LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
LUT School of Engineering Science
Degree Program of Chemical Engineering

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INDIRECT HYDROGENATION OF CO_2 TO METHANOL VIA FORMATE INTERMEDIATE

Examiners: Professor Tuomas Koiranen
Docent Arto Laari

Supervisor: Docent Arto Laari
Harri Nieminen

ABSTRACT

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Methanol is an important chemical compound which finds various applications in industry. Methanol is mostly produced from fossil feedstock such as natural gas, coal and oil. The direct gas phase hydrogenation of syngas - mixture of CO, CO_2 and H_2 over Cu-Zn-oxide based catalysts is presently the main route of methanol synthesis. However, alternative routes of methanol production based on renewable sources, such as utilization of captured CO_2 and renewable H_2 produced from wind and solar energy, are of great interest due to the current increase of oil prices and growing concerns connected to climate change. Direct hydrogenation of syngas mainly consisting of CO_2 to methanol is associated with problems related to thermodynamic limitations. For that reason, indirect hydrogenation of CO_2 via its derivatives is gaining scientific significance. One such process is a low-temperature methanol synthesis in liquid medium. In this method alcohol is used as a catalytic solvent and acts as a promoter for the methanol synthesis reaction proceeding via corresponding formate intermediate.

For this thesis, the alcohol promoted liquid phase methanol synthesis performed in autoclave reactor was studied at laboratory scale. Experiments were carried out at a temperature range of 180-220^{o}C and total pressure of 60 bar. Different alcohol solvents, such as 2-butanol, 1-butanol, 2-propanol and 1-pentanol were tested as promoters in the methanol synthesis. Conventional $CuO/ZnO/Al_2O_3$ catalyst was used as such and in combination with a molecular sieve and a

$Cr_2Cu_2O_5$ catalyst to evaluate the effects of simultaneous water removal and utilization of mixed catalysts on the methanol synthesis.

The specific productivity of methanol was found to increase with decreasing temperature of the process. In-situ water removal from the reaction mixture, as well as utilization of combined catalysts brought positive results regarding methanol synthesis. Maximal catalyst specific productivity of 54.4 g of methanol per kg of catalyst per hour and volumetric specific productivity of 3.36 g of methanol per liter of solvent per hour were obtained during the experiments. The productivity values are low compared to gas-phase synthesis from CO_2. However, milder process conditions and simple operation of alcohol-promoted methanol synthesis could prove useful for small-scale methanol synthesis plant. Additional research is required to make final conclusions about the feasibility of this process.

CONTENTS

Acronyms 6
Nomenclature 8

LITERATURE REVIEW 9

1. Introduction 9
  1.1. Comparison of CCS and CCU strategies 9
  1.2. Renewable energy and synergetic use of “Hydrogen and Methanol Economy” concepts 10
  1.3. Market overview and future perspectives for renewable methanol 11
  1.4. Aims of the thesis 12

2. Conventional gas-phase methanol synthesis via syngas 13
  2.1. Syngas production routes 15
  2.2. Syngas preparation technologies 17
  2.3. Reactors for methanol synthesis 22
  2.4. Methanol purification 28

3. Production of methanol from CO_2 and H_2 29
  3.1. CO_2 and H_2 for methanol production 29
  3.2. Methanol through direct hydrogenation of CO_2 38
  3.3. Catalysts for CO_2 hydrogenation to methanol 38
    3.3.1. Promoted Cu-based catalysts 39
    3.3.2. Other modified catalysts for CO_2 conversion to methanol 41
    3.3.3. Investigations of the reaction pathways and mechanisms 42
    3.3.4. Short summary of catalyst advances 44
  3.4. Indirect hydrogenation of CO_2 to methanol 46
    3.4.1. Hydrogenation of organic carbonates, carbamates and formates to methanol 46
    3.4.2. Hydrogenation of cyclic carbonates to methanol 48
    3.4.3. Hydrogenation of urea derivatives to methanol 49
    3.4.4. Cascade catalysis for the hydrogenation of CO_2 to methanol 50
    3.4.5. Transfer hydrogenation of organic formates and cyclic carbonates to methanol 52
  3.5. Progress and technological advances in methanol synthesis 54
    3.5.1. Two-stage catalyst bed concept of methanol synthesis 54
    3.5.2. Thermally coupled reactor for simultaneous hydrogen and methanol production 55
    3.5.3. CAMERE process 56

3.5.4. BNL method of methanol synthesis 57
3.5.5. Methanol synthesis through methyl formate 58
3.5.6. LPMEOH project 58
3.5.7. Low-temperature alcohol promoted methanol synthesis 60
3.5.8. Coated catalytic reactors for methanol synthesis 62
3.5.9. Reactive distillation 66

EXPERIMENTAL PART 69

4. Aims and content of experimental part 69
4.1. Experimental plan 69

5. Materials and research methods 71
5.1. Experimental setup 71
5.2. Experimental procedure 72
5.2.1. Preparation and activation of catalysts 72
5.2.2. Preparation and activation of molecular sieve 74
5.2.3. Running of experiments and sampling 74
5.2.4. Analysis of liquid samples 76
5.2.5. Particle size distribution analysis 77

6. Results and discussions 78
6.1. Comparison of catalyst activation methods 78
6.2. Effect of temperature on methanol synthesis and formation of by-products 79
6.3. Effect of in-situ water removal on methanol synthesis 86
6.4. Effect of catalyst combination on methanol synthesis 92
6.5. Effect of process conditions on the catalyst size 94
6.6. Summary of experimental section 97

7. Conclusions 99

REFERENCES 101

Appendix I: Analysis of liquid samples
Appendix II: Calculation examples

Acronyms

CCS	Carbon capture and sequestration strategy
CCU	Carbon capture and utilization strategy
MTBE	Methyl tertiary-butyl ether
MMA	Methyl methacrylate
DMT	Dimethyl terephthalate
DME	Dimethyl ether
MTG	Methanol to gasoline process
MTO	Methanol to olefin process
RWGS	Reverse water-gas shift reaction
SN	Stoichiometric number
MTPD	Metric tons per day
ATR	Auto-thermal reforming of methane
PSA	Pressure swing adsorption
TSA	Temperature-swing adsorption
ESA	Electrical-swing adsorption
GHR	Gas-heated reforming
TCC	Tube-cooled converter
A-SRC	Axial steam-raising converter
R-SRC	Radial steam-raising converter
IGCC	Integrated gasification combined cycle
MEA	Monoetanolamine
DEA	Diethanol-amine
MDEA	Methyl diethanol-amine
PEM	Proton exchange membrane
SOEC	Solid-oxide electrolysis cells
YSZ	Yttria stabilized zirconia
YDC	Yttria doped with ceria
DFT	Density functional theory
FTIR	Fourier transform infrared
THF	Tetrahydrofuran
BNL	Brookhaven National Laboratory
LPMEOH	Liquid-phase methanol synthesis process

WHSV	Weight hourly space velocity
TON	Turnover number
CSP	Catalyst specific productivity
VSP	Volume specific productivity

Nomenclature

m_{MeOH}	Mass of methanol produced [g]
$m_{catalyst}$	Mass of catalyst used [kg]
t	Experimental time [h]
c_{MeOH}	Methanol concentration [ppm]
$V_{solvent}$	Volume of the solvent [m^3]
$\rho_{solvent}$	Density of the solvent [kg/m^3]

LITERATURE REVIEW

1. Introduction

Global energy consumption is increasing constantly as a result of population and economic growth. Presently, the major source of energy is the combustion of fossil fuels. It is predicted to observe this trend in the short and middle term due to the low cost, availability, high energy density and existing reliable technologies for the processing and transformation of coal, crude oil and natural gas to the energy and products essential for the humankind [1]. The consequence of burning of fossil fuels is the emissions of carbon dioxide (CO_2) into the atmosphere, the contribution of which to global warming and the greenhouse effect has led to significant concerns among the scientific society. In this context, technologies in the field of CO_2 capture, storage and utilization can be considered as the possible solution to this ongoing issue bringing both economic and environmental benefits. Thus, reliable technologies capable to utilize the great potential of CO_2 are presently a topic of great interest in scientific investigations. [2]

1.1. Comparison of CCS and CCU strategies

Power and process plants are the major sources of CO_2 emissions to the atmosphere [2]. Therefore, the development and integration of technologies for the capture of CO_2 from these sources could be considered a breakthrough and help to decrease the worldwide emissions of CO_2. The solution of this problem can be achieved with two closely related approaches. Namely, Carbon capture and storage or sequestration (CCS) and Carbon capture and utilization (CCU). [3]

The Carbon capture and sequestration approach (CCS) is focused on the long-term storage of the captured carbon dioxide into naturally or anthropogenically formed reservoirs and geologic formations such as depleted oil and gas fields. This strategy can be useful for the initial decrease of CO_2 emissions mitigating the negative climate effects. Nevertheless, obvious drawback of the CCS strategy is that the investments paid for the sequestration and storage of CO_2 often have no economic value. Additionally, the reduction in the power plant efficiency caused by the integration of the latest capturing technologies is another issue. Furthermore, this approach is useless when answering the constantly growing energy demand. [3]

Contrariwise, the objective of the Carbon capture and utilization (CCU) strategy is the use of captured CO_2 as a raw material for conversion into marketable products such as methanol, DME, carbonates, formic acid and others or even into ready fuels such as methane and liquid hydrocarbons [2]. In addition, technologies for the biological conversion such as direct photo-conversion or bacterial fermentation of CO_2 also exist. However, the obvious disadvantage of the CCU technologies is that the captured and converted CO_2 may be emitted when the products are used. [3]

1.2. Renewable energy and synergetic use of "Hydrogen and Methanol Economy" concepts

Technologies focused on the utilization of solar radiation, wind, geothermal and hydrostatic energy as well as biomass energy sources already play a significant role in a modern society. The aforementioned sources can be considered sustainable substitutes for fossil fuels. However, there are several obstacles for shifting to a completely new energy economy based on renewable sources. For instance, renewable sources of energy such as solar and wind are irregular and fluctuate between different seasons of the year [3]. As a consequence, energy obtained in the time of peak activity must be stored and used in the time of intermittency. One possible way is the storage of generated energy in the form of electricity which is convenient from the transportability point of view. However, the limited capacity of the existing batteries is a subsequent problem. Storage and transportation of energy in chemical compounds such as hydrogen and hydrocarbons is another possible solution. [4]

Hydrogen obtained by water electrolysis with the use of electricity from renewable energy sources can be considered environmentally friendly. It could become a reliable energy carrier. Furthermore, it can be used as a pure fuel causing no emissions of CO_2 to the atmosphere. However, hydrogen is volatile, flammable and explosive and requires careful handling. Moreover, significant modifications to the existing infrastructure would be needed for the integration of hydrogen. [2]

Another possibility is to use the renewable hydrogen and captured CO_2 for methanol synthesis. The concept of "Methanol economy" proposed by Olah et al. [2] complements the "Hydrogen economy" concept in the same time solving the emerging issues as methanol is easier to handle, can be stored and transported easily, can be used as a convenient fuel or a feedstock for the synthesis of a large variety of chemicals. Methanol can also be blended with gasoline and diesel for use as a fuel. Another big advantage of methanol is that only minor modifications to the existing infrastructure would be needed. The use of captured CO_2 and renewable hydrogen for methanol synthesis has following advantages: it can help to mitigate the global warming and be profitable considering the constantly growing demand of fuels and energy worldwide. [1]

1.3. Market overview and future perspectives for renewable methanol

Global methanol production is estimated to be 90 million tons in 2016 [5]. China, Middle East, Russia and Trinidad and Tobago are the main producers of methanol and its derivatives. Methanol (MeOH) is an important basic chemical which is mainly used in three markets: chemicals, transportation and power generation [4]. Methanol is mostly produced from fossil feedstock such as natural gas, coal and oil. However, alternative ways of methanol production based on renewable sources, such as utilization of captured CO_2 and renewable H_2 for methanol production, are of great interest due to the current increase of oil prices and growing concerns connected to climate change. Despite different raw materials the technological processes used for the fossil fuel-based methanol synthesis and the production of renewable methanol are similar [4].

Presently, chemical uses are the most important market for methanol [4]. Methanol can be converted to a large variety of products including formaldehyde (approximately 31% of world MeOH demand) – useful for production of polycondensates (urea, melamine and others), methyl tertiary-butyl ether (MTBE) – a good anti-knocking additive for gasoline, acetic acid, methyl methacrylate (MMA), and dimethyl terephthalate (DMT) [5]. Transportation and power generation are the other important markets for methanol. In the transportation sector, methanol can be blended with gasoline in small concentrations as an additive and in concentrations up to 85% as the main fuel component. Use of pure 100 % methanol as a fuel for vehicles is not currently possible due to its toxicity [2]. Methanol can be converted to dimethyl ether (DME) which is a good substitute for conventional diesel. The methanol to gasoline (MTG) and methanol to olefins (MTO) processes are other attractive options. Furthermore, an increasing interest in use of alcohols as fuels in the marine and aviation sectors can be observed. Currently, the fuel applications of methanol create approximately 37 % of the world MeOH demand [5]. In addition, methanol has fuel cells applications used both in transportation and power generation sectors. It is interesting to note that, methanol and DME are superior fuels for electric power generation in gas turbines. It can be also used as a liquid carrier of hydrogen (methanol consists of 3 atoms of hydrogen). These markets are expected to have the biggest interest in renewable methanol. [4]

The production and consumption of methanol is especially attractive for emerging economies such as China. China currently utilizes low-cost coal feedstock to produce relatively cheap methanol. However, the negative consequences of the coal based production include water shortage and significant increase in CO_2 emissions [2]. Synthesis of methanol with the use of renewable energy sources represents an alternative production route which can be considered viable in a long term period due to the constantly growing demand of methanol and issues related to the environment. Moreover, examples of non-fossil fuel based methanol production already exist in Iceland and Japan with demonstration plants operating at capacities at 5000 and 100 tons per year, respectively [6]. For instance, Carbon Recycling International (Iceland) uses geothermal energy, which is the advantageous feature of this region, to produce low-cost heat and electricity for hydrogen generation by water electrolysis and produces methanol from captured CO_2. The only byproduct of this process is oxygen [6]. This substitution of conventional methanol production routes is a good example which shows that production of methanol can be profitable and environmentally sustainable (under specific circumstances).

1.4. Aims of the thesis

The production of methanol by CO_2 hydrogenation can be attractive for the alleviation of diminishing fossil fuels and mitigating the global warming. The direct gas phase hydrogenation of syngas over Cu-Zn-oxide based catalysts is presently the main route of methanol synthesis. This technological process requires high operating temperatures of approximately 200-250^{o}C, which significantly increases the capital investment and operating costs of methanol production. In addition, high temperatures are not favorable for methanol synthesis due to thermodynamic equilibrium limitations. Consequently, it is of great interest to develop a more effective process which can be operated at milder conditions. One possible route for effective methanol production under lower temperatures is liquid phase methanol synthesis. Currently, the indirect hydrogenation of CO_2 via its derivatives is gaining scientific significance and investigated by many research groups all over the world. The biggest objective of the present work is to create an efficient process for the indirect liquid phase alcohol promoted methanol synthesis ensuring sufficient yield, selectivity and conversion of the main reactants (renewable hydrogen and captured CO_2) to methanol. [7]

2. Conventional gas-phase methanol synthesis via syngas

Crude methanol can be produced through a catalytic process by the following reactions (2.1-2.3) where syngas – the mixture of hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) is the main feedstock. Typically, crude methanol is the mixture of methanol, water, higher alcohols, ethers, acetone and methyl-ethyl-ketone which are the by-products. [8]

$$\mathrm{CO} + 2\mathrm{H_2} \rightleftarrows \mathrm{CH_3OH} \qquad \Delta H_{298K} = -21.7\ \mathrm{kcal\ mol^{-1}} \tag{2.1}$$

$$\mathrm{CO_2} + 3\mathrm{H_2} \rightleftarrows \mathrm{CH_3OH} + \mathrm{H_2O} \qquad \Delta H_{298K} = -11.9\ \mathrm{kcal\ mol^{-1}} \tag{2.2}$$

$$\mathrm{CO_2} + \mathrm{H_2} \rightleftarrows \mathrm{CO} + \mathrm{H_2O} \qquad \Delta H_{298K} = 9.8\ \mathrm{kcal\ mol^{-1}} \tag{2.3}$$

The first two reactions are exothermic while the last one, called the reverse water-gas shift reaction (RWGSR), is endothermic. Based on these reversible reactions, methanol synthesis is favorable when the overall pressure of the system is increasing while the temperature is decreasing, with the maximum conversion being determined by the equilibrium composition. The composition of the syngas, which can be characterized by the stoichiometric number (2.4), also plays an important role in this process. [8]

$$\mathrm{SN} = \frac{(\mathrm{moles\ H_2} - \mathrm{moles\ CO_2})}{(\mathrm{moles\ CO} + \mathrm{moles\ CO_2})} \tag{2.4}$$

Where, $\mathrm{SN} \approx 2(\text{slightly above}) \rightarrow$ ideal for methanol synthesis as high hydrogen partial pressure leads to high reaction rate and high carbon efficiency in the synthesis loop;

$\mathrm{SN} > 2 \rightarrow$ Surplus of hydrogen, thus extra reforming or addition of carbon dioxide is needed to achieve the ideal H/C ratio;

$\mathrm{SN} < 2 \rightarrow$ Deficit of hydrogen, thus extra treatment or addition of hydrogen is needed to prevent the formation of undesired by-products.

The CO: CO_2 ratio and the concentration of inert gases are the other crucially important characteristics of syngas. A high CO: CO_2 ratio is useful for the process of methanol synthesis as it can increase the reaction rate and the achievable per pass conversion while also decreasing the formation of water which has a negative impact on the activity of the catalysts. In practice syngas with concentration of CO_2 varying from 2 to 8 % is considered to be optimal for methanol synthesis. The presence of inerts represented by methane (CH_4), argon (Ar) and nitrogen (N_2) can lower the partial pressure of active reactants which is unfavorable as it lowers the possible conversion. [9]

Various fossil-based carbonaceous materials such as natural gas, coal, coke, heavy oils and asphalts can be used to obtain the syngas for methanol synthesis. Syngas obtained from natural gas can be considered preferable due to high content of hydrogen, small content of impurities, technological ease of its production and environmental issues. However, in some regions the other sources are used extensively due to their availability and the absence or limited availability of natural gas. Even though the estimated capital cost of the syngas generation unit is estimated to be 25% higher, when comparing coal based to natural gas based production, the integration of more expensive technologies with more complicated purification systems for syngas production in coal based plants can be justified by the use of low-cost raw materials. [8]

The removal of impurities mostly represented by sulfur in the form of H_2S, COS and mercaptans from the feedstock in syngas production has a positive impact on methanol synthesis as it can be conducted at relatively mild conditions with pressures of 50-100 bar and temperature of 200-300^{o}C (compared to previous high-pressure processes operating at pressures of 250-350 bar and temperatures of 320-450^{o}C with the use of catalysts consisting zinc oxide and chromium oxide). Milder process conditions are directly connected with the lifetime of the heterogeneous catalysts, as intensive sintering and deactivation are possible negative effects of severe process conditions. Copper based catalysts ($CuO/ZnO/Al_2O_3$) are mostly used in the leading low-pressure processes developed by Johnson Matthey (ICI Synetix), Lurgi, MGC and others for gas-phase methanol synthesis due to the high activity and selectivity (above 99%). Typically, lifetime of such a catalysts ranges from two to five years. Deactivation is mainly caused by poisoning due to remaining amount of contaminants in syngas and thermal damage. [8]

There are several points of view on the reaction mechanism of methanol synthesis on the industrial catalysts. The main subject of debate is whether methanol is produced from CO_2 or directly from CO. Different analytic methods have been employed to develop micro-kinetic models of methanol synthesis and it has been found that the most dominant components found on the catalyst surface at low temperatures were formate species (formed from CO_2 and H_2) and methoxy species (hydrogenated from formyl species which formed from CO and H_2) (Figure 1). Thus, it is possible to conclude that both pathways can exist. However, for low temperature methanol synthesis it is proved that dominant reaction is the hydrogenation of CO_2 and the synthesis occurs via surface formates. [9]

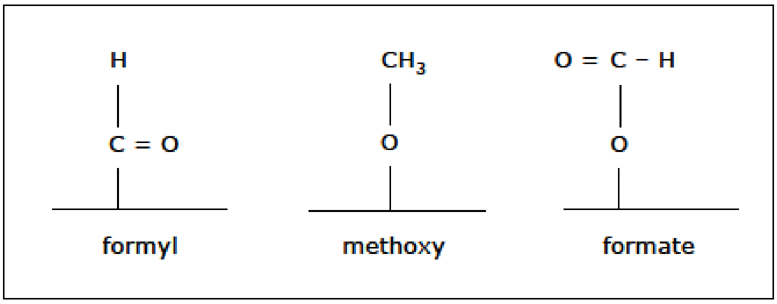


Figure 1 – Most species being found on the catalyst surface. [9]

2.1. Syngas production routes

Steam reforming of methane is the most common process used for the syngas production, represented by following endothermic reaction (2.5). This catalytic reaction is performed under pressures of 20-30 bar and at high temperatures of 800-1000°C over nickel based catalysts (Ni/MgO, $Ni/MgAl_2O_4$) to form CO and H_2. However, RWGSR represented by equation (2.3) also occurs in this process. [8]

$$\mathrm{CH_4 + H_2O \rightleftarrows CO + 3H_2} \qquad \Delta H_{298K} = 49.1\ \mathrm{kcal\ mol^{-1}} \tag{2.5}$$

The increase of temperature and decrease of pressure are favorable for syngas formation in steam reforming of methane. An advantage of this process is that partial combustion of methane can be used to supply the process heat. However, major disadvantage of the process is the surplus of hydrogen in the products, represented by the stoichiometric number SN approximately equal to 3. Thus, further reforming or the addition of carbon dioxide is required to obtain syngas desirable for methanol synthesis. Another disadvantage is that the thermal coking process occurs, clogging the process equipment and catalysts by the formation of soot and coke on the contacting surfaces. The excess of steam and short residence time in the reactor can be used to prevent this negative effect. [8]

Partial oxidation of methane is another technology for the natural gas conversion to syngas, represented by equations (2.6-2.8). The reactions are conducted at temperatures varying from 800°C to 1500°C in catalytic or non-catalytic processes resulting in excess heat which must be utilized afterwards. [8]

- Partial oxidation of methane:

$$\mathrm{CH_4} + \frac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{CO} + 2\mathrm{H_2} \qquad \Delta H_{298K} = -8.6\ \mathrm{kcal\ mol^{-1}} \tag{2.6}$$

- Oxidation of carbon monoxide:

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{CO_2} \qquad \Delta H_{298K} = -67.6\ \mathrm{kcal\ mol^{-1}} \tag{2.7}$$

- Oxidation of hydrogen:

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{H_2O} \qquad \Delta H_{298K} = -57.7\ \mathrm{kcal\ mol^{-1}} \tag{2.8}$$

Although this exothermic reaction can yield syngas with ideal for further methanol synthesis stoichiometric number close to 2, the obtained carbon monoxide (CO) and hydrogen (H_2) can be further oxidized forming undesired water (H_2O) and carbon dioxide (CO_2) in highly exothermic reaction. [8]

Auto-thermal reforming is the combination of the endothermic steam reforming and exothermic partial oxidation of methane in one process. The aim of this technological solution is to create a thermally neutral process for syngas production with no heat consumption or production. Single reactor performing the sequential reactions can be used for this purpose, collecting the excess heat of exothermic partial oxidation of methane and utilizing it for steam reforming. [8]

Syngas production from petroleum oil and higher hydrocarbons involves the basic principles of steam reforming, partial oxidation or their synergetic use and overall can be represented by equations (2.9 and 2.10). Various hydrocarbon sources can be used for syngas production including liquefied petroleum gas, fractions obtained from oil refining, crude oil, heavy oil, tar and asphalt. However, the higher content of impurities compared to natural gas demands more efficient preliminary purification operations to prevent the poisoning of catalysts. [8]

$$\mathrm{C_nH_m} + \mathrm{nH_2O} \rightleftarrows \mathrm{nCO} + \left(\mathrm{n} + \frac{\mathrm{m}}{2}\right)\mathrm{H_2} \tag{2.9}$$

$$\mathrm{C_nH_m} + \frac{\mathrm{n}}{2}\mathrm{O_2} \rightleftarrows \mathrm{nCO} + \left(\frac{\mathrm{m}}{2}\right)\mathrm{H_2} \tag{2.10}$$

Gasification of coal can also be used for syngas production. This process which involves partial oxidation and steam treatment is represented by the following equations (2.11-2.14).

