bar]	Type of reactor
Cu ₇₀ Zn ₃₀ and Cu ₇₀ Zr ₃₀	(1) CO + 2H ₂ ⇌ CH ₃ OH (2) H ₂ + CO + CO ₂ ⇌ CH ₃ OH + H ₂ O	CO: 10- 40 CO ₂ : 0- 10 H ₂ : 40-70	473- 523	10	continuous, tubular, differential

Šetinc and Levec (2001) studied the kinetics of methanol synthesis in a well-mixed slurry reactor. They used a commercial Cu/ZnO/Al₂O₃ catalyst in their experiments and proposed a model for the liquid phase methanol synthesis with Langmuir-Hinshelwood mechanism. They presented that the behaviour of the liquid phase methanol synthesis can be described if Langmuir-Hinshelwood mechanism is used to describe the elementary steps on the catalyst surface. Šetinc and Levec (2001) concluded that the methanol production in the liquid phase is also proportional to the CO₂ concentration and not to the CO concentration. They also noticed that water is significant also in liquid phase synthesis. The operating conditions used in this study are presented in Table 8 and the kinetic equation proposed by Šetinc and Levec (2001) is

$$r_{Me} = A_{Me} e^{\left(\frac{E_{Me}}{RT}\right)} \frac{c_{CO_2} (c_{H_2} - c_{H_2,eq})}{\left(1 + A_W e^{\left(\frac{E_W}{RT}\right)} c_{H_2O}\right)^2}$$

$$r_{H_2O} = A_{H_2O} e^{\left(\frac{E_{H_2O}}{RT}\right)} \frac{c_{CO_2} - c_{CO_2,eq}}{\left(1 + A_W e^{\left(\frac{E_W}{RT}\right)} c_{H_2O}\right)}$$
(17)

Table 8. The operating conditions used by Šetinc and Levec (2001).

Catalyst	Reaction	Feed [mol %]	T [K]	P [bar]	Type of reactor
Commercial Cu/ZnO/Al ₂ O ₃ (C79—5GL; Süd Chemie AG)	(1) CO + 2H ₂ ⇌ CH ₃ OH	CO: 10-	473-	34-	slurry reactor
	(2) CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	20	513	41	
	(3) CO ₂ + H ₂ ⇌ CO + H ₂ O	CO ₂ : 10- 20 H ₂ : 60- 80			

Šetinc and Levec (1999) have presented some other kinetic equations from earlier studies. The equations and used operating conditions are collected in Table 9. The exact references can be found from Šetinc and Levec (1999).

Table 9. Other kinetic models (Šetinc and Levec 1999).

Catalyst	Equation	Feed [mol %]	T [K]	P [bar]	Author
powdered Cu/Zn/Al (5-10 μm)	$r_{CH_3OH} = k \left(c_{CO} c_{H_2}^2 - \frac{c_{CH_3OH}}{K_c} \right)$	CO:25 CO ₂ : 19 H ₂ : 50	473- 543	35- 70	Brown et al. (1984)
United catalyst	$r_{CH_3OH} = k (c_{CO} c_{H_2}^2)^{\frac{1}{3}} \left(1 - \frac{c_{CH_3OH}}{c_{H_2}^2 c_{CO} K_c} \right)$	CO: 19- 51 CO ₂ : 4- 13 H ₂ : 35- 55	523	20- 60	Weimer et al. (1987)
United catalyst EPJ-25 100-120 mesh	$r_{CH_3OH} = k (p_{H_2} - p_{H_2,eq})$ $r_{CH_3OH} = k (c_{H_2} - c_{H_2,eq})$	CO: 15- 50 CO ₂ : 5- 10 H ₂ : 34- 75	478- 523	41,5- 90,2	Lee et al. (1985)
Cu/ZnO/ Al ₂ O ₃ EPJ-25	$r_{CH_3OH} = \frac{k(c_{CO}c_{H_2}^2 - c_{CH_3OH}/K_c)}{(K_0 + K_{H_2}c_{H_2}^{0,82} + K_{CO}c_{CO}^{0,82} + K_{CH_3OH}c_{CH_3OH}^{2,09})^n}$	CO: 4,9- 50 CO ₂ : 6,8- 10 H ₂ : 14- 70 CH ₃ OH: 1,5-23	477- 523	44- 89	Vijayaraghavan & Lee (1993)
Cu/ZnO/ Al ₂ O ₃	$r_{CH_3OH} = k \left(c_{H_2} - \frac{c_{CH_3OH}}{K_c c_{CO} c_{H_2}} \right)$	CO: 26,2; 15 CO ₂ : 6,9; 10 H ₂ : 62,7; 70 CH ₄ : 4,2; 5	493- 513	78,5- 101, 3	Krishnan (1999)

5 METHANOL SYNTHESIS SIMULATOR

Simulators are used to gain knowledge from the studied process. Steady-state or dynamic simulators can be used depending on the aim of the simulations. Steady-state simulations can be used to solve the mass and energy balances of the system and to evaluate different system configurations. Steady-state simulators thus give valuable information for the optimization purposes. Dynamic simulators describe the time-dependent behaviour of the process. As the steady-state simulators provide information for the optimization, the dynamic simulators can be used to evaluate different control strategies and to study the complex, time-dependent interactions of the process variables. The analysis of the process dynamics is an essential task since the steady-state model itself is not adequate for a complete process and control design. Typically, steady-state and dynamic simulators complemented each other in process design.