- Partial oxidation of coal:

$$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{CO} \qquad \Delta H_{298K} = -29.4\ \mathrm{kcal\ mol^{-1}} \tag{2.11}$$

- Steam treatment of coal:

$$\mathrm{C} + \mathrm{H_2O} \rightleftarrows \mathrm{CO} + \mathrm{H_2} \qquad \Delta H_{298K} = 31.3\ \mathrm{kcal\ mol^{-1}} \tag{2.12}$$

- Water-gas shift reaction:

$$\mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta H_{298K} = -9.8\ \mathrm{kcal\ mol^{-1}} \tag{2.13}$$

- Reverse Boudouard reaction:

$$\mathrm{CO_2} + \mathrm{C} \rightleftarrows 2\mathrm{CO} \qquad \Delta H_{298K} = 40.8\ \mathrm{kcal\ mol^{-1}} \tag{2.14}$$

Generally, gasification technology strongly depends on the composition and main characteristics of coal such as water, ash and impurities contents. The surplus of carbon oxides and deficit of hydrogen is the general feature of syngas obtained by gasification of coal. Thus, additional treatment is needed to achieve the ideal H_2/CO ratio for methanol synthesis. Purification is another issue due to the reasons set above. [8]

2.2. Syngas preparation technologies

The carbonaceous feedstock purification and conversion to synthesis gas is the first step of the methanol synthesis process. Different reforming technologies are available for this purpose. It is interesting to note, that reforming process represents approximately 80% of the overall energy consumption and 60% of the total capital investment of the whole methanol synthesis plant. [9]

One step reforming: the syngas is produced by tubular steam reforming without the use of oxygen. The simplified process flow diagram of this process is shown in Figure 2. One step reforming is mostly used in methanol plants with capacities up to 2500 metric tons per day (MTPD). [9]

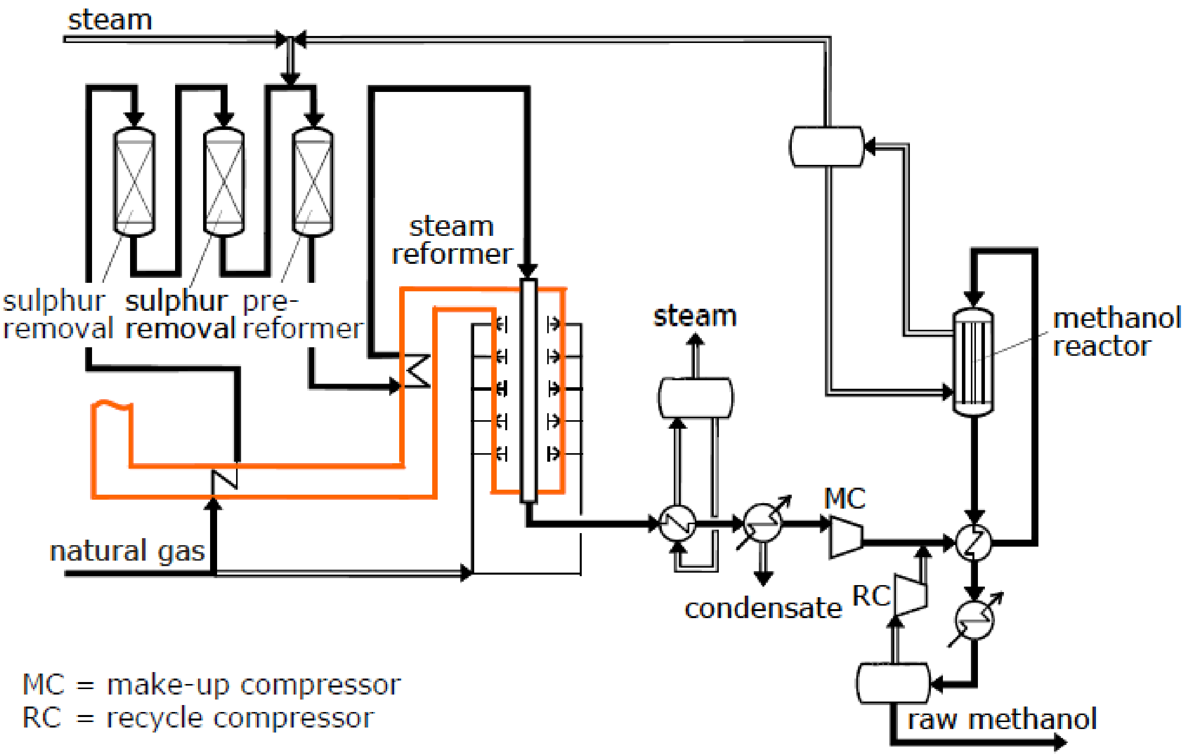


Figure 2- Simplified process flow diagram of methanol manufacture by one step reforming. [9]

Natural gas, which is the carbonaceous feedstock in this process, is supplied to purification units where contaminants are removed. Afterwards, the most energy intensive reactions involving the use of steam at high temperatures are accomplished in the tubular steam reformer (the partial combustion of natural gas can be used to obtain the required energy for this process). The reformer is a draught-fired furnace containing rows of vertical, catalyst-filled tubes (Figure 3). The gas and steam react over the catalyst (typically nickel based) to form a mixture of syngas, residual methane and water in the form of steam. The heat is supplied by the burner located below the roof of the reformer. For this purpose the large radial section in the reformer is needed. The surplus of heat in the conversion section of the furnace and the consequent surplus of steam can be observed as the flow of hot gas from radial section is very intensive. [10]

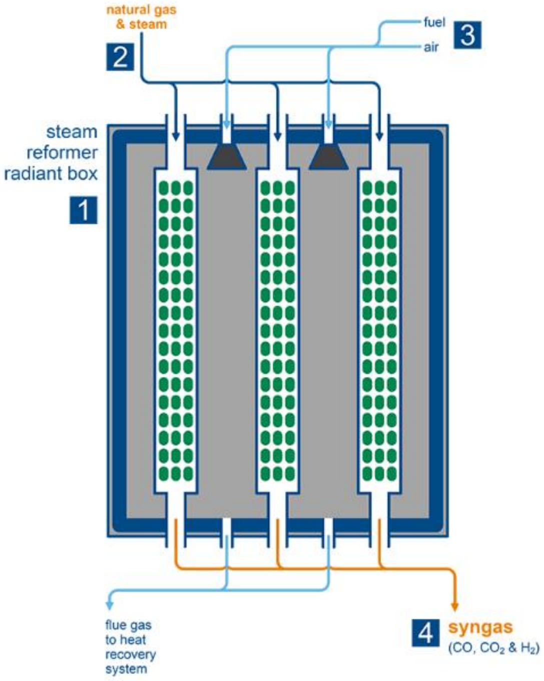


Figure 3 – Tubular steam reformer. [10]

Another effective design of a tubular steam reformer developed in a collaboration of BP and Johnson Matthey process technology is presented in Figure 4. Comparing with the conventional tubular steam reformers it has a smaller footprint but comparative performance due to the employment of counter-current, largely convective heat exchange to intensify the reforming process. [10]

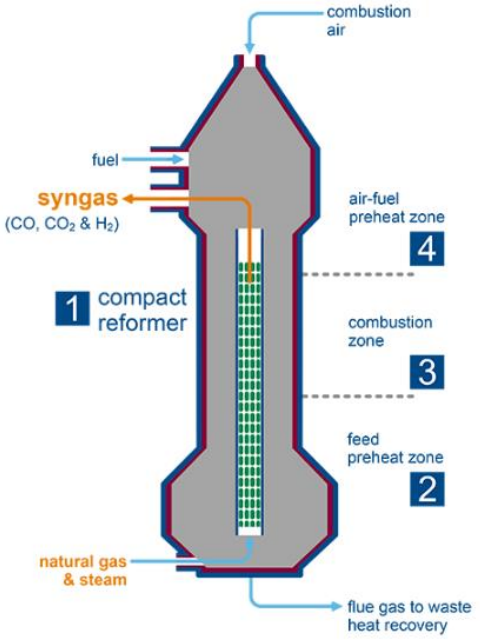


Figure 4 – Compact tubular steam reformer. [10]

Two-step reforming is the combination of primary tubular steam reforming and oxygen-fired secondary reforming which allows to achieve the most suitable composition of syngas for methanol synthesis with SN = 2. This process of syngas preparation is mostly used in the methanol plants with capacities from 2000 to 7000 MTPD. The simplified process flow diagram of this process is represented on Figure 5. [9]

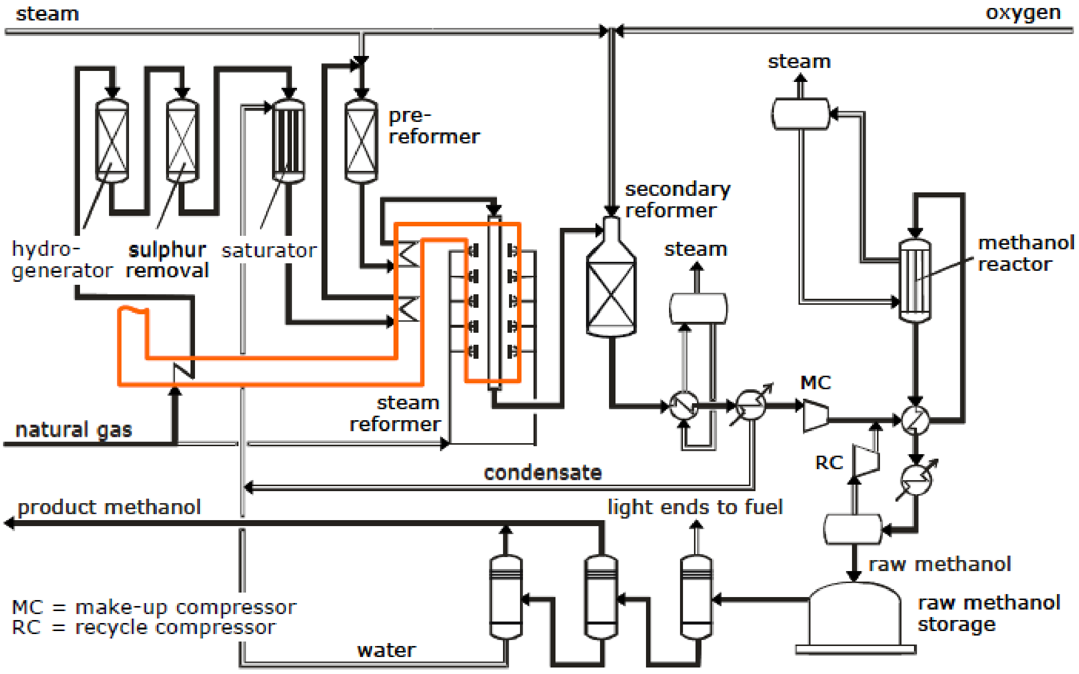


Figure 5 - Simplified process flow diagram of methanol manufacture by two step reforming. [9]

The reforming reactions are divided between two units (primary and secondary reformer) which allow operating the primary reforming under milder conditions and with the use of smaller equipment. This has positive impact on costs of methanol production as the tubular steam reforming is extremely energy consuming. Additionally, the three column distillation of raw methanol is also represented in the process flow diagram shown in Figure 5. [9]

Auto-thermal reforming (ATR) is the process involving the oxygen-fired reforming without any preceding steps. The unique compact design of the auto-thermal reformer makes a significant reduction of the costs of construction possible. Auto-thermal reformer is the unit with a special burner and a fixed catalyst, represented in Figure 6. Typically, auto-thermal reforming produces syngas with SN=1.7-1.8, pointing out the deficit in hydrogen. The application of auto-thermal reforming in methanol plants with large capacities of at least 10000 MTPD is feasible by subsequent addition of H_2 or by CO_2 removal processes (ATR is attractive for large-scale plants).

ATR is mainly used for the production of fuel grade methanol. The production of methanol for conversion to olefins is another widely used industrial purpose. [9]

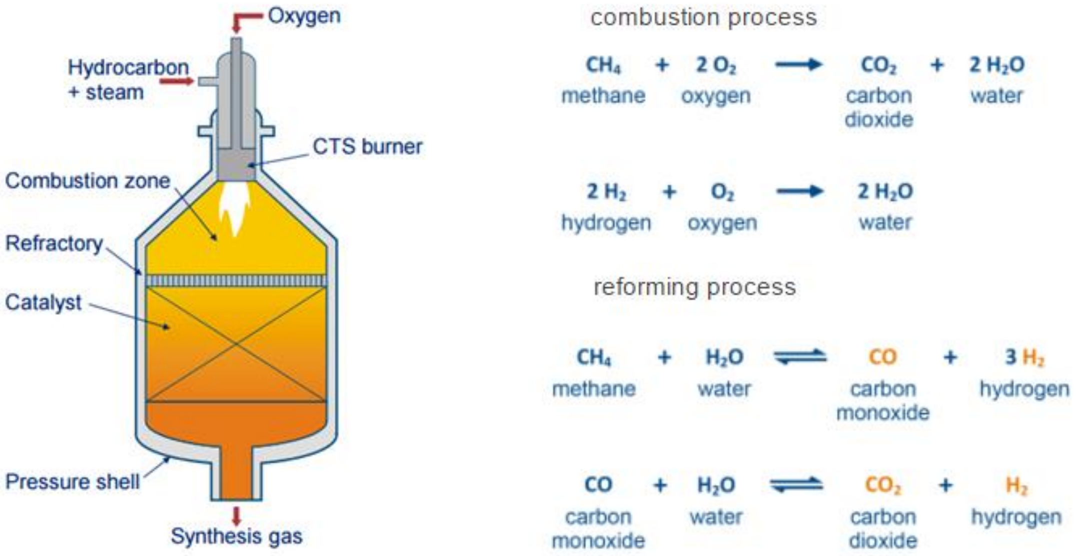


Figure 6 – ATR reactor. [9]

A process flow diagram of the ATR process is presented in Figure 7. In order to adjust the gas composition, hydrogen recovery is performed by a membrane unit. More expensive and effective PSA (pressure swing adsorption) units are also used for this purpose industrially. [9]

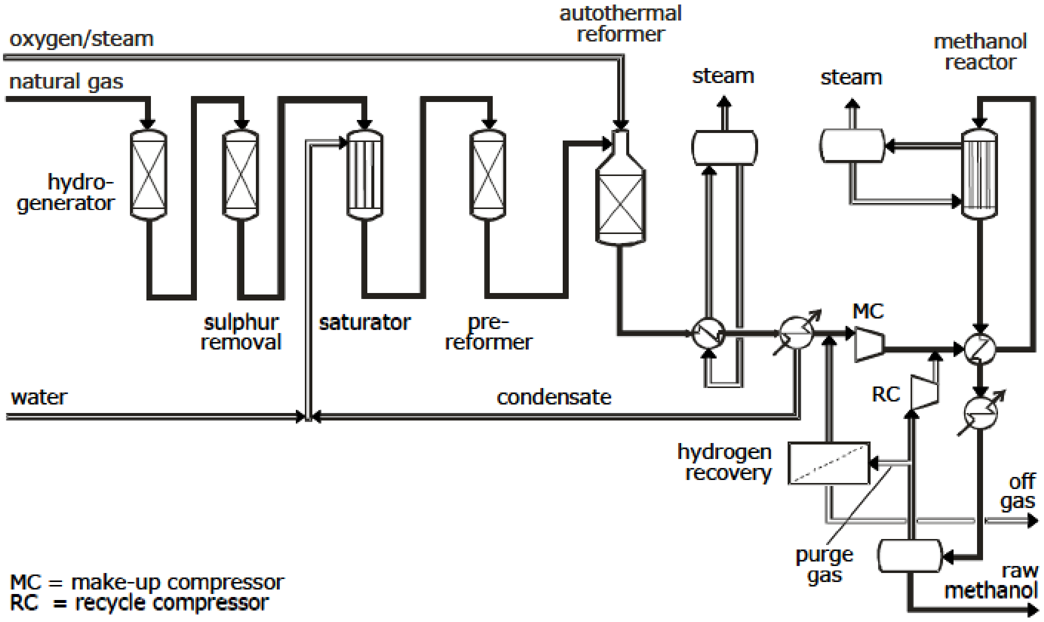


Figure 7 – Simplified process flow diagram of methanol manufacture by ATR. [9]

Gas-heated reforming (GHR) typically works in combination with an auto-thermal reformer to overcome the problem of hydrogen deficit in the produced syngas. Gas-heated reformer is a compact refractory-lined vessel containing vertically-supported tubes filled with catalyst. At the beginning of the process the pre-heated mixture of natural gas and steam enters the top section of the gas heated reformer and passes downwards via the catalyst-filled tubes. The partial reforming of feedstock happens producing the mixture of syngas, unreacted methane and steam. The final conversion into syngas occurs in the auto-thermal reformer. The hot syngas then returns to the gas-heated reformer and flows upwards through the vessel shell-side. The principle of counter-current heat transfer works to drive the endothermic reactions in tubes. A combination of gas-heated and auto-thermal units is represented in Figure 8. [10]

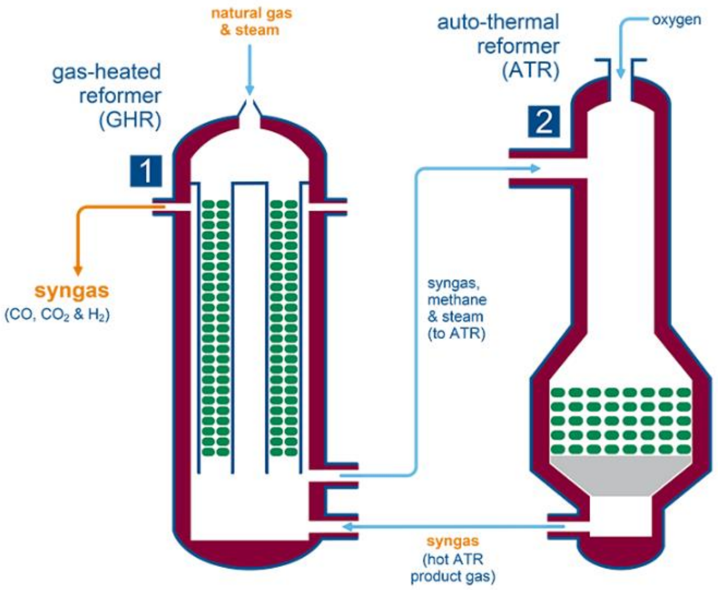


Figure 8 – Combination of ATR and GHR to achieve ideal SN for methanol synthesis. [10]

2.3. Reactors for methanol synthesis

Methanol synthesis is performed after the syngas preparation process. Different designs of methanol synthesis reactors (converters) are available.

The quench converter consists of number of adiabatic catalyst beds installed in series in a common pressure shell (Figure 9). Syngas is injected between the individual catalyst beds and temperature control is conducted by stepwise addition of new syngas inside the reactor. The construction of the reactor is very simple and capacities up to 3000 MTPD can be achieved by its application. This converter is well-proven, reliable and relatively cheap. However, the low per-pass conversion caused by the adiabatic operation resulting in high temperatures is the drawback of this technology. In addition, poor heat recovery and low utilization of catalysts can be observed as not all reactants pass through the entire catalyst volume installed. [9]

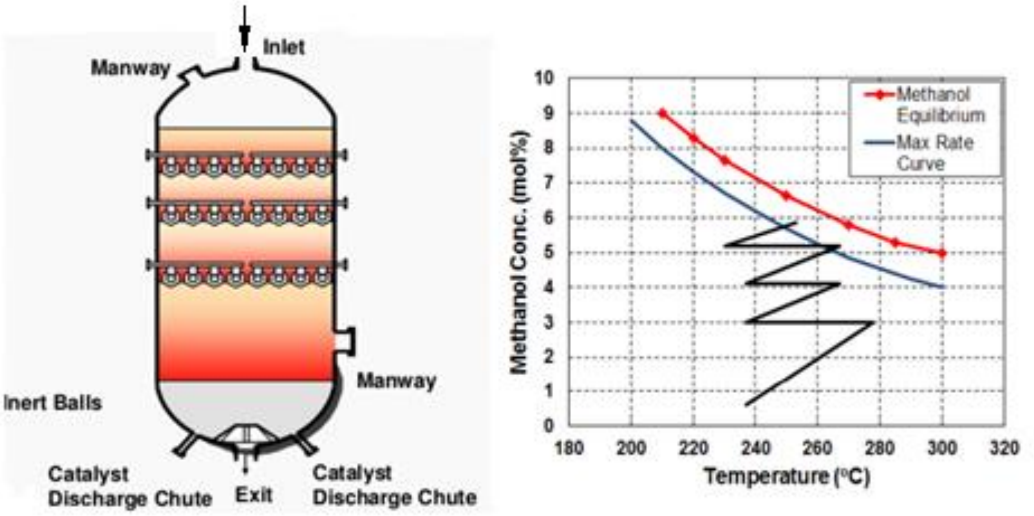


Figure 9 – Quench reactor for methanol synthesis. [11]

The tube-cooled converter (TCC) consists of axial tubes with catalysts on the shell side (Figure 10). It has the following advantages: compact and simple design (small converter volume due to the low catalyst volume), increased heat recovery and simple control. A remarkable drawback is the high weight of the converter which can cause transportation problems when using for large-scale methanol plants. [9]

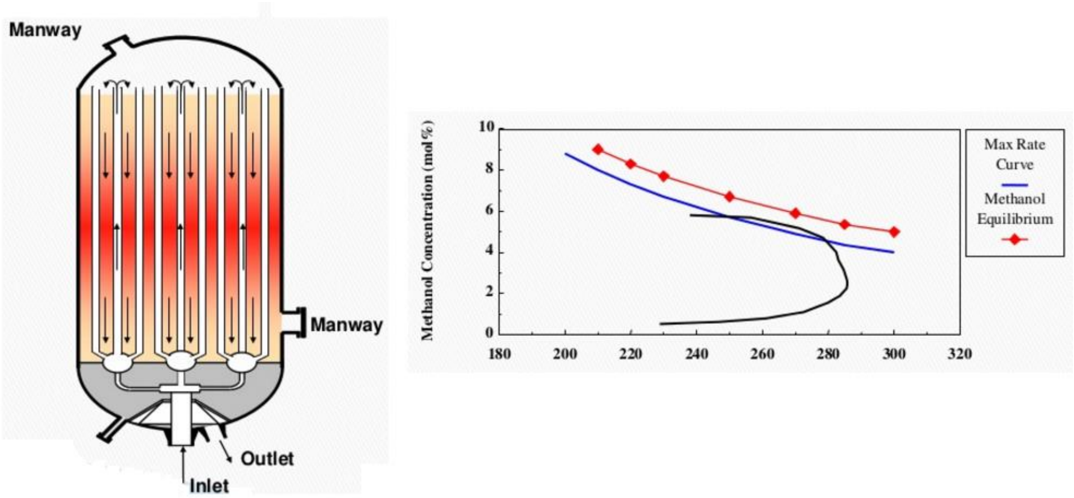


Figure 10 – Tube-cooled converter for methanol synthesis. [11]

The syngas enters the bottom section of the tube-cooled converter and moves upward through tubes embedded in catalyst. The upward stream of syngas is preheated by the exothermic reaction in the catalyst bed. After achieving the top section of the converter, the gas passes down through the catalytic bed forming methanol. Excess heat of this reaction is directed to the fresh syngas by counter-current heat exchange. Vapors of crude methanol, unreacted syngas and inerts exit the bottom section of the converter. Typically, heat recovery and separation of vapors is performed afterwards. Finally, crude methanol and gasses for recycling and transformation are obtained. A tube-cooled converter and additional separation operations are presented in Figure 11. [10]

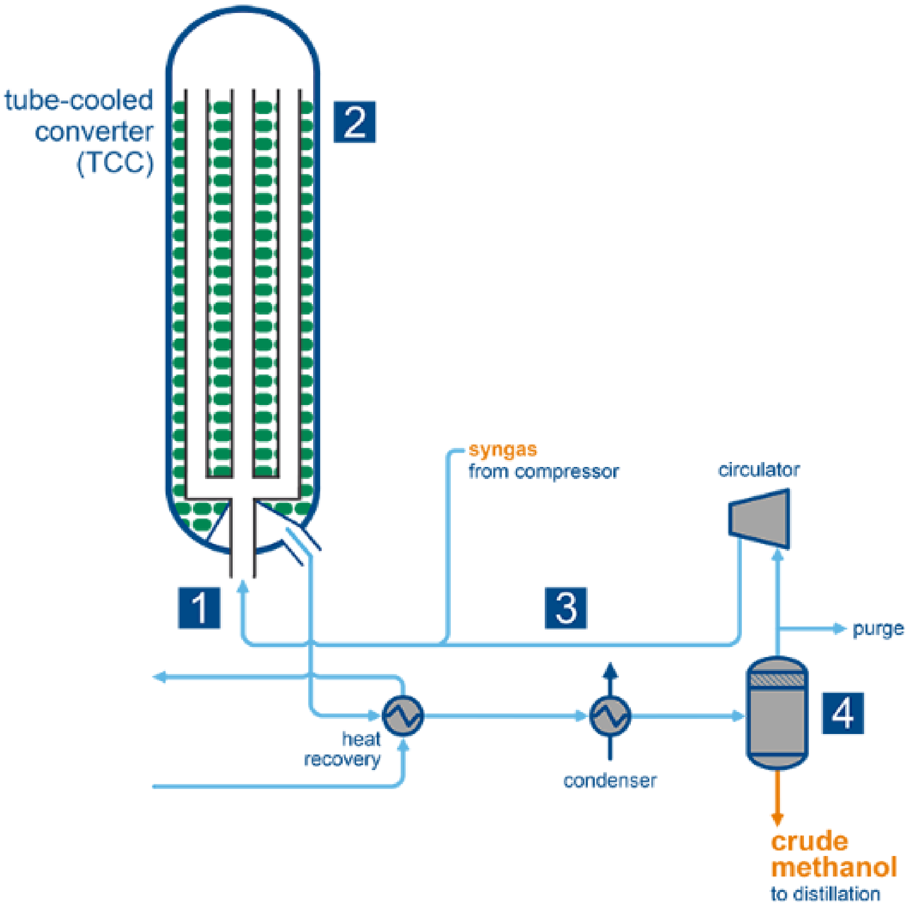


Figure 11 – Process flow diagram of crude methanol synthesis by TCC. [10]

The boiling water converter can be described as a shell and tube heat exchanger containing catalysts. Cooling of the reactor and temperature control is accomplished by the circulating boiling water. Good per-pass conversion of syngas to methanol, high catalyst utilization, low by-products formation and high investment cost are the distinctive features of this type of converter. There are a plenty of boiling water converters designs available which differ in the arrangement of catalyst and cooling water inside the reactor. One good example is the axial steam-raising converter (A-SRC) presented in Figure 12. This converter consists of axial tubes filled with catalysts and circulating water on the shell side. The exothermic conversion of syngas to methanol occurs when the gas pass through the tubes from the top to the bottom section of the reactor. At the same time water from the steam drum flows to the bottom section of the reactor following vaporization, due to heat transfer from the tubes, and returns to the steam drum. The adjustment of steam pressure in the drum can be used to control the catalyst bed temperature in the reaction tubes. Heat recovery and vapors separation are similar to following a TCC. [10]

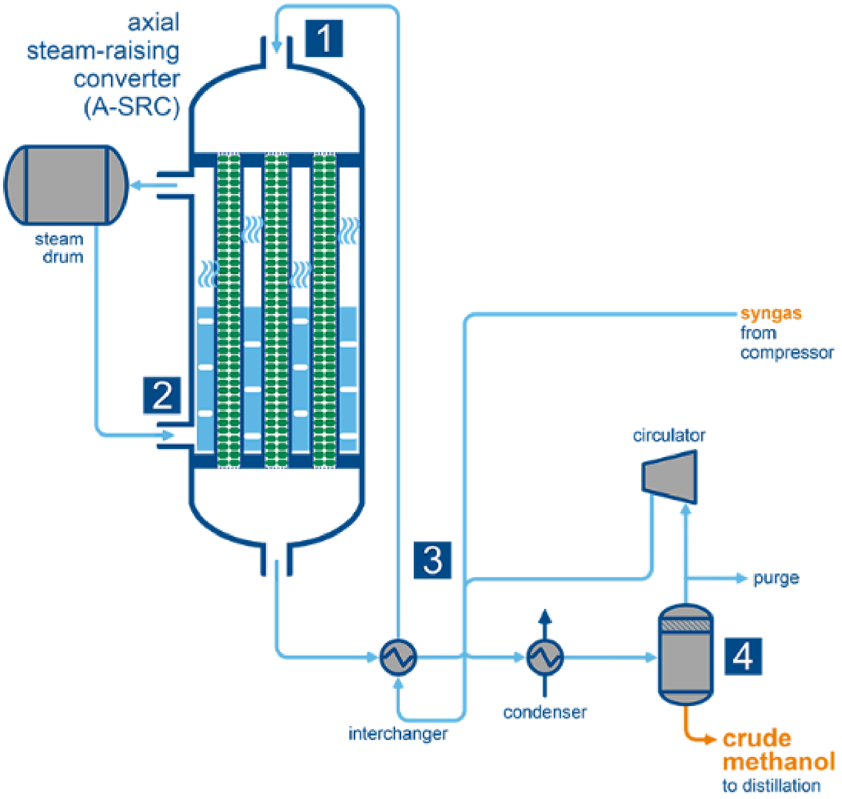


Figure 12 – Process flow diagram of crude methanol synthesis by axial steam-raising converter. [10]

Another example is the radial steam-raising converter (R-SRC) which in contrast has a bed disposition of catalyst within the reactor and cooling water is circulating through tubes in the upward direction (Figure 13). The compressed syngas enters the bottom section of radial steam-raising converter and flows upwards through a vertical distributor pipe which directs it radially outwards through catalyst bed. The mixture of crude methanol, unreacted syngas and inerts exits the middle section of the R-SRC. Then the heat recovery and separation are performed in the methanol loop. [10]

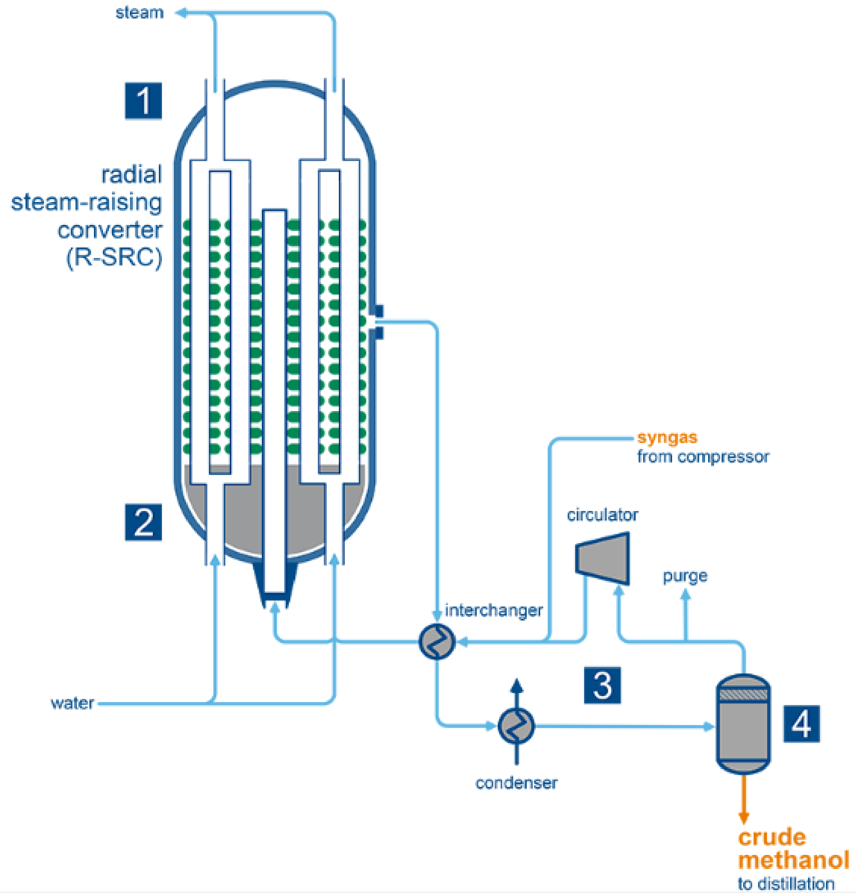


Figure 13 - Process flow diagram of crude methanol synthesis by radial steam-raising converter. [10]

The Casale IMC converter is a pseudo isothermal converter in which plates are used as a heat transfer surfaces. The catalysts are located outside cooling plates. Perfect control of the temperature profile along the catalyst mass is reported to be the advantageous feature of this converter type. This happens due to the ability of selective adjustable heat removal from different parts of the catalyst bed. Furthermore, it is possible to note that the axial-radial flow through the reactor results in low pressure drop values. In addition, elimination of hot spots inside the bed (due to the effective quench mixing) allows the operation of the system at mild inlet temperatures of syngas. Another good feature of this reactor is the drop out pipes that provide simplicity of catalyst loading and replacement. Various cooling fluid flows inside the plates (such as fresh syngas, water or others) can be used to maintain the effective operation temperature. Finally, it is possible to note that the decreased energy consumption and high single vessel capacities are other attractive features of Casale technology. The axial-radial converter is presented in Figure 14. [12]

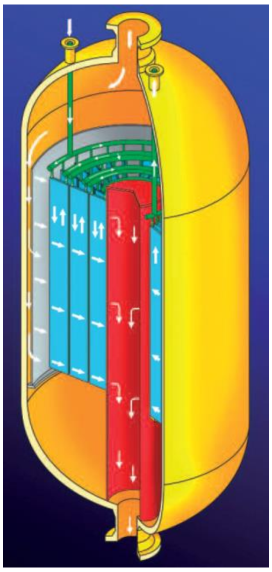


Figure 14 – Axial-radial Casale IMC converter. [12]

The Linde reactor system is an effective isothermal reactor for methanol synthesis. It is possible to note that this system has the benefits associated with the tubular reactor types but at the same time the disadvantages such as thermal stresses resulting in hot spots and decreased production rates are avoided. A spiral-wound cooling tube embedded in the catalyst bed is used for reaction heat flow and overall system temperature is controlled by vapor pressure. The Linde reactor system provides excellent heat transfer coefficients on the catalyst side, decreased values of temperature gradients and require reduced cooling area. Mechanical damage of methanol synthesis catalysts during loading is almost avoided due to the system lay-out. The Linde isothermal converter is presented in Figure 15. [12]

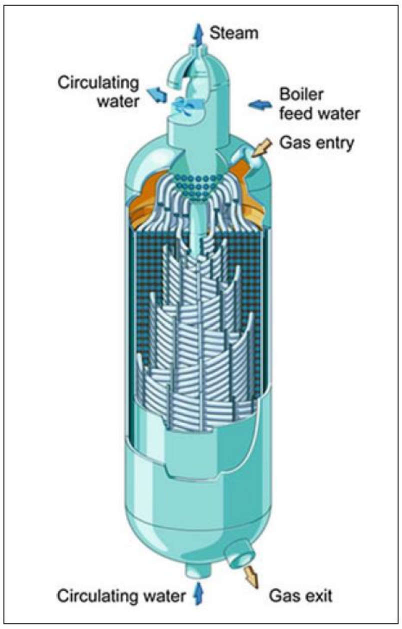


Figure 15 – Linde isothermal converter for methanol synthesis. [12]

2.4. Methanol purification

After synthesis the crude methanol consists of water, undesired by-products and dissolved gases. Distillation of methanol is required for purification of the product. Three grades of purity are available commercially for methanol: fuel grade (also used as a feedstock for olefins manufacture), grade A (widely used as a solvent) and grade AA (chemical grade >99.85 wt% methanol). [8]

Typically, three process steps are used for methanol purification:

- Removal of dissolved gasses (CO, CO_2, CH_4, H_2) by low pressure flashing;
- Removal of the light ends (ketones, ethers, formiates, aldehydes);
- Removal of heavy ends (water, higher alcohols, and ethanol).

A different number of distillation columns can be used for methanol purification. Single column distillation is used for the production of fuel grade methanol. However, presently the most used applications consist of two or three column distillation layouts. The same grade of purity can be achieved by both technological processes (grade A and AA). While two columns distillation is considered to be cost-saving, the three columns distillation (Figure 16) is considered to be an energy saving design. The first stabilizer column is used for removal of light by-products and dissolved gasses. Two concentration columns (in a three column layout) working at elevated and atmospheric pressure, respectively, yield pure methanol and remove water and other undesired by-products. [9]

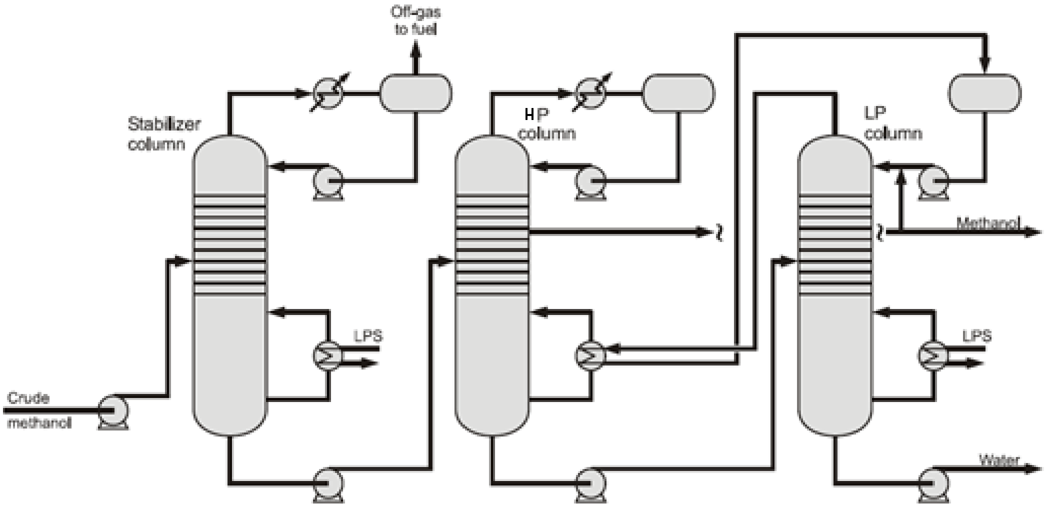


Figure 16 – Purification of methanol by three column distillation. [9]

3. Production of methanol from CO_2 and H_2

3.1. CO_2 and H_2 for methanol production

CO_2 separated from flue gases and H_2 produced by water electrolysis can be used as a feedstock for renewable methanol production. This offers an attractive route capable to decrease emissions of green-house gases into the atmosphere and at the same time answer the constantly growing demand in fuels.

3.1.1. CO_2 capture and separation from flue gasses

Irons et al. [13] investigated the reduction of CO_2 emissions by three capture technologies from flue gases of power plants:

Post-combustion capture

This downstream method involves separation of CO_2 from flue gases after conventional fuel combustion process (analogous to flue gas desulphurization process widely used in coal and oil fired power plants to capture SO_2). The biggest challenge for integration of this method is the low concentration of CO_2 in flue gases, typically varying from 4 – 14 %, which leads to low partial pressure of CO_2 in the gas mixture. As a consequence, large volumes of gas must be handled by large dimensional equipment, leading to high capital investments. Furthermore, powerful chemical solvents must be utilized for capturing purposes. As a result, regeneration of the solvents to release captured CO_2 is associated with huge energy inputs which is also inefficient from the economical point of view. However, the remarkable advantage of this method is that only minor changes are required for the existing power plant allowing the revamping of the process with the CO_2 separation unit. [14]

Pre-combustion capture

This method is based on CO and H_2 formation by means of fuel conversion by reactions with oxygen, air or steam. Subsequently, a catalytic shift converter is used for the conversion of the aforementioned reactants to CO_2 and more H_2. The obtained hydrogen is used as a combustion fuel in a gas turbine combined-cycle plant after separation of CO_2. The main field of application of this technology is in coal gasification power plants (integrated gasification combined cycle, IGCC). However, gasification of biomass, heavy oils and other carbon containing sources is also possible. The remarkable advantage of the pre-combustion capture is the transformation of carbon containing fuel to carbonless fuel. The chemical energy of carbon (C) is transformed to chemical energy of hydrogen (H_2) during the gasification process. Combustion of H_2 in gas boilers, turbines and other technologies can be considered as an environmentally friendly process. Furthermore, the concentration and partial pressure of CO_2 is higher in comparison to post-combustion capture process which simplifies the separation process. The biggest disadvantage of this process is high capital investment required. [14]

Oxy-fuel combustion capture

This method represents the modified post-combustion process. Here, combustion of fuel takes place in the presence of pure oxygen instead of air. Consequently, a high concentration of CO_2 (up to 80%) in the flue gas can be observed. A significant amount of CO_2 is recycled to the combustor to maintain the flame temperature (this temperature is higher in comparison to conventional combustion involving air due to the oxygen used instead). The biggest advantage of this method is that a simple separation method can be integrated due to the high concentration of CO_2 in the flue gas. The suppressed formation of NO_x is another beneficial feature of the oxy-fuel combustion capture. Nevertheless, the expensive process of oxygen generation (which must be constantly supplied for this process) as well as high energy consumption during its processing are the biggest disadvantages of the oxy-fuel combustion capture. Corrosion problems may arise as well [14]. A summary of CO_2 capture technologies is presented in Figure 17.

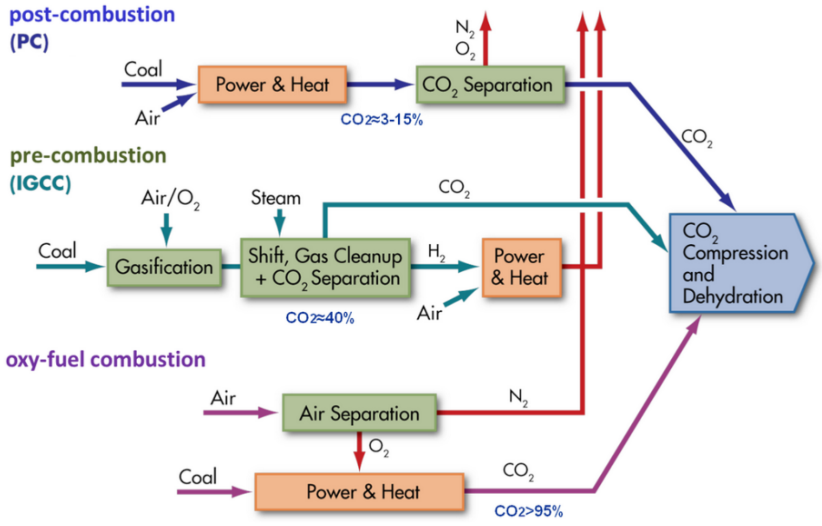


Figure 17 – Summary of CO_2 capture technologies. [14]

The selection of the most suitable capture route is normally connected to such parameters as the concentration of CO_2 in the gas stream, pressure of the gas and combustion fuel type. Various separation techniques including chemical or physical absorption, adsorption on solid material, cryogenic distillation and membrane separation are utilized for that purpose (see below). [14]

Chemical absorption is the preferable method for low and moderate carbon dioxide partial pressures. Typically, basic solvents are used for acid-base neutralization reactions in chemical absorption of CO_2 from flue gases, CO_2 being acidic gas. Chemical absorption processes can be divided to 3 main steps: [14]

- Weakly bonded intermediate is formed during carbon dioxide (CO_2) reaction with chemical solvent.
- Heating is used to break down the formed intermediate.
- Production of pure carbon dioxide (CO_2) stream and regeneration of original solvent.

Currently, a method comprising of amine absorption and steam stripping is the commercialized technology which has been effectively utilized for CO_2 separation in the natural gas industry during the last 60 years. Amine-based solutions (such as MEA – monoetanolamine, DEA – diethanol-amine, MDEA – methyl diethanol-amine or mixtures of them) are commonly used in this process. In this process the flue gas stream containing carbon dioxide (CO_2) is bubbled through the amine-based solvent in packed absorber column where absorption of CO_2 occurs. Subsequently, the absorbed CO_2 is stripped from the amine-based solvent in the regenerator unit by counter-flowing steam (with $T=100\text{-}200^{o}C$). Eventually, the separation with water vapor results in highly concentrated CO_2 stream, which can be compressed and utilized. The main disadvantages of this process are: [14]

- The involvement of large dimensional equipment which leads to high capital and operating costs;
- Intensive energy input is required;
- Low CO_2 loading capacity;
- Corrosion issues;
- Amine degradation by contaminants (SO_x, NO_x, HCl and others).

Investigations of different basic inorganic solvents such as aqueous potassium and sodium carbonate have resulted in lowered absorption temperatures, not exceeding 20°C, as well as lowered regeneration temperatures varying from 100°C to 150°C. Furthermore, rates of solvent degradation and corrosion were also decreased. A typical chemical absorption system for CO_2 recovery from flue gases is presented in Figure 18. [14]

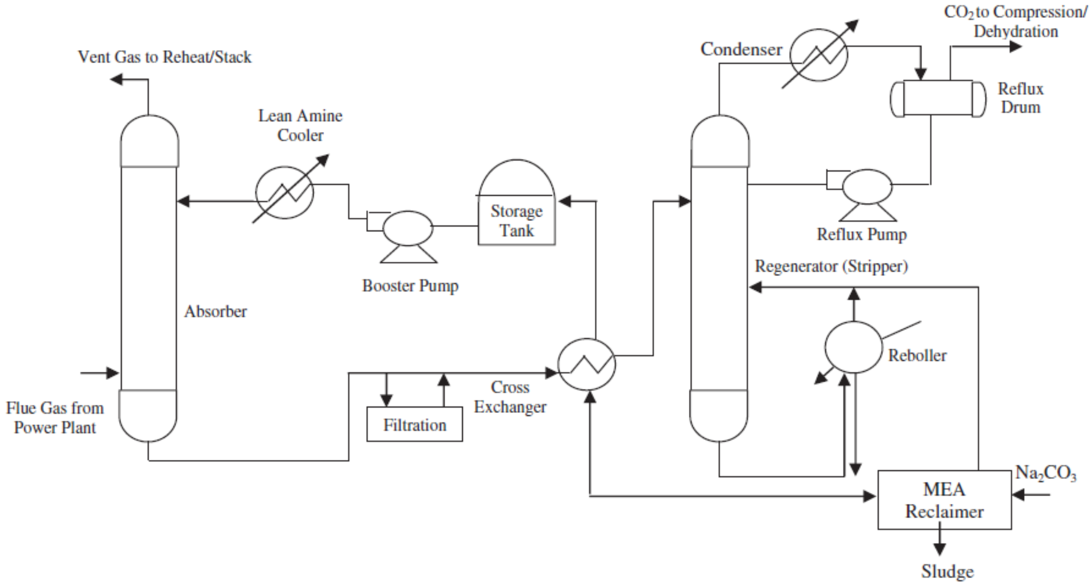


Figure 18 – Typical chemical absorption system for CO_2 recovery from flue gases PFD. [14]

Physical absorption is another method of CO_2 removal from flue gases, based on the solubility of CO_2 in organic solvents. Partial pressure (preferably high) and temperature (preferably low) of the feed gas play an important role in this process. The regeneration of solvents is based on either pressure reduction or heating. Commercialized examples of the utilization of physical absorption method for CO_2 removal from syngas are found in methanol, hydrogen and ammonia production. Removal of CO_2 and H_2S from natural gas is accomplished by solvents such as Selexol (dimethyl ether of polyethylene glycol), Rectisol (cold methanol), propylene carbonate (FLUOR process) and Purisol (N-methyl-2-pyrollidone). The recovery of CO_2 dissolved in the physical solvent is accomplished by pressure reduction in a series of successively installed flash drums (no additional heat is required for this process). A typical physical absorption system for CO_2 recovery from flue gases is presented in Figure 19. [14]

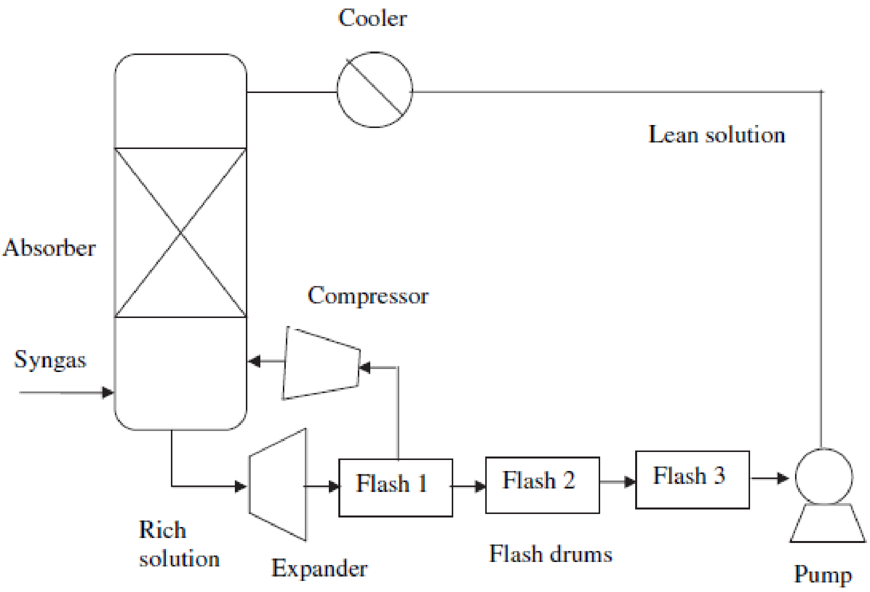


Figure 19 - Typical physical absorption system for CO_2 recovery from flue gases PFD. [14]