This section provides a general representation of the mass balances of methanol synthesis. This section also introduces steady-state and dynamic simulators of the methanol synthesis which utilize the kinetic equation by Vanden Bussche and Froment (1996). The equation is used as a case study because the operational conditions and the feed composition are similar to those that should be used in the studies during the research project CO2UTIL. Naturally, the catalyst is not the same during CO2UTIL and the study carried out by Vanden Bussche and Froment (1996) but the same model structure could be applicable.

5.1 The mass balance model

The mass balances are based on the flow conditions and the assumed reaction scheme. The mass balance can be written as

$$\left[\begin{array}{c} \text{change of the} \\ \text{substance} \end{array} \right] = \left[\begin{array}{c} \text{the flow rate of} \\ \text{the substance in} \end{array} \right] - \left[\begin{array}{c} \text{the flow rate of} \\ \text{the substance out} \end{array} \right] + \left[\begin{array}{c} \text{production of} \\ \text{the substance} \end{array} \right]. \quad (18)$$

The sign of the production term is negative if the substance is consumed in chemical reactions. With mathematical notations, the mass balance for substance i is

$$\frac{dn_i}{dt} = \dot{n}_{i,in} - \dot{n}_i + R_i. \quad (19)$$

Above, n [mol] is the amount of substance, \dot{n} [mol/s] is the molar flow rate, and R [mol/s] is the specific production/consumption rate of the substance. Usually, the mass balance is expressed in concentrations of the substances. Such an equation is obtained through equation

$$n_i = C_i V. \quad (20)$$

Above, C is the concentration and V is the volume. Substituting (20) into (19) and assuming the constant volume results in

$$V \frac{dC_i}{dt} = F(C_{i,in} - C_i) + R_i. \quad (21)$$

Now, the mass balances for methanol synthesis can be written based on (21). The mass balances are

$$\begin{aligned} \frac{dC_{CO}}{dt} &= \frac{F}{V}(C_{CO_{in}} - C_{CO}) - R_1 - R_3 \\ \frac{dC_{H_2}}{dt} &= \frac{F}{V}(C_{H_2_{in}} - C_{H_2}) - 2R_1 - 3R_2 + R_3 \\ \frac{dC_{CO_2}}{dt} &= \frac{F}{V}(C_{CO_2_{in}} - C_{CO_2}) - R_2 + R_3 \\ \frac{dC_{H_2O}}{dt} &= \frac{F}{V}(C_{H_2O_{in}} - C_{H_2O}) + R_2 - R_3 \\ \frac{dC_{CH_3OH}}{dt} &= \frac{F}{V}(C_{CH_3OH_{in}} - C_{CH_3OH}) + R_1 + R_2 \end{aligned} \quad (22)$$

The reaction rate may be calculated in different ways. In the studies concerning methanol synthesis, the reaction rate is typically expressed as

$$R = m_{cat} r. \quad (23)$$

Above, m_{cat} [kg] is the mass of the catalyst and r is the specific reaction rate [mol/s/kg]. The kinetic models derived for methanol synthesis often use the partial pressures of the substances. The concentrations are converted to partial pressures by

$$x_i = \frac{C_i}{\sum C_i} \text{ and} \quad (24)$$

$$p_i = x_i p. \quad (25)$$

Above, x_i is the mole fraction of substance i , p_i is the partial pressure of the substance i and p is the total pressure.

5.2 Steady-state simulator

The steady-state simulator is obtained by setting the derivatives of (22) to zero. The solution of the steady-state concentrations requires a solution of nonlinear algebraic equations. The developed simulator uses the kinetic model proposed by Vanden Bussche et al. (1996) presented in equation 11. It should be noticed that the used kinetic equation

is based on the reactions 2 and 3 and thus the reaction rate R_1 is set to be zero. The parameters for the kinetic equation are given in Appendix 1. Table 10 lists the operating conditions and the feed composition as presented in Vanden Bussche and Froment (1996). Also, the physical measures of the reactor are given in Table 10. The steady-state behaviour of the process as a function of temperature is presented in Figure 3. Figure 4 shows the steady-state behaviour of the process with varying pressure. Figure 4 shows, that higher pressure increases the output concentration of CH_3OH . The optimal temperature concerning the production of methanol is about $520\text{ }^\circ\text{C}$ as shown in Figure 3.

Table 10. The feed composition, operating conditions and reactor size.