Adsorption processes comprise the selective removal (physisorption or chemisorption) of CO_2 from flue gasses to the adsorbent (solid material) followed by regeneration (desorption). PSA (pressure-swing adsorption), TSA (temperature-swing adsorption), ESA (electrical-swing adsorption) and washing are the commonly used methods for desorption process. There are different solid adsorbents available for CO_2 removal from flue gases: [14]

Molecular sieves

This cost-effective method is based on the separation principle according to the molecular size or mass. Typically, adsorbents based on high surface area inorganic supports that incorporate basic organic groups (such as amines) are used. Reaction of basic surface molecules with acidic CO_2 results in formation of surface ammonium carbamates or ammonium bicarbonate, correspondingly for the absence orpresence of water during reaction. Mesoporous substrates (such as silica, SBA-15, MCM-48 and others) can be considered as attractive adsorbents for molecular sieve processes due to the suitable size of their pores (easy access of molecules with amino groups). [14]

Activated carbon

Activated carbon is applicable in a wide range of industrial processes as well as for the capture of CO_2 from flue gases due to the well-developed meso- and micro- porosities. In order to increase adsorption capacity of activated carbons (which is based on physical adsorption), the existing surface chemistry can be modified by impregnation of heteroatoms such as nitrogen functional groups into the carbon structure. This leads to increase in number of basic groups and change the charge distribution of grapheme layers. [14]

Lithium compounds

Lithium zirconate (Li_2ZrO_3) is an effective high temperature CO_2 adsorbent. However, lithium silicate (Li_4SiO_4) possesses even larger adsorption capacity and stability. Furthermore, it can perform at wide range of temperatures and concentrations of CO_2 which make lithium silicate (Li_4SiO_4) an interesting candidate for utilization as a commercially competitive CO_2 adsorbent. [14]

Cryogenic method of CO_2 capture from flue gases involves separation of gas mixtures by fractional condensation and subsequent distillation at low temperature. Liquefaction of CO_2 at a temperature of -73.5^oC and separation by distillation are the main stages of cryogenic separation which is considered to have transportation and storage advantages of the liquid-phase processing. The positive conclusion of the technical viability of the CryCell technology was made after successful implementation in a demonstration plant where cryogenic process of CO_2 removal from the natural gas was used to overcome disadvantages inherent for the conventional acid gas treatment process such as intensive corrosion, consumption of water and chemicals. [14]

Membrane separation technology can be also utilized for CO_2 removal from flue gases. Membranes represent semi-permeable barriers, which can be used for selective separation of substances from gas streams with the help of different mechanisms including solution/diffusion, molecular sieving, adsorption/diffusion, and ionic transport. Beside several advantages that the membrane separation technology possesses in comparison with absorption and adsorption processes such as no regeneration energy requirements, absence of waste streams and simplicity of the modular systems, it also has remarkable disadvantages, such as difficulties in achievement of high degrees of separation leading to multiple stages process requirements, sensitivity to contaminants and some others. Polymeric membranes, porous and non-porous inorganic membranes as well as zeolite and silica membranes represent the available technological solutions for CO_2 removal from flue gases. [14]

3.1.2. Hydrogen production by electrolysis

Electrolysis is a promising process utilizing electricity for splitting of water into gaseous hydrogen (H_2) and oxygen (O_2). In other words, electrolysis is the process for renewable hydrogen production. The basic reaction for water electrolysis is represented by Equation 3.1. [15]

$$\mathrm{H_2O \rightarrow H_2(g) + \frac{1}{2} O_2(g)} \tag{3.1}$$

The fundamental principle of water electrolysis is presented in Figure 20. It can be clearly seen that hydrogen and oxygen bubbles are produced at the cathode (negative electrode) and anode (positive electrode), correspondingly, in the presence of water and high voltage. [15]

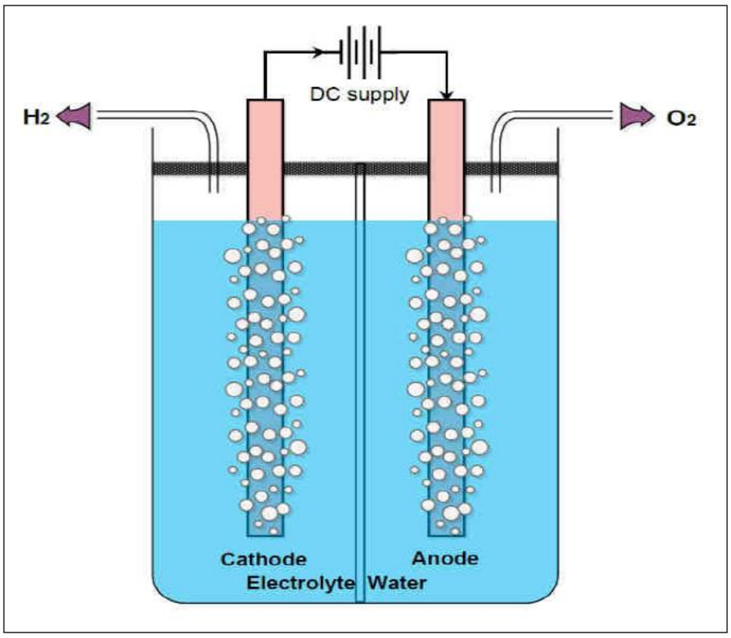


Figure 20 – Principle of water electrolysis for hydrogen production. [15]

It is possible to classify electrolytic cells for hydrogen production based on the nature of electrolyzers used in the process.

Alkaline electrolyzers

Typically, alkaline elecrolyzer consists of electrodes, a microporous separator and a liquid electrolyte (30 wt% KOH or NaOH). The most commonly used material for cathodes in the alkaline systems is nickel (Ni) with catalytic coating (for instance, platinum), while nickel (Ni) or copper (Cu) metals coated with the metal oxides (for instance, ruthenium, tungsten or manganese) are used as materials for anodes. It is interesting to note, that aqueous electrolyte is not consumed during reaction. However, addition of fresh electrolyte is needed due to system losses primarily during recovery of hydrogen. In alkaline cell the decomposition of water into hydrogen and OH^- occurs on the cathode. Subsequently, OH^- is transfered via electrolytic material to the anode where the formation of oxygen (O_2) happens. Hydrogen (H_2) is left in the alkaline solution and can be separated in gas-liquid separation units. Typical current density of this process varies from 100 to 300 mA cm^{-2} and the efficiency varies from 50 to 60%. Alkaline electrolyzer systems are the most developed and lowest in capital investment. However, alkaline systems require huge electricity input for water splitting due to the lowest efficiency in comparison with other existing technologies. The overall reactions of the alkaline electrolysis are represented by Equations 3.2-3.5. [16]

$$\text{Cathode.}\quad 4H_2O_{(l)} + 4e^- \rightarrow 2H_{2(g)} + 4OH^-_{(aq)} \tag{3.2}$$

$$\text{Anode.}\quad 2H_2O_{(l)} \rightarrow O_{2(g)} + H^+_{(aq)} + 4e^- \tag{3.3}$$

$$4OH^-_{(aq)} + 4H^+_{(aq)} \rightarrow 4H_2O_{(l)} \tag{3.4}$$

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{3.5}$$

Proton exchange membrane (PEM) electrolyzers

Proton exchange membrane (PEM) water electrolysis is considered an attractive alternative for conventional alkaline water electrolysis due to the following advantages: higher energy efficiency and production rates as well as more compact design. Typically, proton exchange membrane electrolyzer consists of Pt black, ruthenium, iridium and rhodium catalysts and a Nafion membrane which is used as a separator for both electrodes and gases. In the PEM electrolyzers water is introduced at the anode where the splitting into protons and oxygen occurs.

Subsequently, protons transfer through the membrane to cathode where they are recombined into gaseous hydrogen (H_2) while the unreacted water and gaseous oxygen (O_2) remain behind. It is possible to note, that in comparison to alkaline electrolyzers there is no need for a separation unit. In some cases a drier for residual water removal may be required to achieve high purity requirements. High current densities of more than 1600 mA cm^{-2} and high efficiencies of 55-70% are the remarkable features of proton exchange membrane electrolyzers. The overall reaction taking place at the cathode and anode of the proton exchange membrane electrolyzers are represented by Equations 3.6-3.7. [16]

$$\text{Cathode.} \quad 4H^+ + 4e^- \rightarrow 2H_2 \tag{3.6}$$

$$\text{Anode.} \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{3.7}$$

Solid-oxide electrolysis cells (SOEC)

Solid ceramic material (for instance, yttria stabilized zirconia – YSZ) is used as the electrolyte for selective transmission of negatively charged oxygen ions at elevated temperatures in solid-oxide electrolyzers. Partial replacement of electrical energy required for water splitting by thermal energy can be considered as a distinctive feature of the solid-oxide electrolysis cells. These systems have an ability to become the most energy efficient as the higher process temperature lead to reduced anode and cathode overpotentials which cause power losses in electrolysis. The operational principle of the solid oxide electrolysis cells is essentially similar to the alkaline system as oxygen ions transfer via the electrolyte whereas hydrogen remains in the unreacted steam stream. Solid electrolytes used in this system are not corrosive (in comparison to KOH in alkaline electrolysis) and much easier for handling (no distribution problems inherent to liquid phase processing). However, SOEC technology experiences problems connected to seals, thermal cycling and chrome migration. Efficiencies achieving 85-90% from the electrical input can be found in the literature for this method of water splitting. However, for the overall efficiency estimation, source of thermal energy must be also included. [16]

3.2. Methanol through direct hydrogenation of CO_2

Methanol production from captured CO_2 and renewable H_2 could potentially help to achieve independence from fossil fuels and decrease the emissions of greenhouse gasses to the atmosphere. CO_2 hydrogenation to methanol resembles conventional methanol synthesis from syngas, as represented by equations (2.1 - 2.3). However, the use of syngas mainly consisting of CO_2 for methanol synthesis results in more intensive formation of water (2.2 – 2.3) which negatively affects catalyst activity and increases costs of distillation. In addition, the equilibrium yield of methanol from H_2 and CO_2 is approximately 40% lower due to thermodynamic limitations. Furthermore, low reactivity, thermodynamic stability and highly oxidized state of carbon dioxide are the main barriers for creating effective processes for its utilization. However, it is interesting to note that formation of other undesired by-products is lower (approximately 5 times) and selectivity to methanol is higher in comparison to conventional process of methanol synthesis from CO rich syngas. Thus, production of methanol through hydrogenation of CO_2 offers some attractive benefits even though the yield of methanol from CO is higher. [17]

3.3. Catalysts for CO_2 hydrogenation to methanol

Heterogeneous catalysts are considered preferable for methanol synthesis due to the ease in handling, stability, price and applicability to existing reactor types. The presence of high levels of CO_2 in syngas decreases the selectivity, activity and lifetime of conventional methanol synthesis catalysts based on Cu/ZnO. A number of developments have been made during the last years to create more effective catalysts for CO_2 hydrogenation to methanol. The modification of conventional catalysts (Cu and Zn remain the main active components) with the use of different metals (Zr, Ga, Si, Cr, Pb, B, Mg, Mn and others) is widely used to achieve more effective performance (Figure 21). In addition, different preparation techniques (such as co-precipitation, deposition precipitation, and impregnation) can be used for that purpose as they also play an important role in the behavior of catalysts. [18]

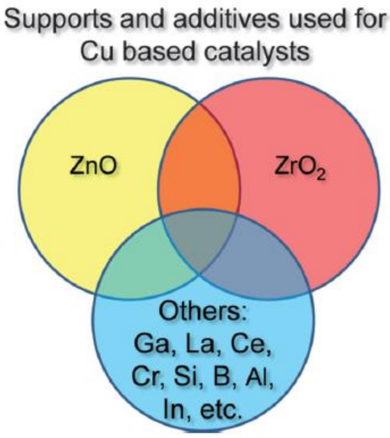


Figure 21 – The mostly used supports and additives for heterogeneous copper-based catalysts. [18]

3.3.1. Promoted Cu-based catalysts

Promoted Cu-based catalysts are considered to be effective for CO_2 hydrogenation to methanol [18]. High dispersion of Cu crystallites is believed to be the main reason for activity and selectivity of Cu-based catalysts. For example, Yang et al. [19] have prepared Cu/ZnO catalysts promoted with ZrO_2 (using successive precipitation) which was found to be useful in enhancing copper dispersion and surface activity. Methanol yield and conversion of CO_2 with the use of Cu/ZnO doped with ZrO_2 catalyst was higher than for conventional Cu/ZnO catalyst in these experiments. Additionally, it is possible to note that lower affinity to water is another beneficial feature of catalysts with Zr in the composition in comparison to $Cu/ZnO/Al_2O_3$. Results gained by An et al. [20] in a series of experiments of methanol synthesis using of catalysts with different ratios of Al/Zr also showed that even small concentration of Zr (5%) added to the composition of conventional catalysts can significantly increase space time yield of methanol. Similar effects were observed with the addition of Y to the composition of conventional $Cu/ZnO/Al_2O_3$ catalysts.

$CuO/ZnO/ZrO_2$ catalysts promoted with Mg and Mn were also found to increase copper dispersion in investigation of adsorptive properties and catalytic activity conducted by Sloczynski et al. [21]. A method involving the decomposition of citrate complexes was used for catalyst preparation and it was discovered that methanol yield and catalyst activity is the highest with $CuO/ZnO/ZrO_2$ catalysts promoted with Mn while the non-promoted catalyst showed the worst results. Addition of Mn to $CuO/ZnO/ZrO_2$ catalysts was also proven to be effective with regard of methanol synthesis rates by Lachowska and Skrzypek [22].

Melian-Cabrera et al. [23] reported positive effects of Pd promotion (in relatively small concentrations varying from 4 to 10 wt %) of Cu/ZnO/Al_2O_3 catalysts resulting in increased reducibility of CuO and higher yield of methanol. In other experiments the positive influence of Pd was proven in CuO/ZnO catalysts prepared with sequential precipitation technique. [17]

The phase of ZrO_2 support is also reported to be important in understanding of Cu-based catalyst activity. For example, Cu/m-ZrO_2 (monoclinic) catalysts showed activity approximately 5 times higher than those with t-ZrO_2 (tetragonal) support. While investigating physicochemical properties Guo et al. [24] found the negative effect of increasing calcination temperature on the future performance of CuO/ZnO/ZrO_2 catalysts prepared by solid-state reaction route. Other investigations by the same scientists were devoted to understanding of the effects of the urea/nitrate ratio on the catalyst activity when preparing CuO/ZnO/ZrO_2 catalysts with combustion techniques [17]. A half of the stoichiometric amount of urea was found to be optimal for catalyst performance.

Co-precipitation preparation methods of CuO/ZnO/ZrO_2 catalysts with the involvement of ultrasound irradiation were tested by Arena et al. [25]. These catalysts showed better activity in different range of pressures and temperatures in comparison to conventional Cu/ZnO/Al_2O_3 catalysts for methanol synthesis. Additionally, surface structure and thermodynamic studies proved the significant importance of ZnO in the catalyst composition (due to strong surface promotion effect) and the dominance of formation of methanol from CO_2, respectively. Another interesting preparation method of gel-network-co-precipitation for ultrafine Cu/ZnO/Al_2O_3 catalysts for methanol synthesis was tested by Hong et al. and resulted in the increase of selectivity and activity of these catalysts. [26]

Zhang et al. [27] and [28] achieved an increase in activity and selectivity to methanol of CuO/γ-Al_2O_3 catalyst by the addition of Zr and V into the catalyst composition. Enhanced performance (due to the synergetic effect between surface O_2 vacancies of CeO_2 and CuO) was also achieved by modification of CuO/γ-Al_2O_3 catalysts with CeO_2 and YDC (yttria doped with ceria) in the experiments by Wang et al. [29].

Hydrogenation of CO_2 and H_2 to methanol with multi-component catalysts (Cu/ZnO/ZrO_2/Al_2O_3 and Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3) has been reported to be more effective than using of conventional Cu/ZnO/Al_2O_3 catalysts. The addition of small concentration of colloidal silica (SiO_2) to the composition of the aforementioned multi-component catalysts was found to have positive effect on their stability. Toyir et al. [30] also found that the addition of hydrophobic SiO_2 in copper-based catalyst increases the selectivity and stability of $CuO/Ga_2O_3/SiO_2$ catalysts while Ga_2O_3 is reported to have positive influence on the surface activity of copper. This composition of catalyst prepared by impregnation technique showed good performance for converting CO_2 to methanol at temperatures varying from 250°C to 270°C.

3.3.2. Other modified catalysts for CO_2 conversion to methanol

Other catalysts for CO_2 conversion to methanol use metal supports different from copper. One example is catalysts based on Pd which show relatively high activity and selectivity to methanol from CO_2. However, as previously it is possible to note that methods of preparation and composition of Pd-based catalysts play an utmost important role for methanol synthesis. Quite a lot of research has been done to achieve high performance of Pd-based catalysts. For example, Liang et al [31] investigated the performance of Pd/ZnO catalysts supported with the usage of multi-walled carbon nanotubes. This novel catalyst showed excellent results for the conversion of CO_2 to methanol at temperature equal to 250°C and pressure equal to 30 atm. Bonivardi et al. [32] found that addition of Ga_2O_3 in the composition of PD/SiO_2 catalysts significantly increased their performance (for instance, selectivity increased by up to 45% with the modified catalyst). The same observations and conclusions were made by Fujitani et al. [18] who tested various supports for Pd-based catalysts and found that modification with Ga_2O_3 brought the best results for methanol synthesis.

The Ni_5Ga_3 catalyst was found to be relatively active and selective to methanol synthesis from CO_2 in the studies of Studt et al. [18]. The performance of Ni-Ga based catalyst was approximately similar in comparison to conventional catalysts for methanol synthesis. However, methanol synthesis with the use of Ni_5Ga_3 catalyst can be conducted at lower pressures due to decreased CO generation. Mechanical and thermal stability of transition metal carbides were found to be attractive for their implementation as catalysts for CO_2 hydrogenation to methanol. In the experiments of Dubois et al. [33] Mo_2C and Fe_3C were found to be effective regarding the CO_2 conversion but poorly selective to methanol. Addition of Au and Ag was found to have a positive influence on the catalyst selectivity to methanol. However, activity of these catalysts was lower compared to Cu-based catalysts. Rh, Ru and Ni-based catalysts were found not to be active for methanol synthesis producing mainly CO and CH_4. [17]

3.3.3. Investigations of the reaction pathways and mechanisms

High activity and selectivity of promoted Cu-based catalysts in hydrogenation of carbon dioxide to methanol generated the interest among the scientific society in understanding of the reaction mechanisms and pathways of the methanol synthesis.

Bell et al. [34] proposed a bifunctional mechanism of methanol synthesis while studying catalytic conversion of CO and CO_2 to methanol over Cu/ZrO_2 similarly to Arena et al. [18] who studied the same processes of methanol synthesis over $Cu/ZnO/ZrO_2$ catalyst. According to the bifunctional mechanism the adsorption and dissociation of H_2 take place on the Cu site while CO_2 adsorption occurs on the ZrO_2 site. In other words, carbon dioxide is adsorbed on bare oxides and hydrogen is dissociated on copper species. Subsequently, the atomic H_2 spillover from the surface of Cu to the surface of ZrO_2, hydrogenating the remaining carbon species (mostly represented by bicarbonates) and forming methanol. The reaction mechanism of CO_2 hydrogenation to methanol over $Cu/ZnO/ZrO_2$ catalyst is presented in Figure 22.

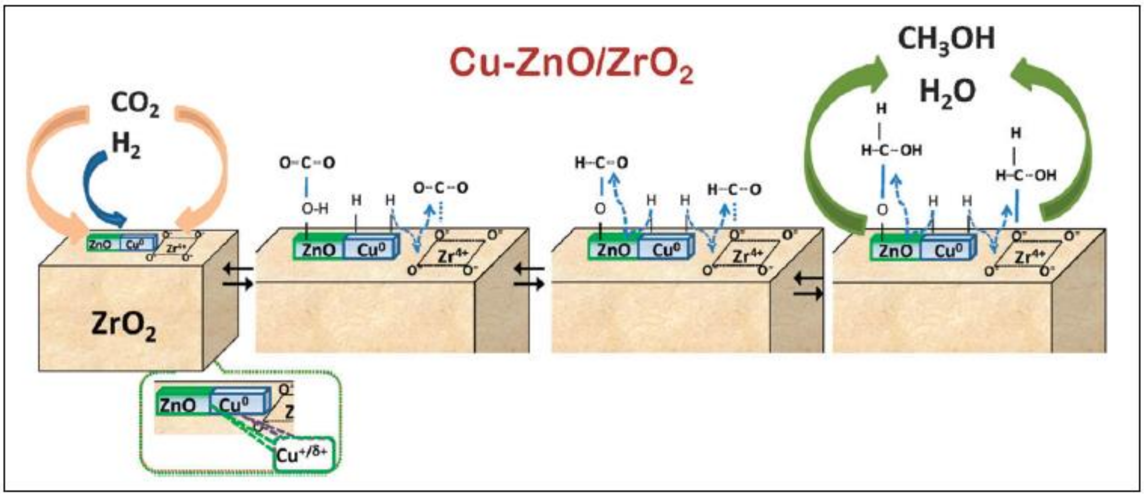


Figure 22 – Bifunctional mechanism of methanol synthesis over $Cu/ZnO/ZrO_2$ catalyst. [18]

However, there are several controversial points of view regarding the active Cu phase. Koeppel et al. [18] found by X-ray diffraction measurements that Cu^o is the most dominant active copper species for the methanol synthesis over Cu/ZrO_2 catalysts. In contrast, Cu^+ was proposed to be the predominantly active component in $Cu/ZnO/SiO_2$ catalysts while studying them in static low-energy ion scatter experiments.

Grabow et al. [18] proposed a micro-kinetic model including 11 individual steps for the methanol synthesis from CO_2 and H_2. These micro-kinetic steps represented on Figure 23 were determined by DFT calculation (* and X* represent the free surface site and the adsorbed atom or molecule X, correspondingly). In the micro-kinetic model proposed by Grabov et al., the hydrogenation of formate ($HCOO^*$) leads to the formation of $HCOOH^*$. Subsequently, the formation of H_2COOH^* occurs by the hydrogenation of $HCOOH^*$. Afterwards, H_2COOH^* splits into H_2CO^* and OH^*. The H_3CO^* can be considered as the final intermediate before methanol (CH_3OH^*) formation. [18]

$$
\begin{array}{rcll}
H_2(g) + 2^* & \rightleftharpoons & 2H^* & (1) \\
CO_2(g) + {}^* & \rightleftharpoons & CO_2^* & (2) \\
CO_2^* + H^* & \rightleftharpoons & HCOO^* + {}^* & (3) \\
HCOO^* + H^* & \rightleftharpoons & HCOOH^* + {}^* & (4) \\
HCOOH^* + H^* & \rightleftharpoons & H_2COOH^* + {}^* & (5) \\
H_2COOH^* + {}^* & \rightleftharpoons & H_2CO^* + OH^* & (6) \\
H_2CO^* + H^* & \rightleftharpoons & H_3CO^* + {}^* & (7) \\
H_3CO^* + H^* & \rightleftharpoons & CH_3OH^* + {}^* & (8) \\
CH_3OH^* & \rightleftharpoons & CH_3OH\ (g) & (9) \\
OH^* + H^* & \rightleftharpoons & H_2O^* + {}^* & (10) \\
H_2O^* & \rightleftharpoons & H_2O\ (g) & (11)
\end{array}
$$

Figure 23 – Micro-kinetic steps of CO_2 hydrogenation to methanol over Cu-based catalyst. [18]

Methanol synthesis via formate intermediate was also proven by in-situ FTIR spectroscopy while studying the reaction mechanism over Pd/β-Ga_2O_3 catalyst as well as the bifunctional reaction mechanism (Figure 24). The determined key components were HCOO, H_2COO (dioxomethylene), CH_3O (methoxy) and finally CH_3OH (methanol). [35]

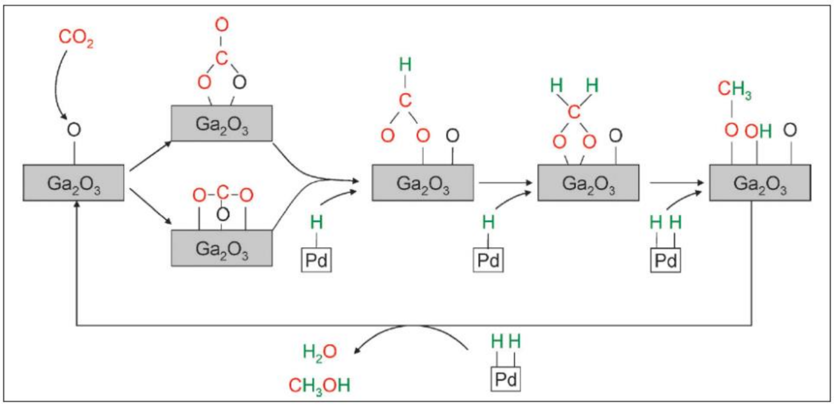


Figure 24 – Reaction mechanism of methanol synthesis over Pd/β-Ga_2O_3 catalyst. [35]

Other reaction routes via RWGS reaction comprising conversion of CO and CO_2 to methanol via HOCO intermediate can be also found in literature. Liu et al. [35] proposed a reaction pathway comprising both the RWGS (via HOCO intermediate) pathway and the formate pathway by implementation of Monte Carlo simulation and DFT calculations for the investigation of methanol synthesis over Cu/ZrO_2 (111) and Cu/ZrO_2 (212) catalysts. Finally, it is possible to note that three-step hydrogenation of CO_2 to methanol on zeolites was proposed by Chan et al. [35] as an alternative approach to understand the mechanism of methanol synthesis. Different routes of CO and CO_2 hydrogenation to methanol are presented in Figure 25.