Reactor	Diameter (m)	Length (m)	Catalyst mass (g)			
	0.016	0.15	34.8			
Operating Conditions	Temperature (K)	Pressure (p)	Mass feed rate (10^{-2} g/s)			
	493.2	50	2.8			
Feed com- position	CO (mol %)	H_2O (mol %)	CH_3OH (mol %)	H_2 (mol %)	CO_2 (mol %)	Inert (mol %)
	4	0	0	82	3	11

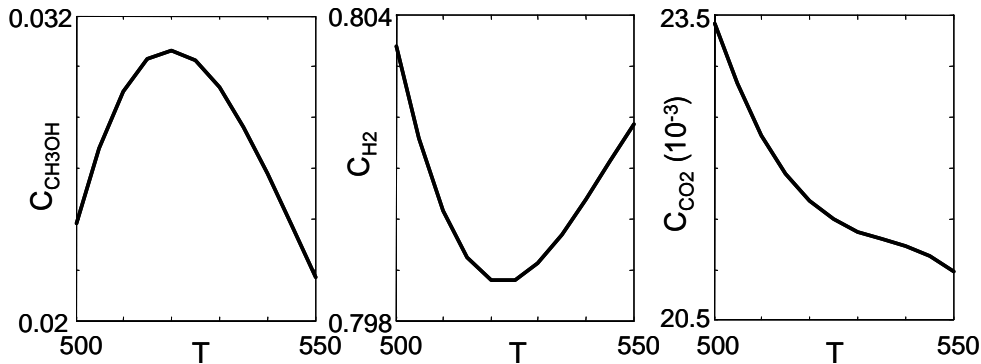


Figure 3. Steady-state concentrations with varying temperature ($p = 50$ bar).

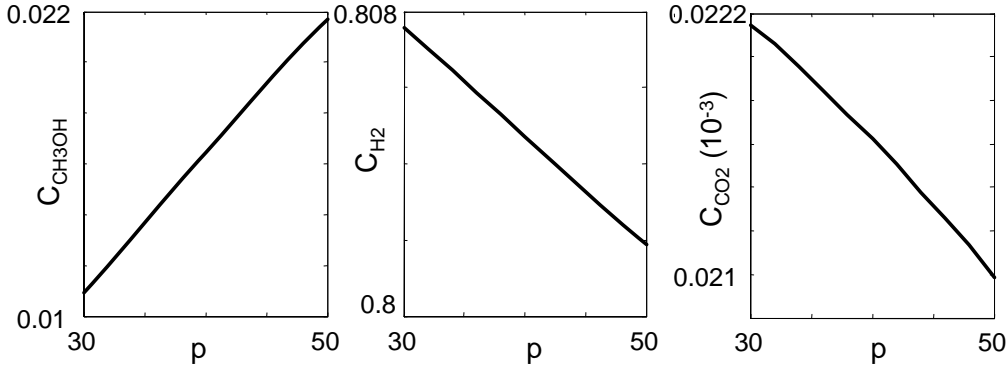


Figure 4. Steady-state concentrations with varying pressure ($T = 493,2 \text{ }^\circ\text{C}$).

5.3 Dynamic simulator

The dynamic simulator for methanol synthesis is based on the mass balances given in equation 22. The simulator is presented in Figure 5. It includes three subsystems: one for defining the inputs, the other for calculating the reaction rates based on the operating conditions (p and T) and the third for solving the mass balances. The subsystem solving the mass balances is given in Figure 6. As can be seen, the mass balances for each substance are built separately. The simulator uses the same kinetic model, parameters and operating conditions as the steady-state simulator. Even though the kinetic equation by Vanden Bussche and Froment is used, the simulator is built in such a way, that other kinetic models can be easily included.

To guarantee the validity of the simulator, the simulations carried out by Vanden Bussche and Froment (1996) were repeated. The results of the simulations are provided in Figure 7. The figure shows the concentrations of the substances with the values given in Table 10. The figure also shows the output concentration of methanol with different operating pressures. All the concentrations in Figure 7 are pretty much the same as presented in Vanden Bussche and Froment (1996) and the simulator can be considered valid.

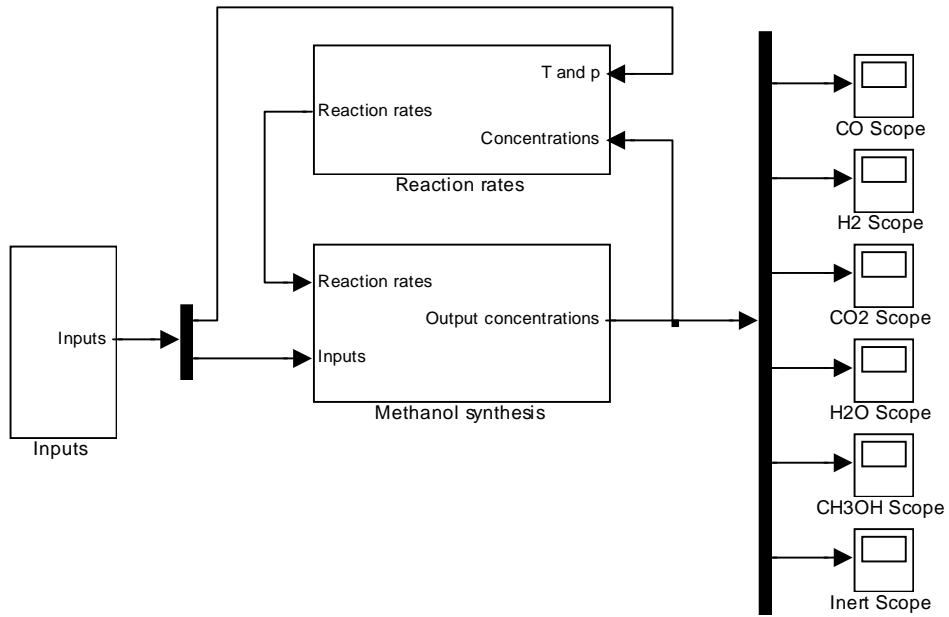


Figure 5. The dynamic simulator of the methanol synthesis.

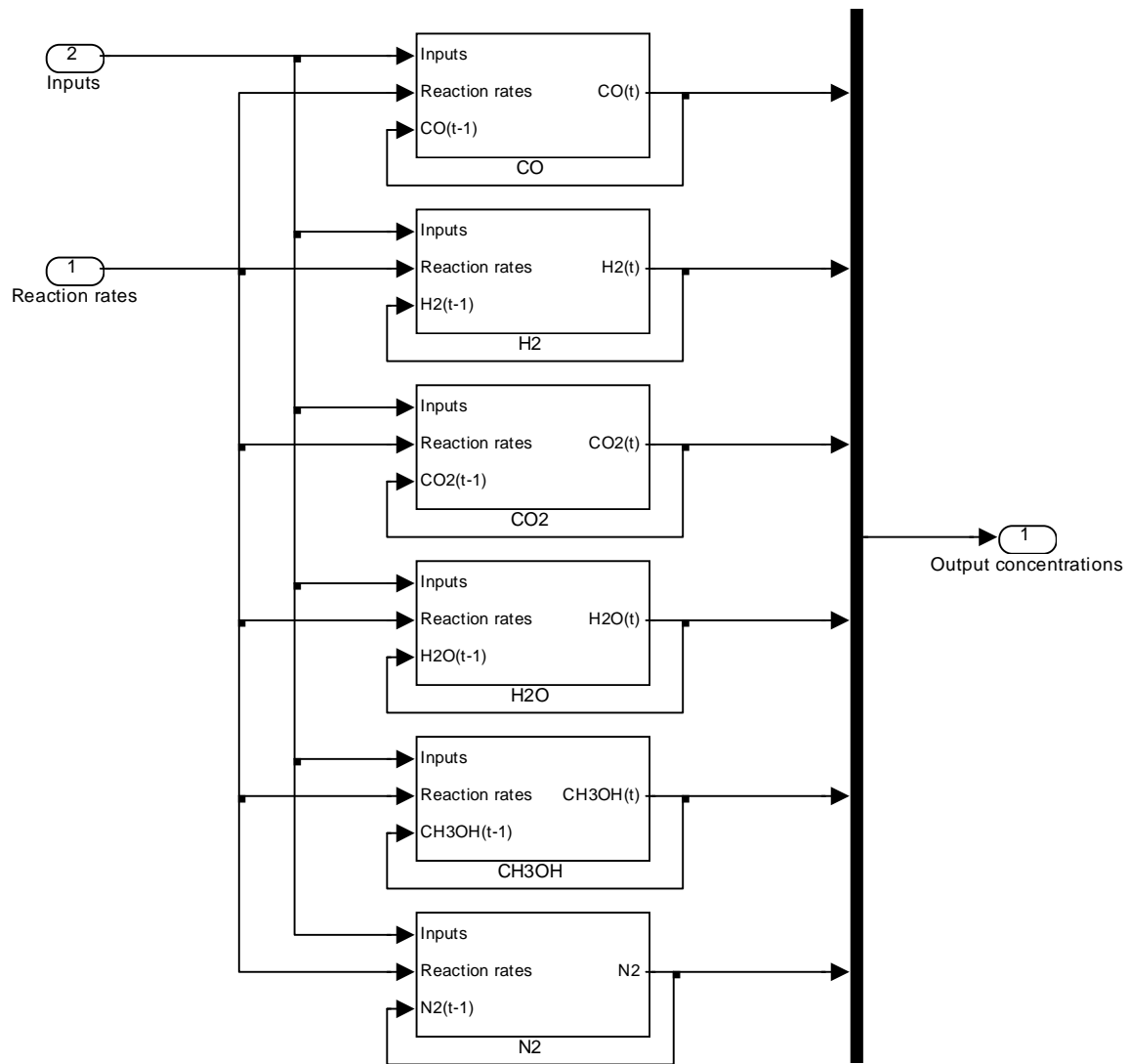


Figure 6. The subsystem for solving the mass balances.

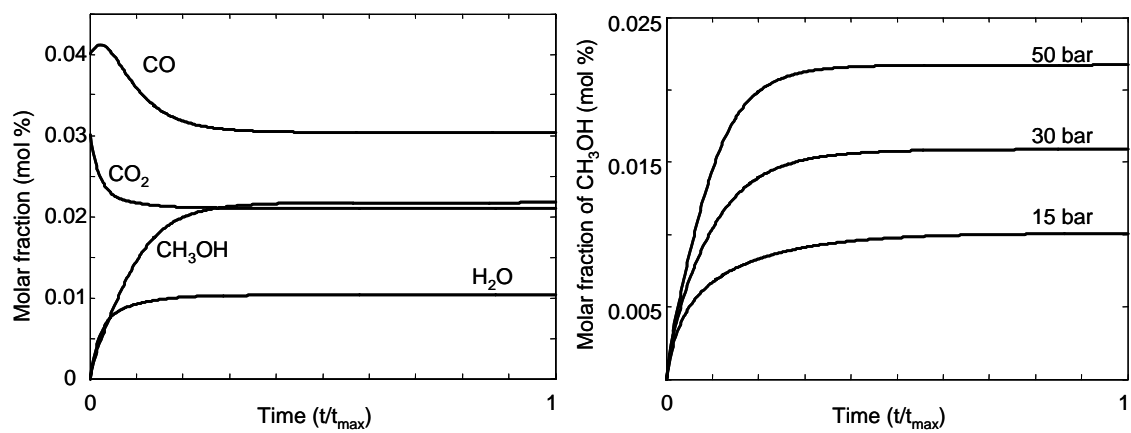


Figure 7. Simulation results with the parameters given in Table 10.