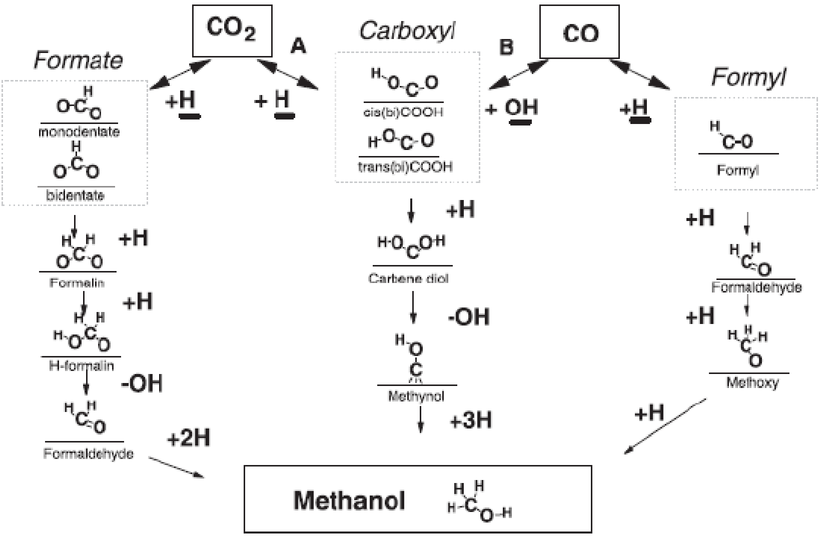


Figure 25 – Pathways of the CO and CO_2 conversion to methanol over Cu. [35]

3.3.4. Short summary of catalyst advances

A short summary of catalyst advances is represented in Table 1. It is possible to conclude that the use of highly selective and active catalysts with higher tolerance to water is of great importance for CO_2 hydrogenation to methanol. Various novel and promising preparation techniques such as solid-state reactions, urea-nitrate combustion and reverse co-precipitation exist to achieve higher performance of catalysts. Modification of the composition of catalysts by different compounds is also widely implemented to increase the efficiency. As a result, conventional Cu/ZnO catalysts promoted with Pd, Zr, Ga, Mg, Mn and others show better selectivity and activity to methanol synthesis from CO_2 rich syngas. Research on the reaction pathways for methanol synthesis indicate mainly two alternative routes: methanol synthesis by RWGS (via HOCO intermediate) and via formate intermediate. However, the bifunctional mechanism is considered to be well-established.

Table 1 – Summary of catalyst advances for CO_2 hydrogenation to methanol [36]

Catalyst	Preparation method	Pressure [bar]	Temperature [ºC]	CO_2 conversion [%]	MeOH selectivity [%]	MeOH space time yield [mmol/g*h]
Cu/ ZrO_2	Deposition-precipitation	20	240	6.3	48.8	11.2
Cu/ZnO/ZrO_2	Co-precipitation	80	220	21	68	5.6
		40	240	-	-	9.2
		30	250	19.4	29.3	-
	Urea-nitrate combustion	30	240	17	56.2	-
	Glycine-nitrate combustion	30	220	12	71.1	-
	Solid-state reaction	30	240	15.7	58	-
Cu/ZnO/Ga_2O_3	Microwave-assisted precipitation	30	270	15.9	29.7	4.2
	Incipient wetness	30	270	6.01	28.2	1.4
Cu/Ga_2O_3/ZnO	Co-impregnation	20	270	6	88	11.8
Cu/ZnO/Al/ZrO_2 (Fibrous)	Co-precipitation	40	240	20.5	61	-
		50	250	25.8	69.4	-
Cu/ZnO/ZrO_2/ Ga_2O_3	Use of citric acid	80	240	17	71	6.6
Cu/ZnO/Ga_2O_3/ZrO_2	Co-precipitation	80	250	-	75	10.1
Cu/ZnO/Ga_2O_3/SiO_2	Co-impregnation	20	270	5.6	99.5	10.9
Cu/B_2O_3/ZrO_2	Deposition-precipitation	20	250	15.8	67.2	1.8
Cu/ Ga_2O_3/ZrO_2	Deposition-precipitation	20	250	13.7	75.5	1.9
Cu/ZnO/Al/Y	Co-precipitation	50	250	26.9	47.1	16.2
Pd/CeO_2	Impregnation	20	250	4	27.7	1.2
Pd/Ga_2O_3	Co-precipitation	50	250	19.6	51.5	10.1
Au/ZnO/ZrO_2	Co-precipitation	80	220	2	100	2
Pd/Ga_2O_3/MWCNTs	Co-precipitation	50	250	16.3	57.5	9.4
Pd/Zn/MWCNTs	Incipient wetness	30	250	7.3	86.3	6.3
Pd/Zn/MWCNTs	Co-precipitation	50	270	19.6	35.6	7
Pt/CeO_2	Impregnation	30	230	8.1	68.2	5.5

3.4.Indirect hydrogenation of CO_2 to methanol

The negative feature of direct CO_2 hydrogenation to methanol with the involvement of Cu/ZnO based heterogeneous catalysts is that this process requires high operating conditions (temperature varying from 200-250°C and pressure in the range of 50-100 bars) which decreases methanol yield due to the thermodynamic limitations. However, reduction of process temperature cannot be used because activation of thermodynamically stable CO_2 can be achieved at the aforementioned temperatures. Desirable milder conditions can be achieved through indirect hydrogenation of CO_2 to methanol through its derivatives such as organic carbonates, formates, carbamates, urea derivatives and others (Figure 26). [7]

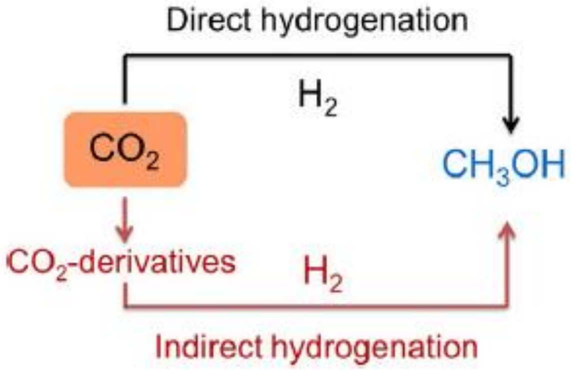


Figure 26 – Scheme of direct and indirect hydrogenation of CO2 to methanol. [7]

3.4.1. Hydrogenation of organic carbonates, carbamates and formates to methanol

A series of experiments on the indirect hydrogenation of CO_2 to methanol via derived organic carbonates, carbamates and formates were conducted by Milstein et al. [37]. Homogeneous Ru-based catalyst was used in the first set of experiments where CO_2 was at first converted to dimethyl carbonate ($C_2H_6O_3$) and then hydrogenated to methanol under mild conditions of T=145°C and P=40 bar. Complete conversion of CO_2 and good selectivity was achieved. Subsequently, even better results (increased turnover number) were achieved with the use of a bipyridine-based pincer complex as a catalyst. Another experiment was conducted with the same catalyst and methanol synthesis was done through methyl carbamate. Mixture of methyl N-benzyl carbamate and hydrogen was heated in THF (solvent - tetrahydrofuran – $(CH_2)_4O$) for 48 h at T=110°C. As a result, methanol and benzylamine were gained. Eventually, methanol was synthesized through reaction of methyl formate and hydrogen conducted with the use of the same catalyst in 1.4-dioxane (solvent) at 145°C and P=50 bars. The synthesis can be also conducted without solvent resulting in green waste-less process. It is of crucial importance to emphasize that the processes of converting of CO_2 to formic acid and derived products are well-established. As a consequence, this promising route of methanol synthesis is of great scientific interest. The aforementioned reactions and catalysts are presented in Figure 27.

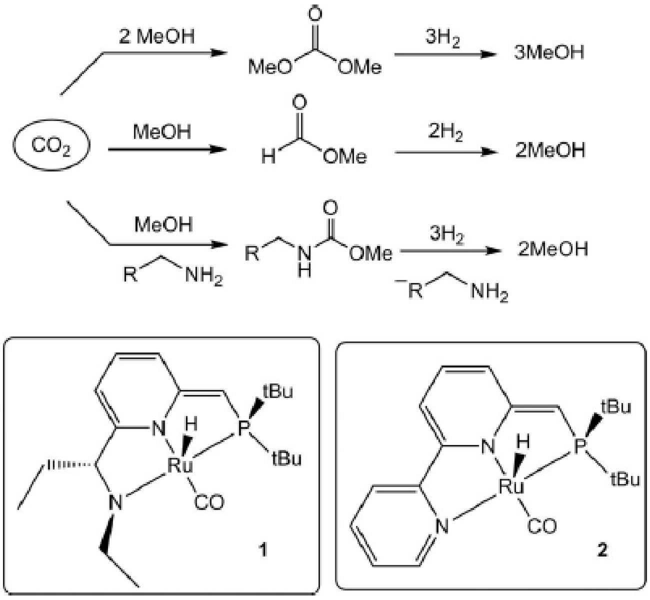


Figure 27 – Indirect hydrogenation of CO_2 to methanol via formic acid derived products (carbomates and formates). [7]

The experiments by Xian-Long Du et al. [7] were conducted with the use of nanocomposite heterogeneous copper-based catalyst prepared by co-precipitation in oxalate-gel (Cu/Al_2O_3-oxalate gel with concentration of copper varying from 10-50 wt %). Hydrogenation of CO_2 to methanol via methyl formate was conducted at T=130°C without solvent and the highest yield of methanol of 92% and turnover number of 1092, which is reported to be the highest found in literature for methyl formate to methanol hydrogenation, were achieved when the copper content in catalyst was 20 wt %. This showed the highest methyl formate hydrogenation activity due to the highest metallic copper dispersion observed for that concentration of copper. Stability of this catalyst was demonstrated by repeated use at least 3 times. Different supports (Cu/ZnO, Cu/CrO_2, $Cu/ZnO-Al_2O_3$, Cu/Cr_2O_3) were also tested, however, Cu/Al_2O_3 showed the highest performance for methyl formate hydrogenation to methanol. The selective hydrogenation of other formates (ethyl-formate, propyl-formate and butyl-formate) to methanol under optimized conditions with the $20-Cu/Al_2O_3$-oxalate gel catalyst resulted in methanol yields approaching 91% for all of formates.

3.4.2. Hydrogenation of cyclic carbonates to methanol

A significantly important step in ethylene glycol production is the omega process which is the subsequent process of CO_2 and ethylene oxide (C_2H_4O) conversion to ethylene carbonate ($C_3H_4O_3$). According to Ding et al. [38], the process of ethylene glycol production can be used as a basis for indirect selective hydrogenation of ethylene carbonate with Ru-based catalyst to methanol. Thus, the production of significantly important chemicals (methanol and ethylene glycol) can be accomplished simultaneously by reactions represented in Figure 28.

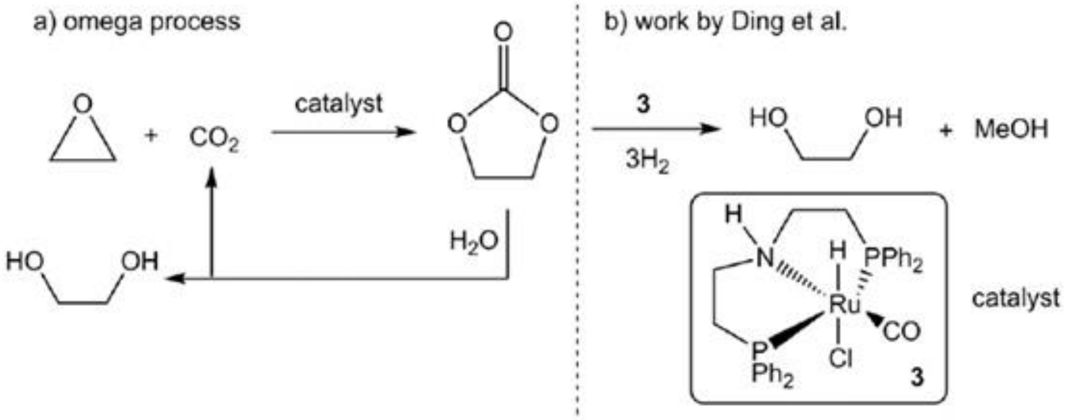


Figure 28 – Co-production of ethylene glycol (omega process) and methanol via indirect hydrogenation of ethylene carbonate. [7]

Some other variations of the Ru-based catalyst were also tested for the aforementioned process (potassium tert-butoxide, iridium-based complex (less effective) and others), and yields of methanol varying from 85 to 99% were obtained while operating at pressures of 60 bar. However, such pressures require reactors with durable construction, which increases capital investment costs, even though the performance of these catalysts (high activity and stability) was sufficiently high. Hence, reactions involving lower pressures of hydrogen are of great interest. For instance, one interesting approach is the utilization of reaction of de-polymerization by hydrogenation of waste poly propylene carbonate (prepared by copolymerization of propylene oxide and carbon dioxide) with the use of Ru-based catalyst (Figure 28) to obtain methanol in high yields and 1,2-propyleneglycol while using lower pressure. The following reaction is presented in Figure 29. [7]

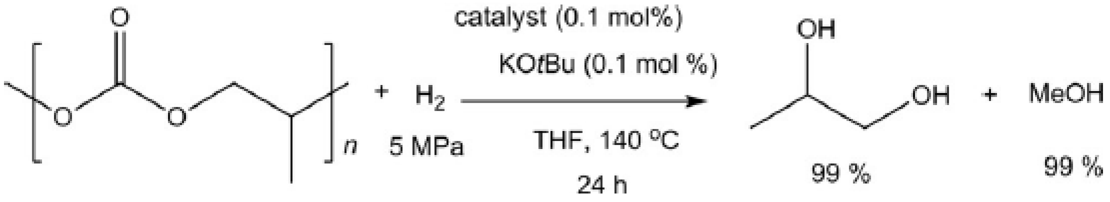


Figure 29 – Alternative approach to use the recovered waste poly-carbonate as feedstock for methanol synthesis. [7]

Nanocatalyst $CuCr_2O_4$ (prepared by hydrothermal method followed by calcination) was developed for the hydrogenation of ethylene carbonate to methanol to overcome the well-known problems in handling of homogeneous Ru-based catalyst. Use of this catalyst let to achieve 60% conversion of ethylene carbonate to methanol and 93% conversion of ethylene carbonate to ethylene glycol at T=180°C and P=50 bar. Subsequently, the surface of this catalyst was studied and it was found that the presence of metallic copper and cubic spinel structure of the aforementioned naonocatalyst is responsible for the high activity and selectivity to methanol. A notable advantage of the $CuCr_2O_4$ catalyst is its ability to be used for several times. Hydrogenation of ethylene carbonate with other heterogeneous catalysts did not show good selectivity to methanol and formation of undesirable by-products occurred intensively. Further investigations of heterogeneous catalysts to increase the conversion of ethylene carbonate to methanol and find catalysts less harmful to nature ($CuCr_2O_4$ cannot be considered environmentally friendly) was conducted by Xian et al. [7] They developed a nano-composite $Cu\text{-}SiO_2$ catalyst (with 70 wt % loading of Cu) prepared by precipitation gel, which was tested for ethylene carbonates hydrogenation at T=160°C and P=60 bars. The yield of methanol was increased to 95%. Afterwards, the significantly important impact of copper valence state on the performance of Cu-based was studied and analyzed with the temperature reduction method by Xian et al. [7]. It was found that Cu^o/Cu^+ ratio plays an utmost important role in obtaining high yield of methanol. Finally, it was found by the same authors that addition of B_2O_3 (by doping) has a positive impact on catalyst stability while hydrogenating ethylene carbonates to methanol.

3.4.3. Hydrogenation of urea derivatives to methanol

Different urea derivatives (which can be catalytically synthesized from CO_2 and amines) can be converted to methanol via hydrogenation. Milstein's group reported the hydrogenation of alkyl and aryl urea derivatives at P=13.6 bars and T=110°C to methanol with the use of a bi-pyridylbased Ru pincer complex as a catalyst. Yield of methanol varied from 46% to 94% and formamide was formed as the by-product of this reaction. [39]

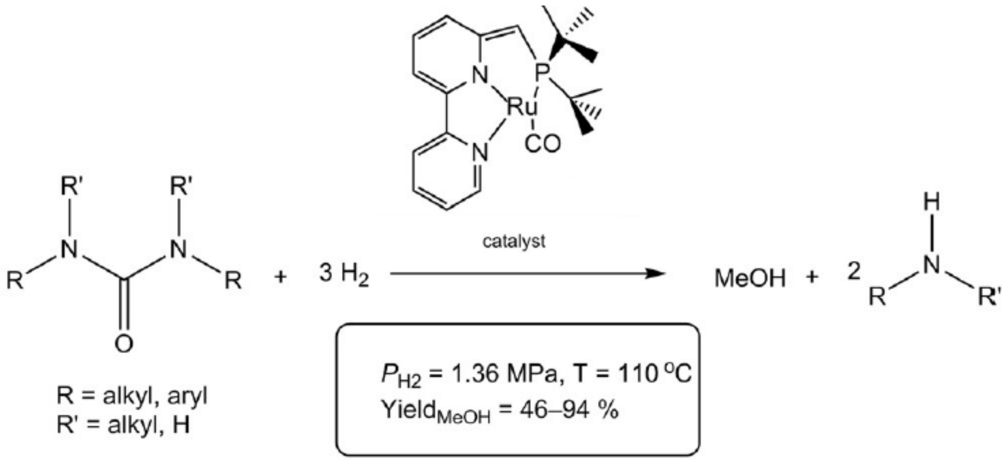


Figure 30 – Hydrogenation of alkyl and aryl urea derivatives to methanol. [7]

3.4.4. Cascade catalysis for the hydrogenation of CO_2 to methanol

Concept of “cascade catalysis” developed by Sanford and Huff [40] is another interesting approach which is focused on the indirect catalytic (homogeneous) hydrogenation of formic acid and formate ester intermediates to methanol. The cascade catalysis comprises the following consecutive steps (reactions):

- Hydrogenation of carbon dioxide to formic acid;
- Esterification (to obtain formate esters);
- Methanol synthesis via hydrogenation of the ester.

These cascade catalysis steps are presented in Figure 31. It can be noted that each step requires a specific catalyst. Thereby, a challenge to overcome is to choose the appropriate set (combination) of catalysts which can work in good interaction with each other not affecting negatively the overall process. For that reason, authors [7] tested a series of different catalysts and found the best combination which is presented in Figure 31.

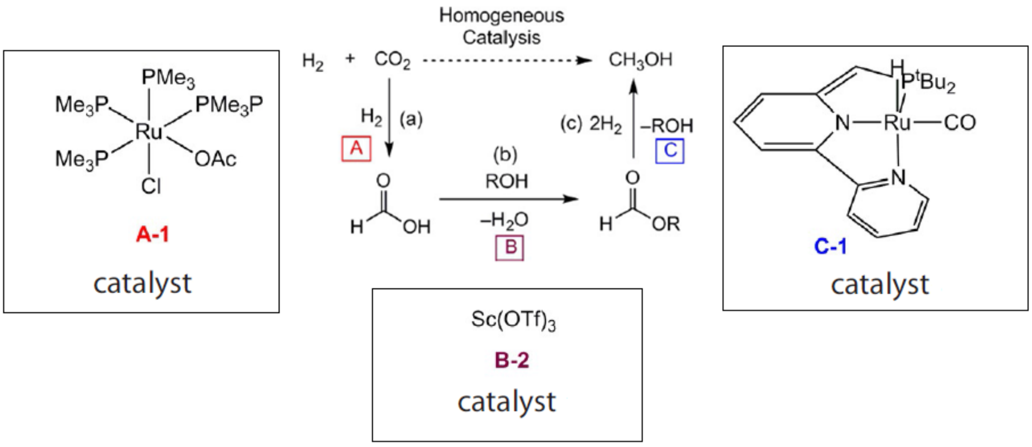


Figure 31 – Methanol synthesis from CO_2 and H_2 with cascade catalysis. [7]

Even though the aforementioned catalysts were found to be the best in holding the separate steps of the cascade catalysis, the negative deactivation effect of catalysts for the subsequent steps B and C by each other occurred. For that reason, separate disposition of catalysts within the reactor was used to overcome this problem (catalysts A and B were located in the center (inner vial) and catalyst C in the outer shell of the reactor). The whole reaction of the methanol synthesis by cascade catalysis of CO_2 and H_2 is presented in Figure 32.

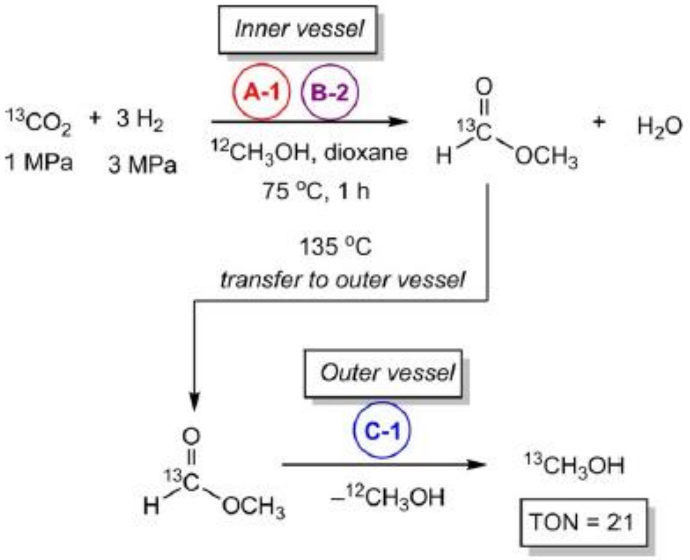


Figure 32 – Separate disposition of catalysts to prevent deactivation in cascade catalysis. [7]

Thompson et al. [41] developed an effective cascade heterogeneous system to overcome the difficulties in separation and poor compatibility, problems intrinsic to homogeneous catalysts. Methanol was synthesized by three separate steps and two different heterogeneous catalysts at T=135°C, P=10 bars (CO_2) and P=30 bars (H_2). Firstly, carbon dioxide (CO_2) was hydrogenated to formate intermediate with a Cu/Cr_2CuO_4 catalyst. Subsequently, the formate intermediate was hydrogenated to methanol with a Cu/Mo_2C catalyst. The cascade reaction route for carbon dioxide hydrogenation to methanol via formic acid and formate intermediate is represented in Figure 33.

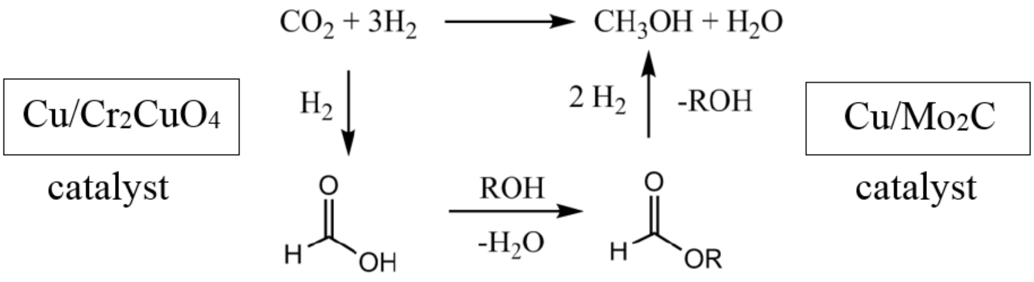


Figure 33 – Indirect methanol synthesis (by cascade heterogeneous catalytic system) via formic acid and formate intermediate. [7]

The same group of researchers found that addition of ethanol (C_2H_6O) into the CO_2 and H_2 reactants can significantly increase the conversion rates (here methanol was formed via ethyl formate intermediate). Different catalysts were tested and Cu/Cr_2CuO_4 catalyst showed the best performance in converting the CO_2 to ethyl formate in the presence of ethanol. Even though the activity and selectivity of Cu/Cr_2CuO_4 catalyst was high regarding conversion of CO_2 to ethyl formate, the subsequent formation of methanol from ethyl formate was not efficient with the use of the aforementioned catalyst. To solve this problem the Cu/Mo_2C catalyst was used and showed high activity and selectivity in the conversion of ethyl formate to methanol. Thus, it is possible to conclude that synergetic use of the mixture of Cu/Cr_2CuO_4 and Cu/Mo_2C catalysts in the presence of ethanol can have positive effect on methanol synthesis (increase productivity) while hydrogenating CO_2 by cascade catalysis. [41]

3.4.5. Transfer hydrogenation of organic formates and cyclic carbonates to methanol

Even though the hydrogenation of various formates and carbonates indicates an attractive route of methanol synthesis from CO_2, the use of pressurized and extremely flammable hydrogen in these processes bring some obvious difficulties making the whole process hazardous. Transfer hydrogenation with the use of hydrogen donors (instead of hydrogen) can be used to increase safety. For that reason, Hong et al. [42] developed the process of transfer hydrogenation of formates and carbonates to methanol in C_3H_8O (2-propanol which was used as a solvent and hydrogen donor) with a commercial Ru-based catalyst with metal loading of 0.1 mol -%, in the presence of a base (K_2CO_3), which played the utmost important role in the catalyst performance at 140°C for 12 h. Other alkyl formates (isopropyl-, benzyl- and ethyl-) were slightly reduced to form methanol, as well. The reaction of transfer hydrogenation of methyl formate to methanol and the catalyst used in the process are presented in Figure 34.

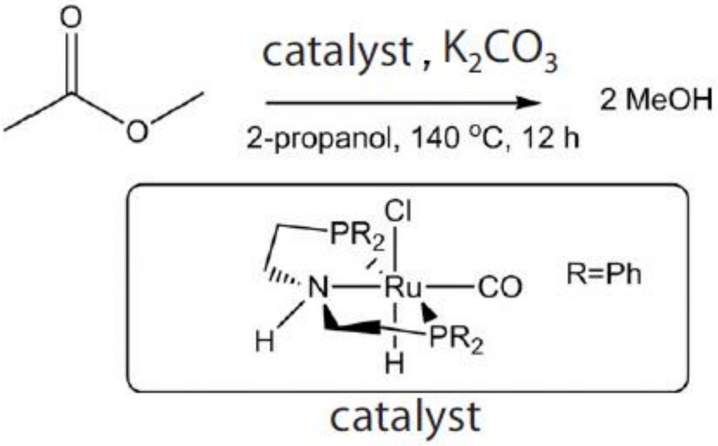


Figure 34 – Transfer hydrogenation of methyl formate to methanol. [7]

After that, a series of experiments were conducted by the same researchers [42] to quantitatively convert cyclic carbonate, which can be easily gained by inserting carbon dioxide into epoxides, to methanol via transfer hydrogenation. The same solvent (2-butanol), Ru-based catalyst and process conditions were used. However, methanol formation occurred from 4-methyl-1,3-dioxolan-2-one which was the intermediate substance of transfer hydrogenation of cyclic carbonate. In addition to that, other substitutes of cyclic carbonates (butyl, ethyl and phenyl) were effectively reduced to methanol as well. Methanol and propylene glycol were the final products of the reaction represented in Figure 35.

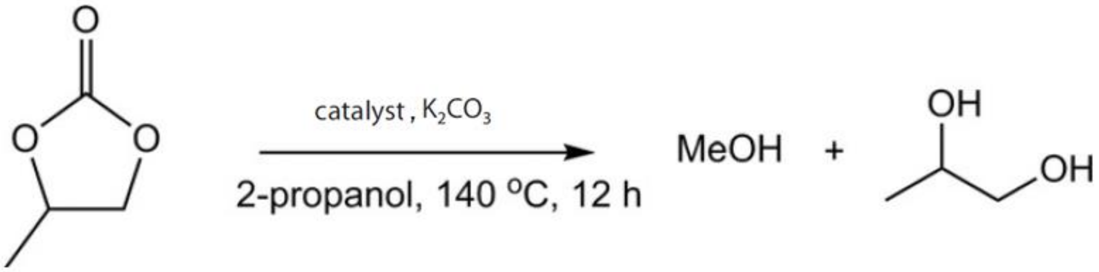


Figure 35 – Transfer hydrogenation of 4-methyl-1,3-dioxolan-2-one to methanol. [7]

3.5. Progress and technological advances in methanol synthesis

It is of crucial importance to note, that many efforts are concentrated all over the world on finding alternative and more effective solutions of methanol synthesis (especially from CO_2 and H_2). For instance, the cooperation of Lurgi and Süd-Chemie led to the development of highly effective catalysts for methanol synthesis from CO_2 and H_2 at $T=260^oC$. A pilot plant in Japan utilizes CO_2 and H_2 as raw materials to produce methanol catalytically over SiO_2 modified Cu/ZnO catalyst at a capacity of 50 kg per hour. Pressure of 50 bar and temperature of 250^oC are used in this process. Another pilot plant in Japan built by Mitsui Chemicals also operates effectively and produces 100 ton of green methanol per year. Photochemical splitting of water is used for hydrogen production in this process. Carbon Recycling International built the first commercial plant in Iceland producing methanol from CO_2 and H_2. The distinctive features of this plant are that utilization of cheap geothermal energy is used for energy generation and water electrolysis is used for hydrogen production. Other significantly important developments are presented below. [17]

3.5.1. Two-stage catalyst bed concept of methanol synthesis

Rahimpour [43] developed a two-stage catalyst bed system (instead of the conventional single catalyst bed) applicable for methanol synthesis from CO_2. Partial conversion of syngas to methanol at high yield and at higher than normal operating conditions happens in the first catalyst bed which is represented by a water-cooled reactor with catalyst packed in the tubes. Subsequently, second catalyst bed represented by a gas-cooled reactor with catalyst packed in the shell side uses the excess heat of the first stage to pre-heat the feed gas for the first reactor. In other words, the whole system works as a heat exchanger:

- 1st heat exchange occur when the fresh syngas flows upwards through the second converter tubes while the reaction of methanol synthesis occurs on the shell side. Excess heat of the exothermic methanol synthesis is used for pre-heating of the fresh syngas and leads to the enhanced conversion rate of the reaction.
- 2nd heat exchange happens when the pre-heated syngas flow downwards through the tubes of the first converter filled with the catalyst. Excess heat is transferred to the cooling water circulating inside the shell.

The estimation of the potential of two-stage catalyst bed system and numerical comparison with conventional single bed system was done with the help of one-dimensional heterogeneous dynamic model. A favorable temperature profile of catalyst was found along the two-stage catalyst bed system. Enhanced catalyst activity, increased production rate of methanol and prolonged catalyst life time were the remarkable consequences of the favorable temperature profile. A schematic diagram of the two-stage catalyst bed system developed by Rahimpour (applied as an industrial dual-type reactor) is presented in Figure 36.

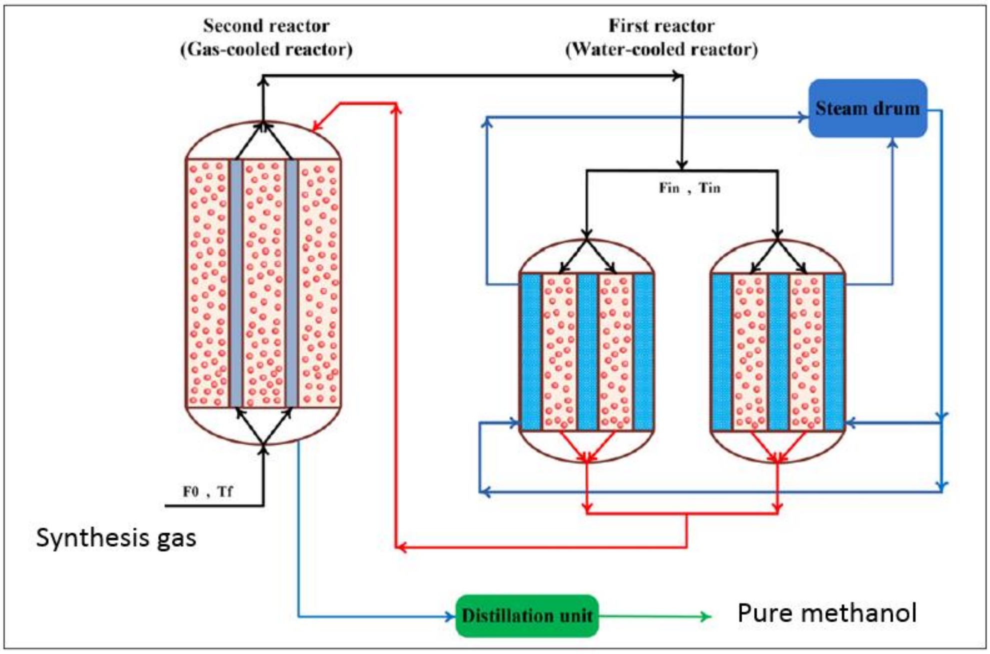


Figure 36 - Two-stage catalyst bed system (dual-type methanol synthesis reactor). [44]

3.5.2. Thermally coupled reactor for simultaneous hydrogen and methanol production

A promising idea for process intensification is the coupling of endothermic and exothermic reactions in reactors using heat exchange between different fluids. Vakili et al. [45] developed a superior method which can be applied for simultaneous methanol synthesis and hydrogen production by cyclohexane dehydrogenation in the heat exchanger reactor represented in Figure 37.

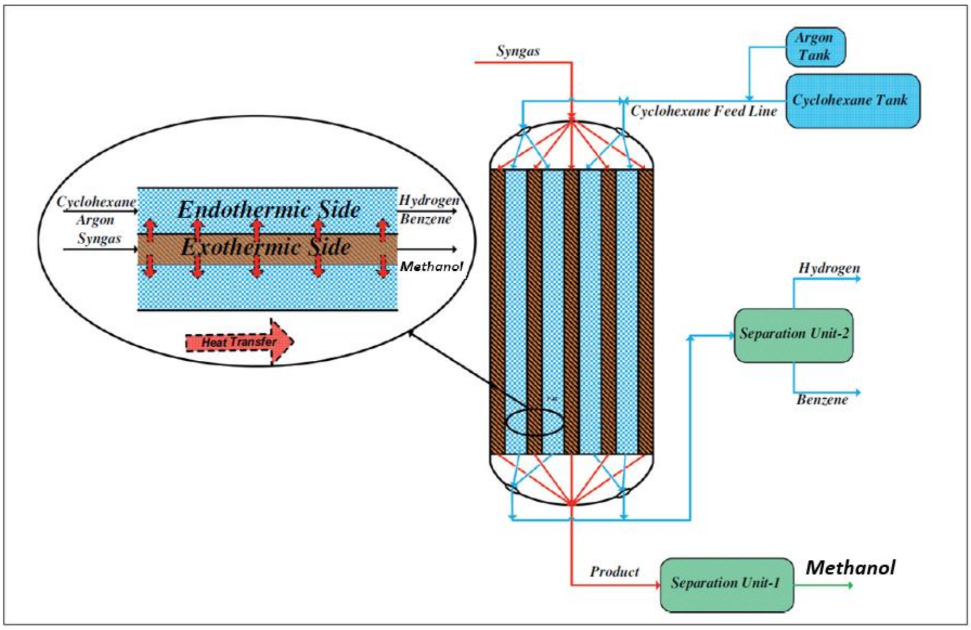


Figure 37 – Simultaneous methanol and hydrogen production in heat exchanger reactor. [45]

In this technology, the whole system works in co-current mode. The exothermic methanol synthesis from CO_2 and H_2 occurs on the first side of the heat exchanger reactor while the endothermic reaction of hydrogenation of cyclohexane (which is used as the coolant medium instead of water) to benzene takes place over Pt/Al_2O_3. Consequently, the heat is transferred constantly from the exothermic synthesis favoring enhanced conversion of syngas to methanol (due to thermodynamic aspects) and driving the endothermic reaction, producing hydrogen This is also beneficial as hydrogen is one of the main reactants and can be subsequently utilized for synthesis purposes.

3.5.3. CAMERE process

The Korean Institute of Science and Technology developed the process for the utilization of CO_2 emissions by using them as a feedstock for methanol synthesis. This process has the status of a pilot plant and methanol synthesis occurs by two subsequent steps:

- Conversion of CO_2 to CO and H_2O by RWGS reaction in the first operation unit over $ZnAl_2O_4$ catalysts at T=600-700°C and ambient pressure;
- Methanol synthesis in the second operation unit by using the CO-rich syngas over Cu-based catalysts at T=250-300°C and P=50-70 bar.

A simplified process flow diagram of the CAMERE process is presented in Figure 38.

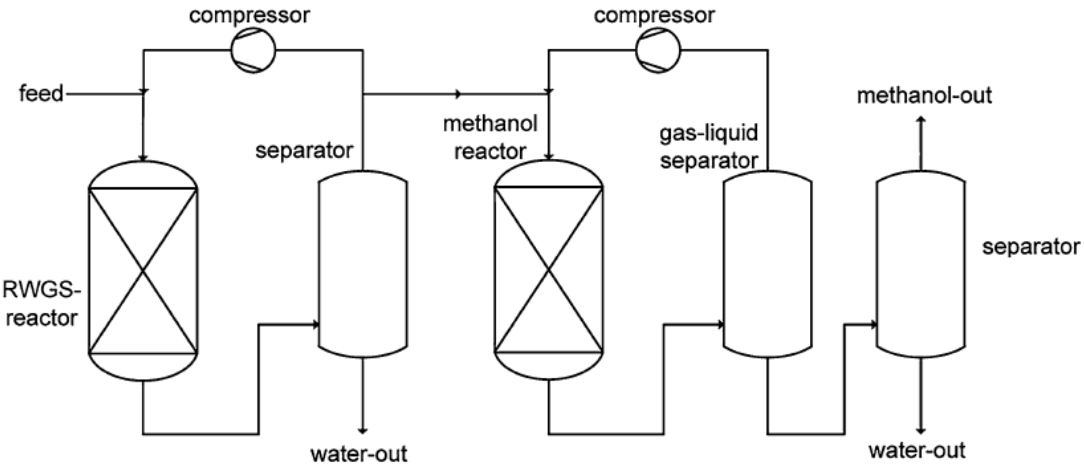


Figure 38 – Simplified process flow diagram of CAMERE process. [46]

Even though this method can be used for CO_2 conversion to methanol (yield =70%), it requires highly stable catalysts for the first process step. In addition, high temperatures lead to high operating costs. The second step involves typical conditions and catalysts for the conventional methanol synthesis. Thus, the CAMERE process provides a possible solution for the conversion of CO_2 to methanol. [46]

3.5.4. BNL method of methanol synthesis

Brookhaven National Laboratory (BNL) developed a new method of low-temperature methanol synthesis from syngas to overcome the thermodynamic limitations of the conventional methanol synthesis. This process can be conducted at mild temperatures varying from 100^{o}C to 130^{o}C and pressures varying from 10 bars to 50 bars with the use of very strong base catalysts (NaH or a mixture of nickel acetate, t-amyl alcohol and sodium hydride). A high yield of up to 70% and good selectivity to methanol is reported for this method. However, the commercialization of this process is highly unlikely due to the fast deactivation of the developed catalysts in the presence of trace amounts of CO_2 and H_2O in the feed gas or reaction system, necessitating utilization of complicated systems for syngas purification or reactivation of catalysts, leading to high capital and operating costs. [17]

3.5.5. Methanol synthesis through methyl formate

This alternative process of methanol synthesis from syngas is considered a low-temperature (100°C) process and can be conducted by the following chemical reactions at pressures varying from 30 to 60 bars:

- Carbonylation of methanol to form methyl formate:

$$\mathrm{CO + CH_3OH = HCOOCH_3} \tag{3.8}$$

- Hydrogenation of methyl formate to form 2 moles of methanol:

$$\mathrm{HCOOCH_3 + 2H_2 = 2CH_3OH} \tag{3.9}$$

- Net reaction – hydrogenation of carbon monoxide to form methanol:

$$\mathrm{CO + 2H_2 = CH_3OH} \tag{3.10}$$

The carbonylation reaction is carried with the use of homogeneous catalysts such as sodium methoxide ($NaOCH_3$) or potassium methoxide ($KOCH_3$) in the liquid phase. Other heterogeneous catalysts such as Amberlyst and Amberlite resins are also reported to be active for methanol carbonylation. Subsequently, the reaction of hydrogenation of methyl formate can be carried out in the gas or liquid phase on Cu-based catalysts yielding methanol. It is possible to conduct the carbonylation and hydrogenation reactions separately in two reactors, which is good from the effectivity point of view, or together in one reactor, which can be considered as a cost saving option. However, for the latter case, combined catalysts such as CH_3ONa/Cu or CH_3ONa/Ni are needed. Nevertheless, similarly to the BNL method, this process requires pure syngas without CO_2 and H_2O, which significantly affects the activity of catalyst by poisoning, making this process challenging for commercialization and ineffective in terms of utilization of CO_2 emissions. [47]

3.5.6. LPMEOH project

Air Products [48] has developed a liquid-phase methanol synthesis process (LPMEOH) when looking for more effective alternatives for the conversion of coal-derived syngas (which is typically rich in carbon oxides) to methanol. This process is reported to be effective in terms of process heat removal and temperature control, which leads to enhanced syngas conversion to methanol due to favorable thermodynamics. A slurry bubble column reactor presented in Figure 39, where syngas is bubbled into the liquid, is used in the LPMEOH process. Use of powdered catalyst suspended in inert oil, which acts as a temperature moderator, can be considered as a distinctive feature of this process as well as a robustness, flexible operation, and high quality of the methanol product.

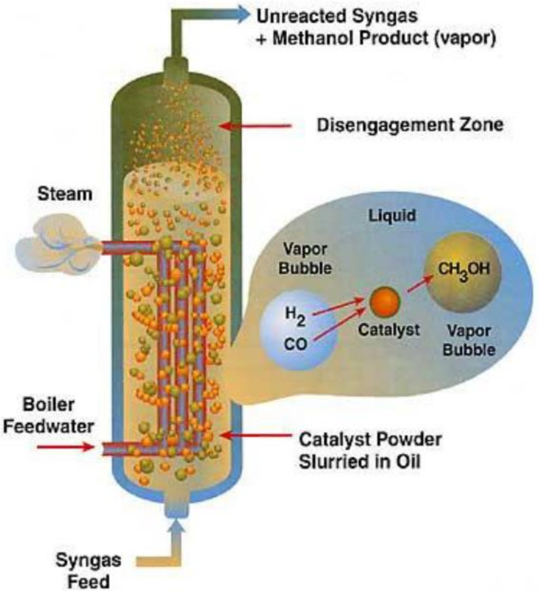


Figure 39 – LPMEOH slurry bubble column reactor used for the methanol synthesis. [48]

In order to show the efficiency of the developed process, Air Products opened a demonstration plant in 1997 with methanol capacity of 235 tons per day. The main objective of the demonstration period was the identification of bottlenecks and achievement of stable operation conditions and parameters (superficial gas velocity, slurry concentration, catalyst lifetime). The simplified process flow diagram of this plant is presented in Figure 40.

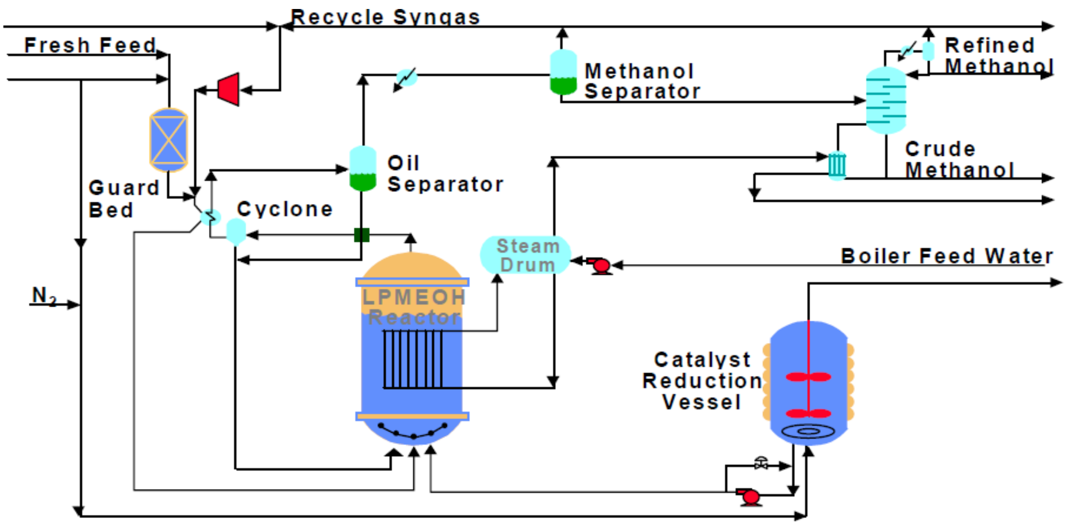


Figure 40 – The simplified process flow diagram of the LPMEOH demonstration plant. [48]

The heart of this system is the slurry bubble column reactor which is used for the methanol synthesis. The contaminants harmful for the catalyst, such as iron and nickel carbonyls, are removed from syngas in activated carbon guard bed. A catalyst reduction vessel equipped with a heating/cooling jacket, utility oil skid and agitator is used for catalyst slurry activation. Entrained slurry droplets and condensed oil droplets are separated in cyclone and oil separator, correspondingly, and recycled back to the LPMEOH reactor. Finally, crude methanol separation and distillation steps take place. The LPMEOH demonstration plant was reported to be effective and capable to be integrated to gasification combined cycle power plant (IGCC). The obstacles to overcome are the costs of coal-derived syngas purification, catalyst activity and scaling up issues. [48]

3.5.7. Low-temperature alcohol promoted methanol synthesis

Liu et al. [49] developed a new method for methanol synthesis from syngas over Cu-based catalyst in alcohol liquid medium to overcome the thermodynamic limitations of the conventional gas-phase synthesis. In this method alcohol is used as a catalytic solvent and acts as a promoter for the methanol synthesis reaction which can be conducted at $T=170^oC$ and $P=30\text{-}50$ bars achieving high per pass conversion of CO to methanol. One big advantage of this process is the ability to use low-grade syngas not affecting negatively the catalyst stability and activity, which is attractive in terms of utilization of CO_2. In addition, efficient removal of reaction heat, due to large heat capacity of the liquid medium, can favor increased methanol yield and reduce production costs. The conventional Cu-based catalysts can be used in this process, showing good activity for CO_2 conversion (close to 26%) and selectivity to methanol (close to 73%). Formate intermediate is known to be the key species found on the surface of Cu-based catalysts during methanol synthesis from syngas. Hydrogenation of the formate intermediate to methanol can be done via direct route where subsequent formation of H_2COO, H_3COO and H_3COH from HCOO occur, or indirect route, where the reaction proceeds via the following two steps:

- Alcohol (ROH) and formate intermediate (HCOO) react to form HCOOR on the catalyst support.

$$\mathrm{HCOO} + \mathrm{ROH} = \mathrm{HCOOR} + \mathrm{OH} \tag{3.11}$$

- Hydrogenolysis of HCOOR to methanol on the catalyst surface.

$$\mathrm{HCOOR} + 4\mathrm{H} = \mathrm{CH_3OH} + \mathrm{ROH} \tag{3.12}$$

Various alcohols were tested as the catalytic solvents (alcohols promote and in the same time not consumed during reaction). For instance, Fan et al. [50] investigated methanol synthesis from CO_2 and H_2 over different heterogeneous catalysts (Cu/ZnO, Cu-Cr-O and Pb-Cu-Cr-O) in ethanol using a moderate pressure of 30 bars and a relatively high temperature of 200°C in a batch reactor. It was found that conventional Cu-based catalysts showed the best selectivity to methanol (73.3%) and conversion of CO_2 (7.5%) compared to the other catalysts. Ethyl formate was found to be the main side product in these experiments and was pointed as the key intermediate to methanol formation. The hydrogenation of ethyl formate can be considered as the rate-determining step in methanol synthesis. Diffuse reflectance infrared Fourier transform spectroscopy was applied for the investigation of the reaction mechanism of the dual catalysis of methanol synthesis (catalyst Cu/ZnO + ethanol). The proposed reaction mechanism for ethanol promoted methanol synthesis is presented in Figure 41. It can be noted, that for other alcohols this mechanism is similar but with the corresponding intermediate formates.