6 SENSITIVITY ANALYSIS

Through sensitivity analysis, information about the importance of the input variables and model parameters can be obtained. Such information is useful while assessing the modelling results. The input variables and model parameters include a lot of uncertainty arising from different sources. This uncertainty passes through the model to the output variables. Understanding the sensitivity of the model outputs to uncertainty is essential while developing reliable models. (Campolongo and Braddock 1999) Whitcombe et al. (2003) used sensitivity analysis to gain knowledge from the interactions between operational parameters and emissions in fluidising catalytic cracking units employed in the petroleum industry. Sensitivity analysis has been used for the same purpose also by other authors. Quina and Quinta Ferreira (1999) used sensitivity analysis for the catalytic fixed bed reactors while Zafir and Gavrilidis (2002) used it for catalytic plate reactors. Nagel et al. (2008) and Corrêa et al. (2005) have used sensitivity analysis to gain knowledge from the fuel cell applications. The starting point for each of the investigations mentioned above is the lack of understanding of the interactions/phenomena within the studied process. The results from the applied sensitivity analysis have typically revealed some new information about the processes.

6.1 Applied sensitivity analysis

The process model can be expressed as a function of the variables defining the operational conditions (temperature, pressure, composition of the feed) of the reactor and the set of the parameter values. The model is given by

$$y = f(x, p) + e. \quad (26)$$

Above, x is the set of variables defining the operational conditions, p is the parameter set identified for the model and e is the modelling residuals. The predictions of the model are calculated from

$$\hat{y} = f(x, \hat{p}). \quad (27)$$

The objective function used in the sensitivity analysis is simply the sum of the squared errors between the observed and the predicted values. The observed value may also be produced by a simulator as done in Correa et al. (2005). The objective function corresponding to the k :th value of the studied variable is (Correa et al. 2005)

$$J_k = \sum_{i=1}^N [y_k - f(x_k, \hat{p}_i)]^2. \quad (28)$$

The relative importance of each parameter corresponding to the k :th value of the studied variable is (Correa et al. 2005)

$$\delta_k = \frac{J_k}{y_k}. \quad (29)$$

Finally, the overall sensitivity of the parameter is calculated from (Correa et al. 2005)

$$\gamma = \sum_{k=1}^K \delta_k. \quad (30)$$

In the equations above, y_k is the observed output, x_i is the test set generated for each variable, N is the number of tests in the testing set and K is the number of values for the studied variable.

The basic procedure for the sensitivity analysis includes the following steps (Correa et al. 2005):

1. Selection of the N parameters for testing.
2. Select the studied values for the variable.
3. Define the ranges of the parameters.
4. Generate a random (uniform distribution) testing set with i experiments for each parameter within the defined range.
5. Execute the tests with the model and calculate the value of the objective function (J_k).
6. Determine the relative importance of the parameters with different values of the studied variable (δ_k).
7. Evaluate the sensitivity of each parameter (γ).

6.2 Results

The kinetic equation proposed by Vanden Bussche and Froment (1996) has five parameters. All the parameters are temperature dependent and follow equation

$$\text{Parameter} = A \exp\left(\frac{B}{RT}\right). \quad (31)$$

The sensitivity is analysed for each parameters' A and B terms. The sensitivities were calculated to several outputs. The studied outputs were the reaction rates and the yield of methanol. The relative importance (δ) were calculated with varying operational conditions (temperature and pressure). The temperature and pressure were varied between [500 550] and [30 50], respectively. The overall sensitivity (γ) of each parameter was also determined. The studied parameters and their ranges are presented in Table 11.

First, the relative importance of each parameter to each output variable was calculated for each studied level of temperature and pressure. It was noticed that the relative importance of parameters corresponding any of the output variables behaved in a very same manner

with different temperatures. This is shown in Table 12, which presents the correlation coefficients between the relative importances of the parameters to each output variable with the varying temperature. Thus it is enough to analyse the sensitivity of the parameters to any of the output variables. For further analysis of sensitivity with different temperature levels, the reaction rate R_2 is studied.

The relative importance with the varying pressure shows a bit different behaviour. It was noticed that the relative importance of the reaction rate R_2 and the methanol yield behaved similarly but the reaction rate R_3 did not. Table 13 presents the correlation coefficients between the relative importances of the parameters with the varying pressure. For further studies of the sensitivity, reaction rates R_2 and R_3 were selected.

Table 11. The ranges for the studied parameters.

Parameter		Range
k_1	A	$\pm 15\%$
	B	$\pm 15\%$
k_2	A	$\pm 15\%$
	B	$\pm 15\%$
k_3	-	$\pm 15\%$
k_4	A	$\pm 15\%$
	B	$\pm 15\%$
k_5	A	$\pm 15\%$
	B	$\pm 15\%$

Table 12. Correlation coefficients between the relative importance of the parameters to each output variable with the varying temperature.