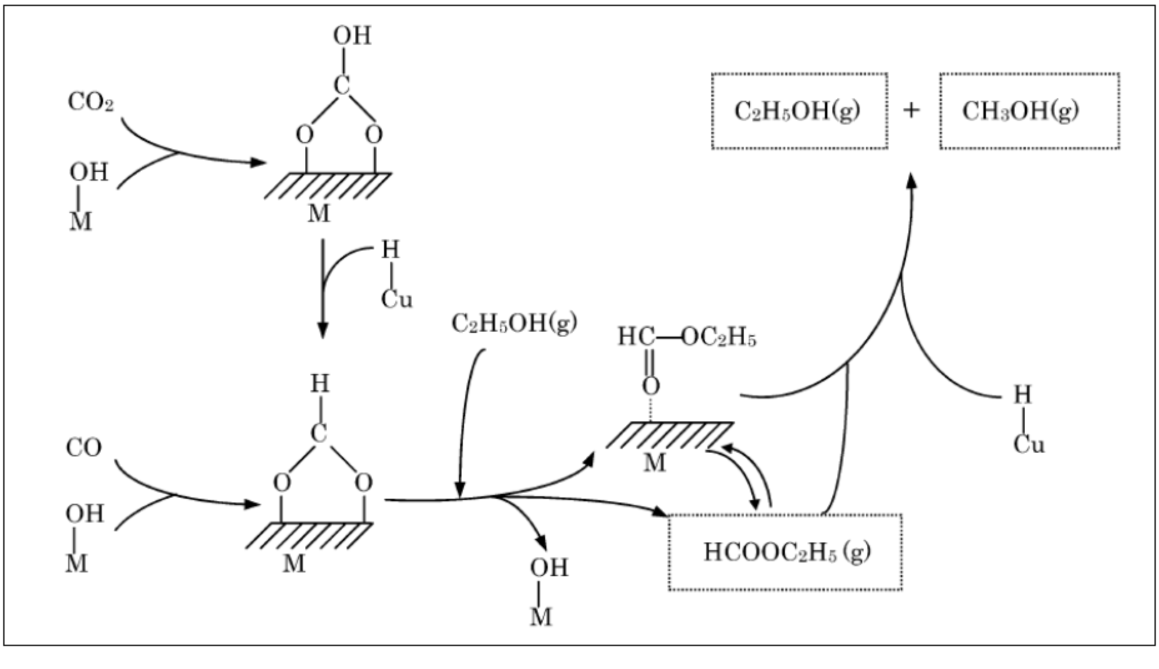


Figure 41 – Reaction mechanism for alcohol promoted methanol synthesis (with ethanol) from syngas over Cu/ZnO catalyst.

Zeng et al. [47] conducted series of experiments in the batch reactor hydrogenating mixture of $CO/CO_2/H_2/Ar$ (32/5/60/3) in 13 different alcohols to form methanol at T=170°C and P=30-50 bars over Cu/ZnO catalyst. The following reaction route was suggested for this process.

$$\mathrm{CO + H_2O = CO_2 + H_2} \tag{3.13}$$

$$\mathrm{CO_2 + \frac{1}{2}H_2 + Cu = HCOOCu} \tag{3.14}$$

$$\mathrm{HCOOCu + ROH = HCOOR + CuOH} \tag{3.15}$$

$$\mathrm{HCOOR + 2H_2 = ROH + CH_3OH} \tag{3.16}$$

$$\mathrm{CuOH + \frac{1}{2}H_2 = H_2O + Cu} \tag{3.17}$$

$$\mathrm{CO + 2H_2 = CH_3OH} \tag{3.18}$$

Remarkably, there was no activity for methanol synthesis when using cyclohexane or ethanol without the solid catalyst. Benzyl alcohol and ethylene glycol had no activity for methanol synthesis. The yields of CH_3OH and HCOOR (liquid products) were the highest at 23.46% and 21.48% respectively when using 2-propanol and 2-butanol as solvents for catalytic methanol synthesis in the liquid medium. 2-pentanol and ethanol showed results approximately two times lower (yields of 11.81% and 11.35%, correspondingly). Such alcohol solvents as 1-propanol, 1-butanol, iso-butanol and 1-pentanol showed yield varying from 7.74% to 9.43%. Worst yields of CH_3OH and HCOOR were obtained for cyclohexanol and t-butanol. Thus, it is possible to conclude that 2-alcohols showed the best performance while hydrogenating a mixture of $CO/CO_2/H_2/Ar$ catalytically to form methanol. In addition to that, it is possible to note that net reactions do not depend on the alcohol type. [47]

3.5.8. Coated catalytic reactors for methanol synthesis

Different process intensification options are implemented to modify the catalytic processes which involve highly endothermic and exothermic reactions, for instance, methanol synthesis. The main consequences of the large temperature gradient occurring in this process are the selectivity and catalyst deactivation issues. Coated catalytic reactors can be used to solve this issue by to the following advantages:

- Compact design due to improved heat transfer coefficient (main reason is the shift from convective to conductive mechanism);
- Enhanced mass transfer due to increased surface area of the catalyst (porous layers of the catalyst coat the walls of the reactor);
- Smaller pressure drops compared to the conventional types of methanol converters;

- Attractive for small scale plants;
- Easy to scale-up by simple numbering-up.

Monolithic and micro-structured reactors are good examples of coated catalytic reactors. Mechanical and thermal stability are the most important parameters for coated catalysts. The main parts (layers) of the coated catalyst are presented in Figure 42. Typical overall layer thickness varies from 15 to 100 μm. Washcoating is the most commonly used technique for creating these layers. However, there are a lot of other techniques for coating including growth of catalyst layers from various liquid solutions on a substrate, growth from vapor phase and electronic film growth. [36]

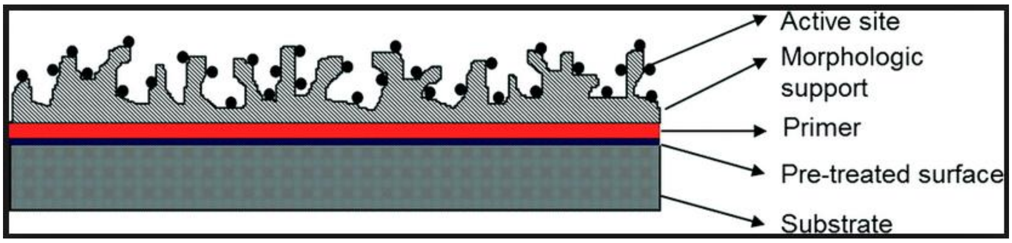


Figure 42 – Main layers of coated catalyst. [36]

Monolithic reactors

A typical monolithic reactor consists of several pieces of cylindrical monoliths with square channels (other designs of channels such as circular, triangular etc. are also possible) coated with the catalyst. A schematic picture of a shell and tube monolithic reactor is presented in Figure 43.

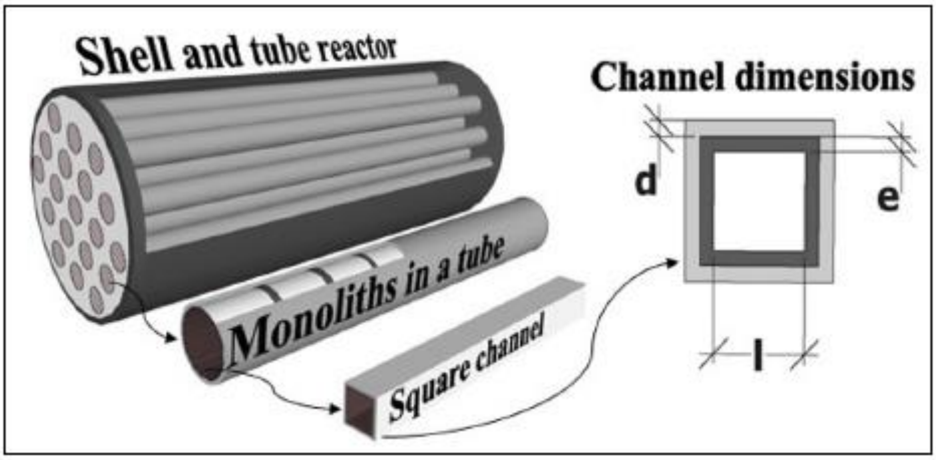


Figure 43 – Monolithic reactor for methanol synthesis. [51]

Arab et al. [51] found some interesting features while comparing the performance of a conventional packed-bed reactor and a coated monolithic reactor for methanol synthesis from CO_2 and H_2 under the same operating conditions. After modeling they found that for small WHSV (weight hourly space velocity) the conventional packed-bed reactor and coated monolithic reactor perform identically. Thus, installation of a more expensive coated monolithic reactor is unnecessary. At high WHSV the use of more complicated and expensive monolithic reactors is advisable and can be considered as the best option due to the negligible pressure drop and better performance in comparison to the packed-bed system. However, despite the benefits that monolithic reactor offers, there are several drawbacks: low radial heat transfer (especially in ceramic reactors), difficulties related with the catalyst coating and replacement and some others. The aforementioned researchers emphasized that additional technical and economical investigations are needed to make conclusions about the viability and applicability of the monolithic reactors for methanol synthesis.

Micro-structured reactors

The advantages of using micro-structured reactors are very similar to those of monolithic reactors. However, there are some significant differences in their designs. For instance, the thickness of the channels of micro-structured reactors varies from 0.001 mm to 1 mm (sub-millimeter range) which is much smaller than for monolithic reactors. In addition to that, the design of the channels in micro-structured reactor can have non-regular shapes giving a high degree of freedom for the moving fluids whereas the channels of the monolithic reactors are typically straight in their direction. Furthermore, micro-structured reactors offer excellent controllability of the reaction conditions due to the small hold-up value. High surface to volume ratio varying from 10 000 to 50 000 m^2/m^3 can be considered as another distinctive feature of the micro-structured reactors. Excellent heat and mass transfer make these reactors attractive for exothermic reactions, such as methanol synthesis, and endothermic reactions, such as steam reforming of methane for the syngas manufacture. High price of the micro-structured reactors can be considered as the biggest disadvantage. A simplified scheme of a typical micro-structured reactor for Fischer-Tropsch synthesis is presented in Figure 44. [36]

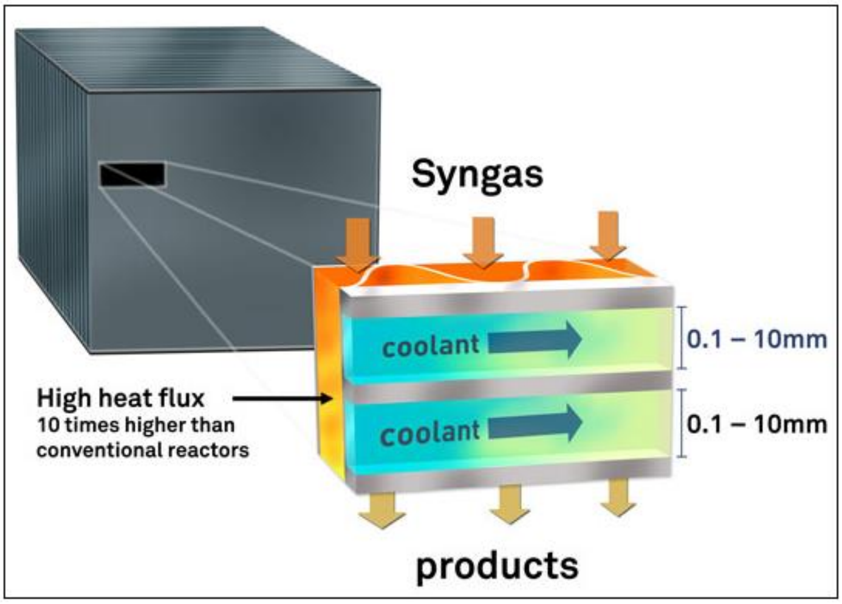


Figure 44 - Micro-structured reactor for Fischer-Tropsch synthesis. [36]

Membrane reactors

Typically, membrane reactor represents the concept of integrated reaction and separation process in one unit. This is particularly good for equilibrium limited reactions, such as methanol synthesis, due to efficient selective removal of by-products from the convertor by membrane. Thus, higher per-pass conversion and increased selectivity can be achieved. Struis et al. [52] firstly applied the membrane reactor for methanol synthesis at 200^oC and 4.3 bar pressure to show the opportunity of its effective utilization. Afterwards, this method has gained a lot of scientific interest. Galucci et al. [53] conducted a series of experiments of methanol synthesis from CO_2 and H_2 comparing the performace of a traditional converter and a zeolite membrane reactor. They found that the zeolite membrane reactor can be utilized effectively for methanol synthesis from CO_2 and H_2 due to enhanced in-situ separation effect of the water-alcohol mixture, which favors increased methanol yield in equilibrium reaction. Chen et al. [54] simulated the reactions of CO_2 hydrogenation to methanol in silicone rubber/ceramic composite membrane reactor and noticed enhanced conversion of CO_2 to methanol (22% more in comparison with the conventional fixed bed reactor). It is interesting to note, that membranes consisting of zeolite show the best adsorption-diffusion separation mechanism in comparison with other selective layer materials used in membrane reactors. This makes zeolite membrane reactors preferable for CO_2 hydrogenation due to selective removal of H_2O and CH_3OH and effective rejection of H_2. Remarkable challenge of the membrane reactors is that H_2, which is the main reactant in methanol synthesis, has small kinetic diameter and can easily pass through the selective layer. The aforementioned features make utilization of zeolite membrane potential in methanol synthesis from CO_2. A scheme of the membrane reactor is presented in Figure 45.

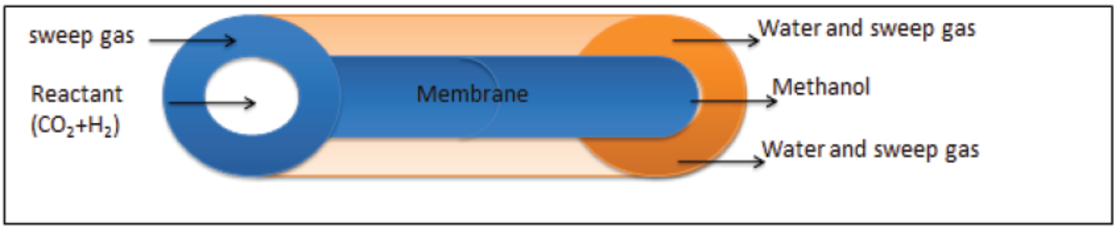


Figure 45 – Scheme of membrane reactor for methanol synthesis. [55]

3.5.9. Reactive distillation

Reactive distillation (catalytic distillation) is a process intensification concept which has become popular during the last decades. Various applications of this technology in chemical and process engineering field appear frequently due to the potential for capital investment and operating costs reduction, productivity and selectivity improvements, and reduced consumption of energy and polluting solvents. This concept represents the idea of synergetic simultaneous use of separation and reaction processes integrated in one operation unit. [56]

There are several examples of successful application of reactive distillation for several reactions:

- Hydrogenation (for instance, synthesis of cyclohexane from benzene and hydrogen);
- Esterification (for instance, synthesis of high purity methyl acetate from methanol and acetic acid);
- Etherification (for instance, synthesis of methyl tert-butyl ether);
- Dehydration (for instance, DME synthesis form methanol)
- Polymerization, hydrodesulphurization, hydrolysis, alkylation, etc.

Remarkably, it is possible in principle to apply the concept of reactive distillation also for methanol synthesis from captured CO_2 and renewable H_2. The single catalytic vessel divided into three sections might be used in terms of intensification of the exothermic reaction of methanol synthesis. The middle catalytic zone can be used for the reactions of methanol synthesis in which the continuous removal of products will be used to overcome the equilibrium limitations. In this way, catalyst poisoning by water can be also avoided. Methanol and water can be collected in the top (stripping) and bottom (rectifying) section of the reactive distillation column, correspondingly. The recycling process of unreacted products can be accomplished by the condenser and reboiler. The principal idea of the reactive distillation concept is presented in Figure 46.

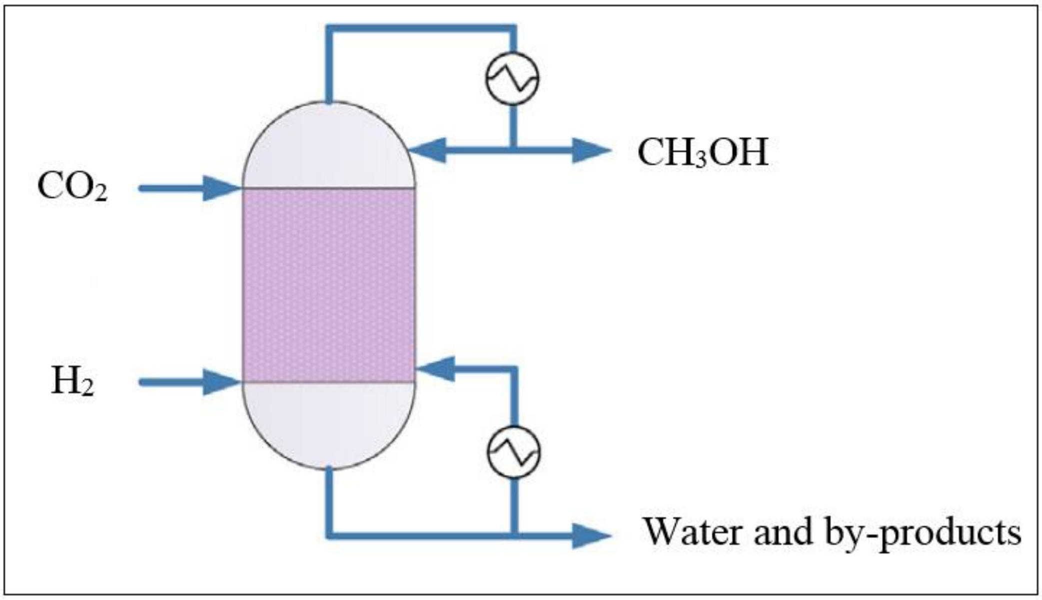


Figure 46 – Reactive distillation concept in methanol synthesis from CO_2 and H_2. [57]

Even though there is scarce information in the literature regarding catalytic distillation applied for methanol synthesis from captured CO_2 and H_2, there are some patents [58] of this technology for the conventional methanol synthesis from syngas including the following points:

- Catalytic distillation reactor is used as a single apparatus to achieve the simultaneous formation of alcohol (methanol) from syngas and the separation of the alcohol (methanol) with water;
- Methanol synthesis process includes the contact of syngas with the catalyst (which can be liquid or solid) in a reaction chamber operated at methanol conversion-promoting conditions to achieve high yield;
- Simultaneous separation of alcohol (methanol) from reaction by-products in the single vessel is used to overcome the limitations of thermodynamic equilibrium of the reaction.

In addition to that, some other technological solutions exist to overcome the drawbacks of energy-consuming conventional distillation process such as thermally coupled distillation columns, dividing wall-columns, heat-integrated or cyclic distillation. Reactive dividing wall-column distillation (R-DWC) can be considered as the most recent technological progress in this field. Kiss et al. [57] reported that this technology can be effectively utilized for the DME synthesis by dehydration of methanol in terms of reduced foot-print of the plant, enhanced performance, energy savings and reduced emissions of carbon dioxide. It is interesting to note, that reactive distillation and conventional process of DME synthesis showed similar performance while doing the simulation studies in Aspen Plus. However, considerations regarding the feasibility of reactive distillation in DME synthesis led to the conclusion that this technology can be considered a more preferable option than the conventional method due to milder operating conditions (in case of building a new plant). As a conclusion, one can emphasize that the reactive distillation concept has potential to be successfully integrated to methanol synthesis from CO_2 and H_2 to increase process efficiency. [57]

EXPERIMENTAL PART

The experimental part of the thesis consists of laboratory scale experiments on the alcohol promoted methanol synthesis process. The description of the synthesis process can be found in Section 3.5.7 of the literature review. The following experimental part provides information about methods, procedure and results of the experiments.

4. Aims and content of the experimental part

The following aims were assigned to the experimental work. The general objective of the thesis was to confirm the feasibility of the methanol synthesis promoted by alcohols. The indirect route via formate intermediate was to be confirmed by finding supporting evidence. For this purpose, different solvents (alcohols) and solvent mixtures (alcohol + non-alcohol solvent) were tested and their effect on the productivity of methanol and on the side reactions were assessed. Furthermore, optimal process conditions were clarified, as well as the best activation method for the commercial Cu-based catalyst utilized in the process. Testing of a dual catalyst – a mixture of $CuO/ZnO/Al_2O_3$ and $Cr_2Cu_2O_5$ was carried out to evaluate its effect on methanol productivity. Finally, the effects of simultaneous water removal by molecular sieve on the productivity of methanol were evaluated.

4.1. Experimental plan

The experimental plan is presented in Table 2. The experiments were performed at a temperature range from 180°C to 220°C. A constant total pressure of 60 bars was set for all experiments. It is reported in literature that 2-alcohols are the best promoters for methanol synthesis. Therefore, 2-butanol was utilized as a solvent in the first 3 experiments. At the beginning, different catalyst activation methods were compared. The first method was performed in a heated tubular contactor while the second method was performed *in-situ* in the autoclave reactor (*vide infra*). Subsequently, 1-butanol (boiling point of 117°C and solubility in water of 0.07 g/L at 20°C) was tested as an alternative to 2-butanol (boiling point of 100°C and solubility in water of 125 g/L at 20°C) at a temperature range from 180°C to 220°C. This was related to the potential advantages of 1-butanol in the separation of water, in comparison to 2-butanol.

Other potentially attractive solvents such as 2-propanol (boiling point of 83°C and miscible in water) and 1-pentanol (boiling point of 137°C and solubility in water of 22 g/L at 20°C) were also tested. A mixture of 1-butanol and hexane (a solvent with increased H_2 solubility) was tested to estimate the effect of H_2 solubility on the methanol synthesis. Simultaneous in-situ removal of water from the reaction mixture was performed by a series of experiments with the molecular sieve UOP type 3Å. In the first step, the molecular sieve was used in beads. Thereafter, it was decided to grind it in the same manner as the catalyst in order to decrease the internal diffusion resistance. One experiment, in which molecular sieve, catalyst and 1-butanol were utilized simultaneously, was carried out with increased reaction time to evaluate the effect of water adsorption on methanol productivity. Mixtures of the commercial Cu-based catalyst and a catalyst modified with Cr were tested in different proportions with addition of 2-butanol to estimate the effect on methanol productivity.

Table 2 – Experimental plan.

Experiment	Solvent	Process conditions		Solid phase			Activation method
		T [°C]	$P_{total}/P_{partial}$ [bar]	$CuO/ZnO/Al_2O_3$ [g]	$Cr_2Cu_2O_5$ [g]	UOP type 3Å [g]	
1	2-butanol	180	60/50	20	-	-	Tube
2	2-butanol	180	60/50	20	-	-	Reactor
3	2-butanol	180	60/50	20	-	20 (beads)	Reactor
4	1-butanol	180	60/54	20	-	-	Reactor
5	1-butanol	200	60/50	20	-	-	Reactor
6	1-butanol	220	60/46	20	-	-	Reactor
7	2-propanol	200	60/34	20	-	-	Reactor
8	1-pentanol	200	60/55	20	-	-	Reactor
9	1-butanol + hexane	180	60	20	-	-	Reactor
10	2-butanol	180	60/50	10	-	40 (ground)	Reactor
11	2-butanol	180	60/50	20	-	30 (ground)	Reactor
12	2-butanol	180	60/50	25	-	25 (ground)	Reactor
13	2-butanol	180	60/50	20	10	-	Reactor
14	2-butanol	180	60/50	10	20	-	Reactor
15	1-butanol (8 hours)	180	60/54	20	-	30 (ground)	Reactor

5. Materials and methods

5.1. Experimental setup

The experimental set-up process flow diagram is depicted in Figure 47. The set-up consists of a steel constructed, mechanically mixed, Parr 4520 autoclave reactor with an inner volume of 450 ml. The maximum pressure rating of the reactor is 138 bar while the maximum temperature rating is 300^{o}C. A rupture-disk set to fail at pressures above 138 bar is installed to provide pressure relief. The reactor is connected to Parr 4848 control unit. SpecView software is used to record temperature and pressure data during reaction. Combination of external electric heating (heating jacket) and a cooling water coil inside the reactor is used for temperature control. Mixing is accomplished by a magnetic-driven stirrer with controlled frequency of rotation. The frequency was set to 600 rpm for all experiments. The reactor is equipped with a pressure-proof sampling vessel, which allows collection of liquid samples during the experiments. The sampling vessel is cooled by water, which allows the condensation of vapor products. Three gas cylinders are connected to the reactor gas inlet line, each followed by a separate closing valve. Check valves are also installed to prevent reverse gas flow into the cylinders. The cylinders contain pure CO_2, mixture of H_2/N_2 (5:95), and a mixture of H_2/CO_2 (3:1). Additionally, nitrogen (N_2) is available from the laboratory supply line.