	$\delta(R_2)$	$\delta(R_3)$	MeOH yield
$\delta(R_2)$	1.00	0.95	1.00
$\delta(R_3)$	0.95	1.00	0.95
MeOH yield	1.00	0.95	1.00

Table 13. Correlation coefficients between the relative importance of the parameters to each output variable with the varying pressure.

	$\delta(R_2)$	$\delta(R_3)$	MeOH yield
$\delta(R_2)$	1.00	0.60	1.00
$\delta(R_3)$	0.60	1.00	0.60
MeOH yield	1.00	0.60	1.00

6.2.1 Varying temperature

To identify the most sensitive parameters, the histogram of the overall sensitivity of the parameters is studied. Figure 8 shows the overall sensitivity for all the parameters to

reaction rate R_2 with different temperatures. The histogram in Figure 8 reveals four significant parameters. The significant parameters are all the B terms of the equations. This is quite obvious result, because the B terms are in the exponents while the A terms are only multipliers.

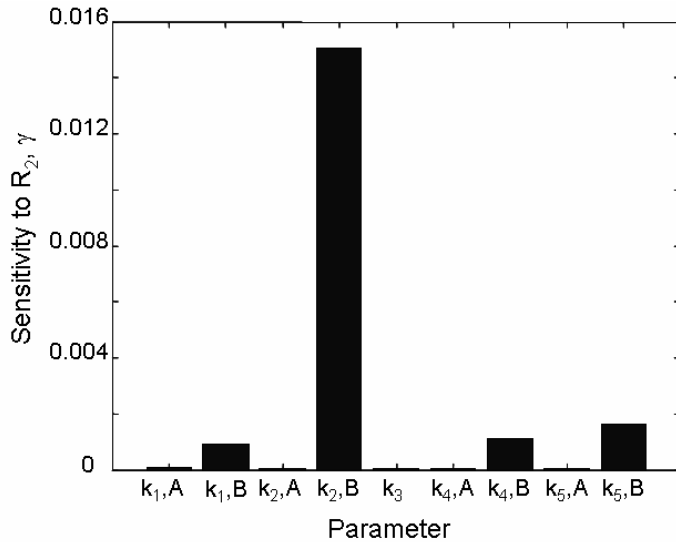


Figure 8. The sensitivity of the parameters to the reaction rate R_2 with the varying temperature.

The significant parameters are studied more carefully to find the temperature dependency of the sensitivity. Figure 9 shows the relative importance of the parameters as a function of temperature. It can be seen that the sensitivity is at highest with lower temperatures. It can also be noticed that the relative importance of the parameter B of k_2 is the greatest for all temperatures. The relative importances of the other parameters are more or less the same.

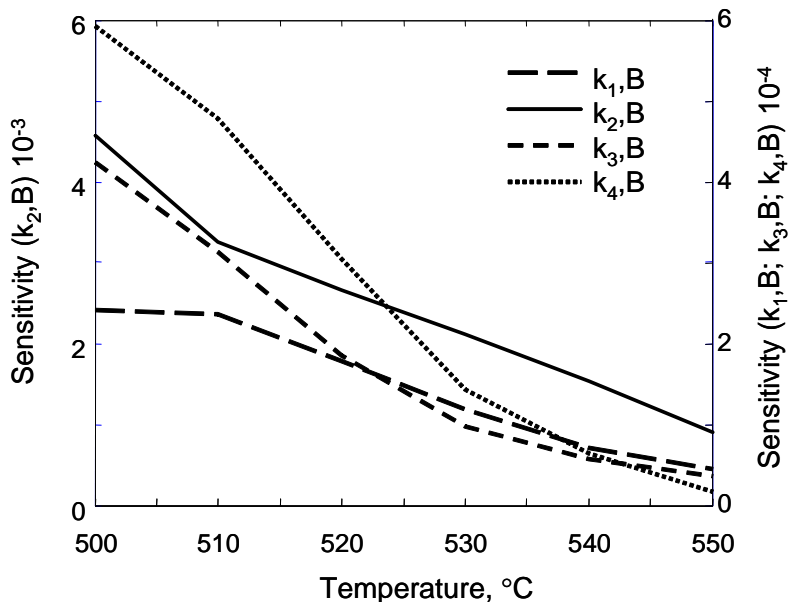


Figure 9. The relative importance as the function of the temperature.

6.2.2 Varying pressure

Figure 10 shows the sensitivities of the parameters to the reaction rates R_2 and R_3 when the pressure is changed. The histogram for R_2 shows that the most sensitive parameters are the B terms for k_1 and k_2 . Also, it seems that all the other B terms are more sensitive than the A terms, but the difference is not as clear as with the varying temperature. Thus the B terms for k_1 and k_2 are studied more carefully (Figure 11). Figure 11 shows that the increasing pressure also increases the relative importance of the studied parameters. The results given in Figure 10 are not that clear for the reaction rate R_3 . First of all, it can be noticed that the sensitivities are higher than for R_2 . Second, there is not that big difference between the most sensitive parameters. Still, the same parameters as before (the B terms of k_1 and k_2) are the most sensitive. The other parameters that show a bit higher sensitivity are the A terms of k_1 and k_3 .

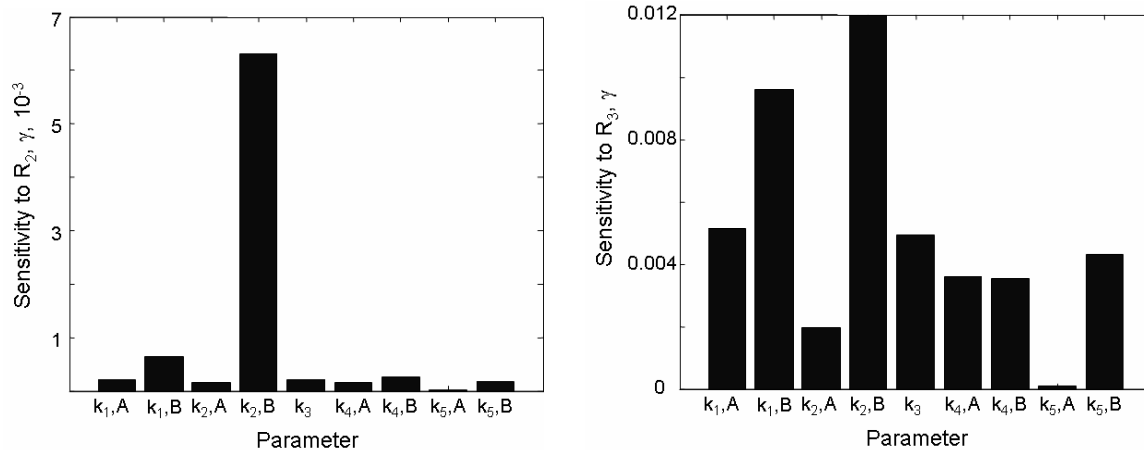


Figure 10. The sensitivity of the parameters to the reaction rates R_2 and R_3 with the varying pressure.

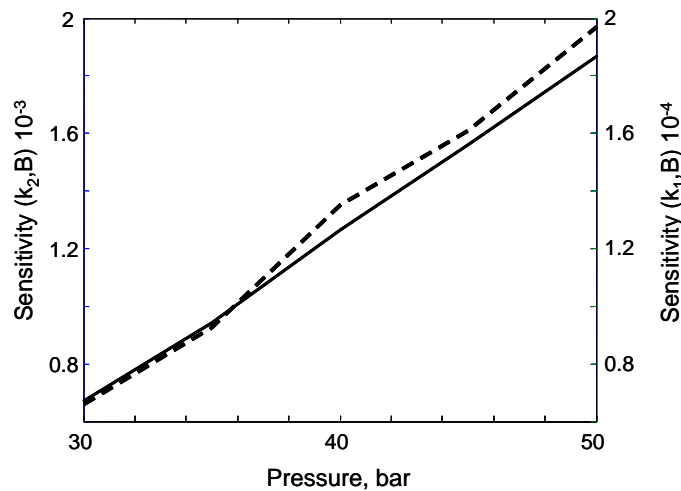


Figure 11. The relative importance to R_2 as the function of the pressure.

7 FUTURE WORK

The simulator introduced in this report uses the kinetic model proposed by Vanden Bussche and Froment (1996) and does not include the energy balance. In the future, the energy balance will be added to predict the temperature changes in the reactor. The temperature is an important variable considering the performance of the process and thus it should be taken into consideration. Other kinetic models presented in this report will be added to the simulator. The additions are made in order to compare the results from different kinetic models and to evaluate the suitability of the existing kinetic models to the data obtained from laboratory experiments.

Some data can be generated with the simulator presented in this report. The data are used to study possible techniques (such as genetic algorithms) for the identification of the model parameters. The data can be used also to study the possibilities of using alternative methods (such as neural networks) for the kinetic modelling.

As the data are available from the laboratory experiments, the experiences obtained with the generated data are implemented with the real-life data. The aim is to develop the simulator that can be used for predicting the dynamic behaviour of the methanol synthesis process.

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APPENDIX 1

Kinetic models from the literature.

The values of the parameters are based on the equation:

$$\text{Parameter} = A \exp(B/RT)$$

expect the equation by Coteron and Hayhurst (1994) follows the equation:

$$\text{Parameter} = A \exp[B(1/T_M + 1/T)].$$

Klier et al. 1982

$$r_1 = k_1 \left(1 + \frac{1}{K_{redox}^{eq}} \frac{p_{CO}}{p_{CO_2}} \right)^{-3} \frac{K_{CO} K_{H_2}^2 (p_{CO} p_{H_2}^2 - p_{CH_3OH} / K_1^{eq})}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2})}$$

$$r_2 = k_2 \left(p_{CO_2} - \frac{1}{K_2^{eq}} \frac{p_{CH_3OH} p_{H_2O}}{p_{H_2}^3} \right)$$

Graaf et al. 1996

$$r_{CH_3OH} = \frac{k_1 K_{CO} (c_{CO} c_{H_2}^{3/2} - c_{CH_3OH} / c_{H_2}^{1/2} K_1^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O}}$$

$$r_{H_2O} = \frac{k_2 K_{CO_2} (c_{CO_2} c_{H_2} - c_{H_2O} c_{CO} / K_2^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O}}$$

$$r_{CH_3OH}^* = \frac{k_3 K_{CO_2} (c_{CO_2} c_{H_2}^{3/2} - c_{CH_3OH} c_{H_2O} / c_{H_2}^{3/2} K_3^{eq})}{(1 + K_{CO} c_{CO} + K_{CO_2} c_{CO_2}) c_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) c_{H_2O}}$$

	A	B
k_1	1,66e5	-93925
k_2	7,21e17	-215130
k_3	8,52e-1	43425
K_{CO}	9,01e-12	92138
K_{CO_2}	3,15e-5	34053
$K_{H_2O}/K_{H_2}^{0.5}$	2,71e-12	103030
K_1^{eq}	2,391e-13	98388
K_2^{eq}	1,068e2	-39683
K_3^{eq}	2,554e-11	58705

von Wedel et al. 1988

$$r_{CH_3OH} = k C_{H_2}^{0,4} C_{CO}^{0,18} - k_{-1} C_{CH_3OH}^{0,13}$$

	A	B
k	1,98e7	-56343
k_{-1}	2,15e10	-85930

Skrzypek et al. 1991

$$r_1 = k_1 K_{H_2}^2 K_{CO} \left[\frac{p_{H_2}^2 p_{CO_2} - \frac{p_{CH_3OH} p_{H_2O}}{K_2^{eq} p_{H_2}}}{(1 + K_{H_2} p_{H_2} + K_{CO_2} p_{CO_2} + K_{CH_3OH} p_{CH_3OH} + K_{H_2O} p_{H_2O} + K_{CO} p_{CO})} \right]$$

$$r_2 = k_2 K_{H_2} K_{CO_2} \left[\frac{p_{H_2} p_{CO_2} - \frac{p_{CO} p_{H_2O}}{K_2^{eq} p_{H_2}}}{(1 + K_{H_2} p_{H_2} + K_{CO_2} p_{CO_2} + K_{CH_3OH} p_{CH_3OH} + K_{H_2O} p_{H_2O} + K_{CO} p_{CO})} \right]$$

	A	B
k_1	3e9	-104700
k_2	2,5e9	-104700
K_{CO}	4,93e-16	75400
K_{CO_2}	4,34e-14	75400
K_{H_2}	1,38e-14	75400
K_{H_2O}	3,45e-14	75400
K_{CH_3OH}	1,09e-15	29300
K_1^{eq}	2,391e-13	98388
K_2^{eq}	1,068e2	-39683

Ledakowicz et al 1992

$$r_{CH_3OH} = k \left[\left(c_{H_2}^2 c_{CO} \right) - \left(\frac{c_{CH_3OH}}{K_c} \right) \right]$$

	A	B
k	9,08e5	-62,9
K_c	2,391e-13	98388

APPENDIX 1

Kinetic models from the literature.

	From H2 and CO			
Coteron and Hayhurst 1994	$r_M = \frac{k_{f_1} K_{CO} K_H^2 K_{CH} P_{CO} P_{H_2}^2}{1 + K_{CO} P_{CO} + K_{CO} K_H^{3/2} K_{CH} P_{CO} P_{H_2}^{3/2}}$	k_{f_1}	A	B
	Form H2, CO and CO2	K_{CO_2}	3,717e-5	5144
	$r_M = \frac{k_{f_1} K_{CO_2} K_H K_{HCO_2} P_{CO_2} P_{H_2}}{1 + K_{CO_2} P_{CO_2} + K_{CO_2} K_H^2 K_{HCO_2} P_{CO_2} P_{H_2}^2 + \frac{K_{CO_2} P_{CO_2}}{K'_{CO} P_{CO}}}$	K_H	5,207e-1	-
		K_{HCO_2}	3,579	-1328
		K'_{CO}	1,758	-
			2,857e-3	-1225
Vanden Bussche and Froment 1996	$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} (1 - P_{CH_3OH} P_{H_2O} / K_1^{eq} P_{CO_2} P_{H_2}^3)}{(1 + K_{WH} P_{H_2O} / P_{H_2} + \sqrt{K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}})^3}$	k_1	A	B
	$r_{RWGSR} = \frac{k_2 P_{CO_2} [1 - K_3^{eq} (P_{H_2O} P_{CO} / P_{CO_2} P_{H_2})]}{(1 + K_{WH} P_{H_2O} / P_{H_2} + \sqrt{K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}})^3}$	k_2	0,499	17197
		K_{WH}	6,62e-11	124119
		K_{H_2}	3453,38	-
		K_{H_2O}	1,07	36696
		K_1^{eq}	1,22e10	-94765
		K_3^{eq}	2,391e-13	98388
			2,554e-11	58705
Šetinc and Levec 2001	$r_{Me} = k_1 \frac{c_{CO_2} (c_{H_2} - c_{H_2,eq})}{(1 + K_{H_2O} c_{H_2O})^2}$	k_1	A	B
	$r_{H_2O} = k_2 \frac{c_{CO_2} - c_{CO_2,eq}}{(1 + K_{H_2O} c_{H_2O})}$	k_2	9,25e13	-82250
		K_{H_2O}	3,91e7	-54640
			1,32e2	9550