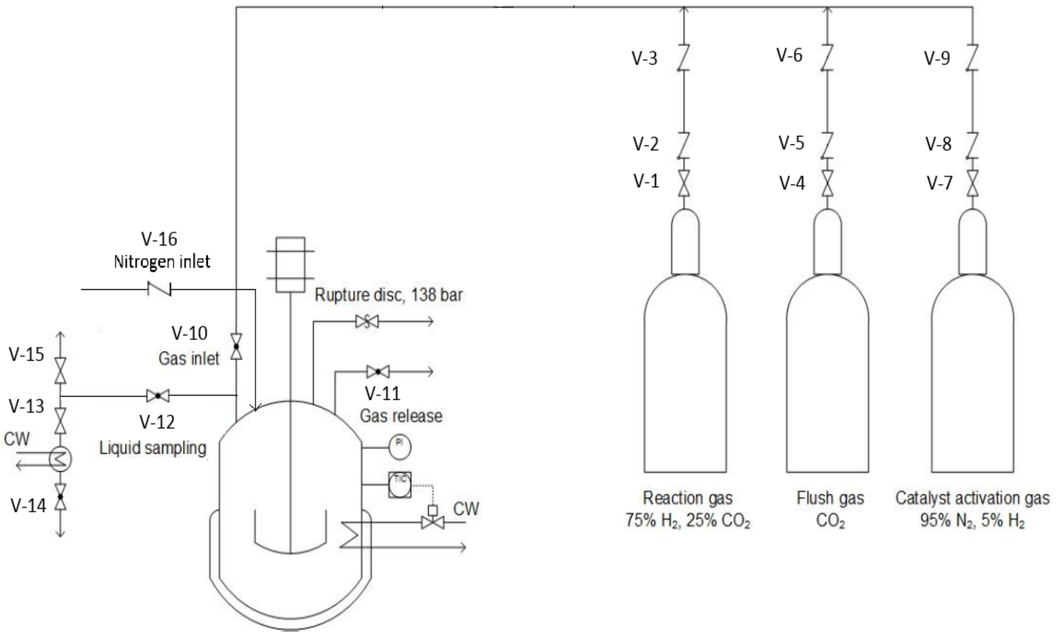


Figure 47 – The experimental set-up.

5.2. Experimental procedure

The following provides detailed information about the experimental procedure, analysis methods and materials involved.

5.2.1. Preparation and activation of the catalysts

A commercially supplied copper-based methanol synthesis catalyst with the reported composition of 63.5% CuO, 24.7% ZnO, 10.1% Al_2O_3 and 1.3% MgO was used for the experiments. The preparation of catalyst consisted of grinding of cylindrical pellets with 5.4 × 3.6 mm size and sieving to a particle size of 150-500 µm (Figure 48). 5 extra grams of grinded and sieved catalysts were taken before each experiment for particle size distribution analysis (*vide infra*).

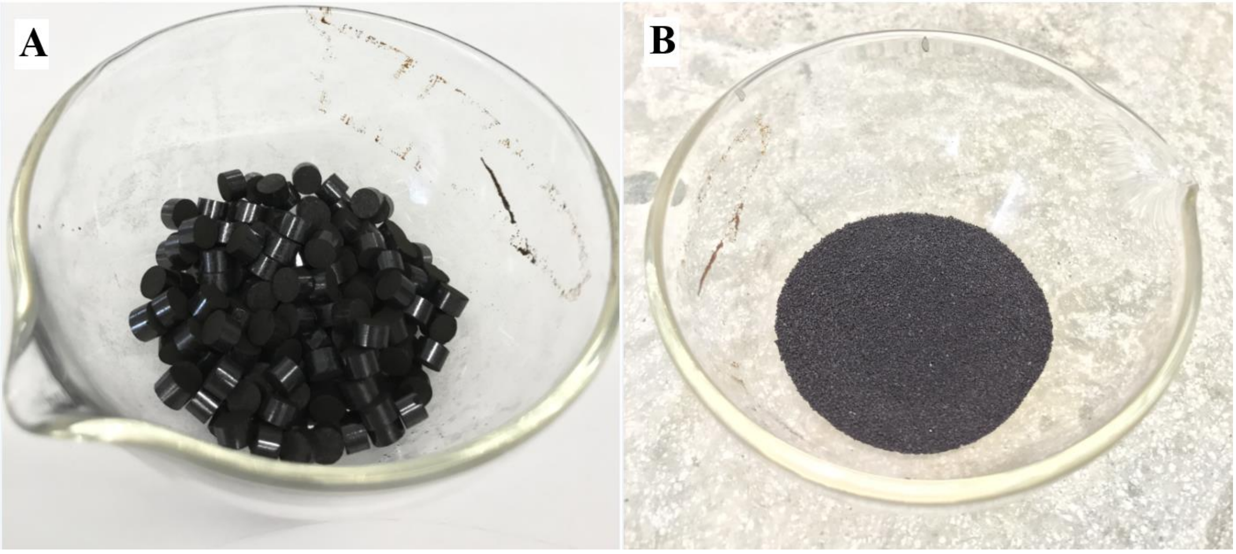


Figure 48 – (A) - pellets of Cu-based catalyst before preparation; (B) – Ground and sieved Cu-based catalysts before activation.

Subsequently, a required quantity of catalyst was placed inside the reactor where the activation was performed *in-situ*. The activation of the catalyst is based on the reduction of copper oxide (CuO) by hydrogen (H_2). The aim is to reduce the passivated metal catalyst, forming the active catalyst sites for the reaction. For that purpose, the activation gas, mixture of H_2/N_2 (5:95), was used at the pressure of 5 bar and temperature of 200°C for 2 hours. Each activation started with purging of the reactor with nitrogen to replace oxygen from the reactor volume. At this point, the mixing speed was set to 600 rpm. After purging, the reactor was pressurized with 5 bar of the activation gas and heated to the targeted temperature of 200°C. When the targeted temperature was reached, the gas inside the reactor was replaced with fresh activation gas.

Additionally, 3 more replacements of the activation gas were performed periodically after 30 minutes intervals. After 2 hours of activation time, the activation gas was removed from the reactor. The reactor was purged with nitrogen and an excess pressure of 0.5 bar was left for overnight to prevent contact with oxygen (to avoid passivation). The same activation procedure was used for the experiments with the catalyst mixture (Cu-based + $Cr_2Cu_2O_5$). However, the copper-chromite catalyst did not require any additional grinding and sieving as it was commercially provided in the powdered form. It is interesting to note that reduction of the Cu-based catalyst under flow of 5% H_2 in a heated tubular contactor was tested as an alternative activation method. The heated tubular contactor consisted of a tube filled with the catalyst and an oven. The activation gas - mixture of H_2/N_2 (5:95) - flowed during two hours through the tube while the oven was used to heat the catalyst to 200°C. The flow of the gas was controlled by a flow meter. Subsequently, all valves were closed and the catalyst was left inside the tube for overnight. The heated tubular contactor is presented in Figure 49.

Figure 49 - Heated tubular contactor used for the catalyst activation.

5.2.2. Preparation and activation of the molecular sieve

A molecular sieve (UOP type, 3Å pore diameter) was used for the experiments with the *in-situ* removal of water from the reaction media. Beads with a diameter of 2 mm were ground and sieved to a particle size of 150-500 µm (Figure 50).

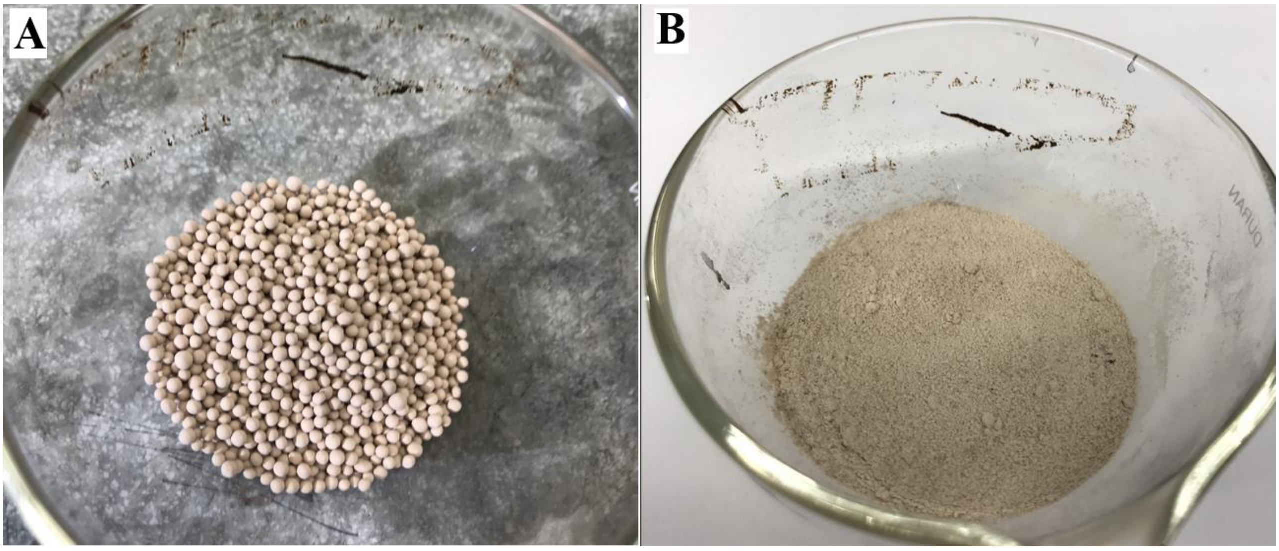


Figure 50 – (A) Molecular sieve beads before grinding and sieving; (B) – Molecular sieve particles 150-500 µm.

After sieving, a required amount of molecular sieve was dried during overnight in the oven at T=250°C to remove water from the adsorbent. On the day of the experiment, the sieve was removed from the oven and cooled for 1 hour in a desiccator. After that, the dried and cooled molecular sieve was ready for use.

5.2.3. Running of experiments and sampling

Before the experiment, sampling device was at first purged with nitrogen. After purging of the sampling device, the reactor was removed and 200 ml of alcohol solvent (or mixture with hexane) was poured quickly (to minimize contact with oxygen) on the top of the activated catalyst. The molecular sieve was also added at this point of the experimental procedure. After this, the reactor was installed and again carefully purged with nitrogen to remove oxygen. At this point, the mixing speed was set to 600 rpm. After partial releasing of nitrogen from the reactor (0.5 bar left), the reactor was heated to the targeted temperature. The temperature and pressure rise was monitored. When the reaction temperature was reached, the initial liquid sample was collected (Figure 50).

Figure 50 – Collected sample.

For that purpose, the mixer and heater were switched off. The catalyst and molecular sieve particles were allowed to settle for 1 minute. This was followed by the addition of small amount of reaction gas - mixture of H_2/CO_2 (3:1) - through the gas dip inlet tube - to clean the sampling tube. Subsequently, the sampling device was filled with the liquid from the reactor by opening the corresponding valve (V-12). The liquid sample was allowed to cool for 30 seconds to condense the vapors present in the sample. Subsequently, the liquid sample was collected from the sampling device by opening the sample collection valve (V-14).

After the initial sample was collected, the reaction was started by feeding the reaction gas into the reactor at a constant pressure of 60 bar (the reactor inlet valve V-10 was left open for continuous feed of reaction gas) and turning on the heater. As the reactor contents were cooled by the cool reaction gas, a period of few minutes was allowed for the temperature to increase. At this point, the reaction time (typically 6 hours) was considered to start. Further liquid samples were collected at intervals of 2 hours according to the procedure described above (Figure 50). All the collected samples were stored below $0^{o}C$ until the day of the analysis (*vide infra*). After the reaction time had finished, the pressure of the reaction gas was released from the reactor and the reactor was cooled. The pipelines and the reactor were purged with nitrogen and removed. Filtration was used to collect the used catalyst and/or the molecular sieve for particle size distribution analysis (*vide infra*).

5.2.4. Analysis of liquid samples

Agilent Technologies 6890N gas chromatograph with a thermal conductivity detector (TCC) and capillary columns was used for the analysis of the liquid samples. Zebron ZB-WAXplus (polar) and HP-1MS (non-polar) columns were used for the analysis of 2-butanol (2-propanol, 1-pentanol) and 1-butanol liquid samples, respectively. An isothermal method with a column temperature of 70 °C and detector temperature of 250°C was employed for analysis of the 2-butanol, 2-propanol and 1-pentanol samples. The hold on time was set to 5 min. The column temperature of 30°C and the same detector temperature of 250°C as before were used for the analysis of 1-butanol samples. The hold on time was set to 10 min. The sample injection volume was 0.2 μl and helium (1.1 ml/min) was used as the carrier gas for both columns.

At the beginning of the analysis procedure, the retention time of the expected compounds (alcohol solvent, corresponding formate, methanol and water) was determined for both methods by preparation and analysis of mixed solutions containing equal parts of the expected compounds. The obtained retention times were used for the identification of the compounds in the actual samples. Subsequently, mixed standard solutions in the relevant range for each compound (high concentration for the alcohol solvents and small for the expected reaction products) were prepared to create calibration curves for concentration calculations. The calculated concentration results obtained with the calibration equations were compared with the calculations based on the weight of the compounds in the mixed standard solutions. The deviation was assumed insignificant. Hence, the error caused by the calibration equations can be justified due to the various potential sources of error in the experimental and analysis procedure.

Each analysis started with the removal of contaminants harmful for the analysis equipment (particles of catalyst and molecular sieve) by filtration of the samples. PHENEX PTFE 0.45μm filters and syringes were used to inject the alcohol inside the 1.5 ml chromatography vials (Figure 51). In the end, the chromatogram of each sample was analyzed and the concentrations were calculated based on the calibration equations (Appendix I).

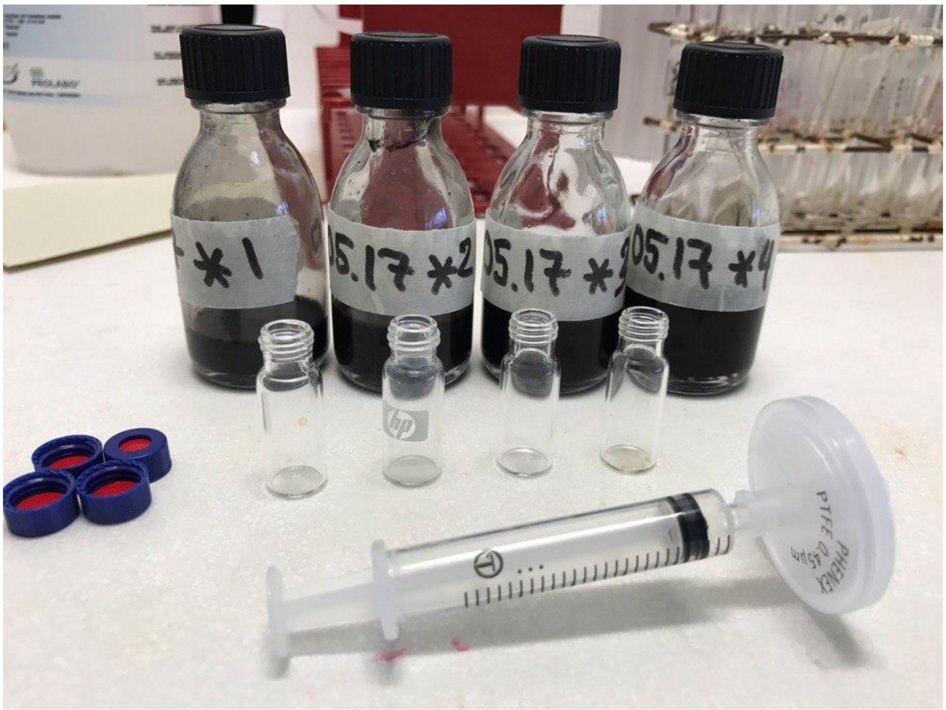


Figure 51 – Preparation of samples for gas chromatography analysis.

5.2.5. Particle size distribution analysis

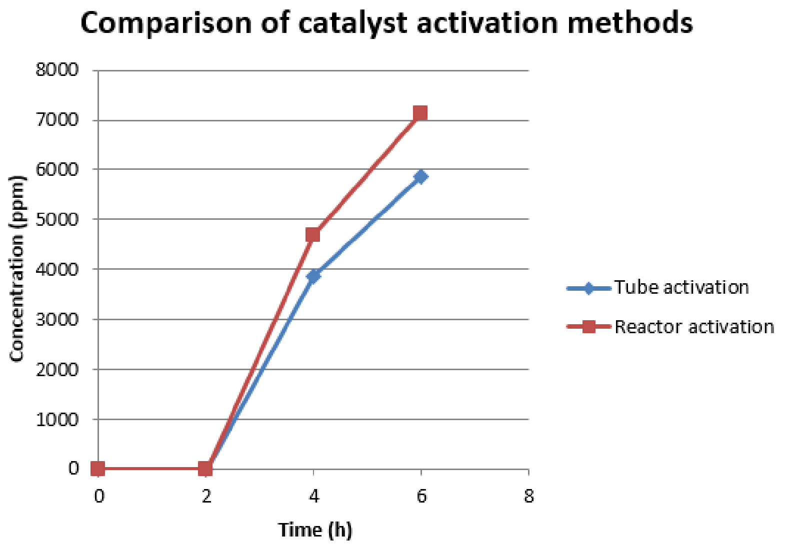
Mastersizer 3000 which uses laser diffraction measurement method was used for particle size distribution analysis. The laser diffraction measurement technique is based on a laser beam (optics and solid state blue light source with power of 10mW) passing through a dispersed particulate sample. Subsequently, angular variation in the intensity of the scattered light is measured (small particles scatter light at large angles and *vice versa* for large particles). This data is analyzed and used for the calculation of the particle size (particle size range from 10nm up to 3.5mm is available). The particle size is reported as a volume equivalent sphere diameter. Sample dispersion was controlled by Hydro EV (semi-automated wet dispersion unit) to ensure particles delivery to the measurement area of the optical bench at suitable concentrations.

At the beginning of the particle size distribution analysis, the samples of the catalyst and/or molecular sieve collected before and after experiments were placed in the beaker of the Hydro EV filled with a dispersant (pure water). The sample was dispersed with the stirrer and distributed to the measurement area by a dip-in centrifugal pump. Five measurements were done for each sample. Finally, the data was collected with the help of Mastersizer – V3.62 software.

6. Results and discussion

6.1. Comparison of catalyst activation methods

As it was discussed previously in Section 5.2.1, two different catalyst activation methods were tested: activation in the heated tubular contactor (tube activation) and *in-situ* activation of the catalyst in the autoclave reactor. After activation of the same amounts of catalyst (20g), alcohol-promoted methanol synthesis was performed at T=180°C and P=60 bar for both cases. Figure 52 presents the methanol concentration results during reaction time (6 hours). From the graph, it can be clearly seen, that the *in-situ* activation of the catalyst in the reactor was more efficient regarding methanol production as the final concentration of methanol (7141 ppm) was approximately by 1100 ppm higher than when tube activation was used (5864 ppm). Consequently, the *in-situ* catalyst activation method was selected for all the rest of the experiments.

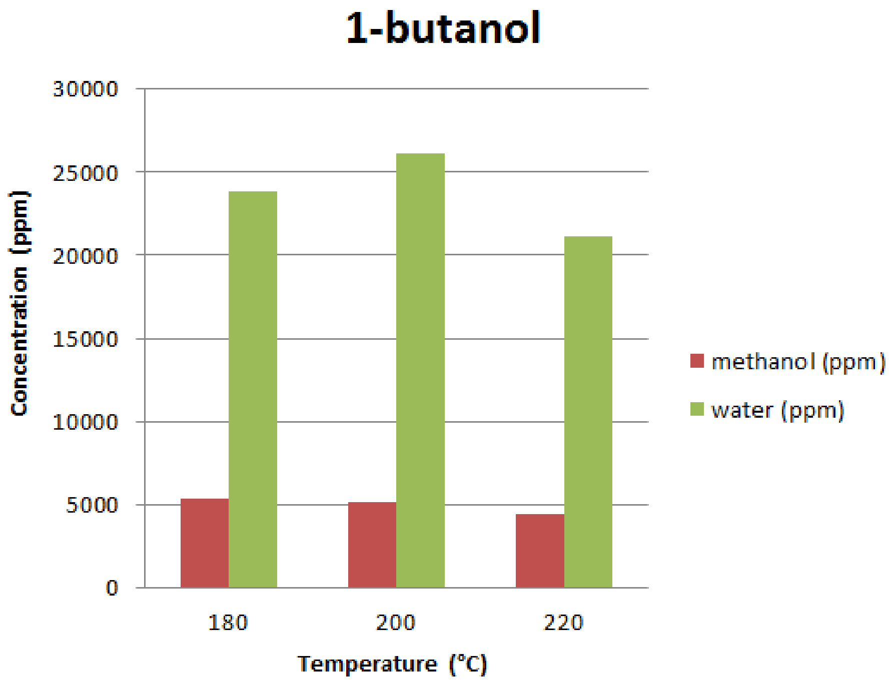


Comparison of activation methods, T=200°C, P=60 bar		
Time (h)	Tube activation	Reactor activation
	methanol (ppm)	
0	0	0
2	0	0
4	3864	4683
6	5864	7141

Figure 52 – Comparison of catalyst activation methods.

6.2. Effect of temperature on methanol synthesis and formation of by-products

A temperature range from 180ºC to 220ºC and a constant total pressure of 60 bar were tested for the experiments with 1-butanol. The same amount of $CuO/ZnO/Al_2O_3$ of 20 g was used for all experiments. The main purpose of these experiments was to clarify optimal process conditions for the alcohol promoted methanol synthesis and to assess the influence of temperature on the methanol productivity, formation of water and other by-products. Figures 53 depicts the final concentrations of methanol and water in the end of reaction time for the experiments with 1-butanol.



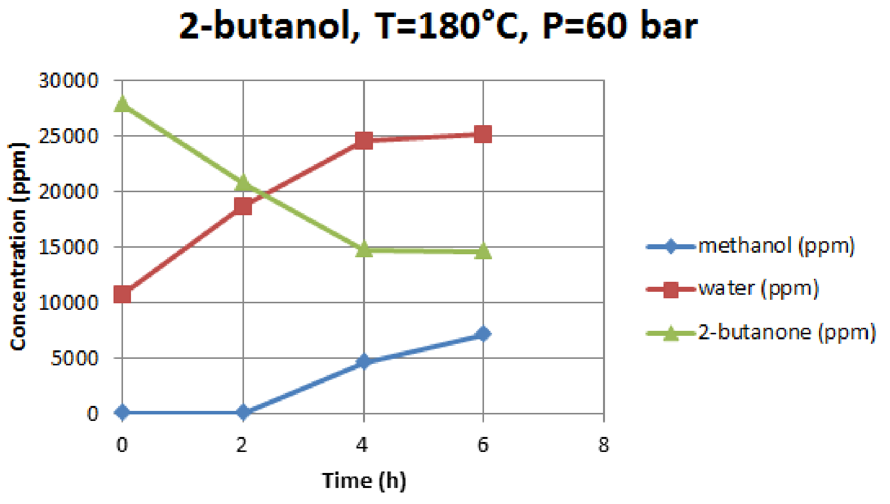
1-butanol		
Temperature (°C)	methanol (ppm)	water (ppm)
180	5320	23814
200	5120	26155
220	4420	21083

Figure 53 – Methanol and water concentrations (ppm) after 6 hours of reaction time in 1-butanol, temperature range from 180ºC to 220ºC and total pressure of 60 bar.

It can be clearly seen from the graphs that for alcohol solvent lower temperature of the process favor methanol synthesis. As an overall trend, it can be clearly seen that the final concentrations of methanol were the highest for experiment with 1-butanol at temperature of 180^{o}C. Slightly smaller concentrations of methanol were observed in experiment at temperature of 200^{o}C while the lowest values were found in the sample obtained from the experiments with 220^{o}C temperature. It should be noted that reaction kinetics depends on the partial pressure of the feed gas. At the higher temperatures, the vapor pressure of the alcohol increased, and thus the partial pressure of feed gas decreased. This can explain the decreasing methanol formation rate with the increasing reaction temperature. The information about the partial pressure of the feed gas can be found in Table 2, while calculation example can be seen in Appendix II.

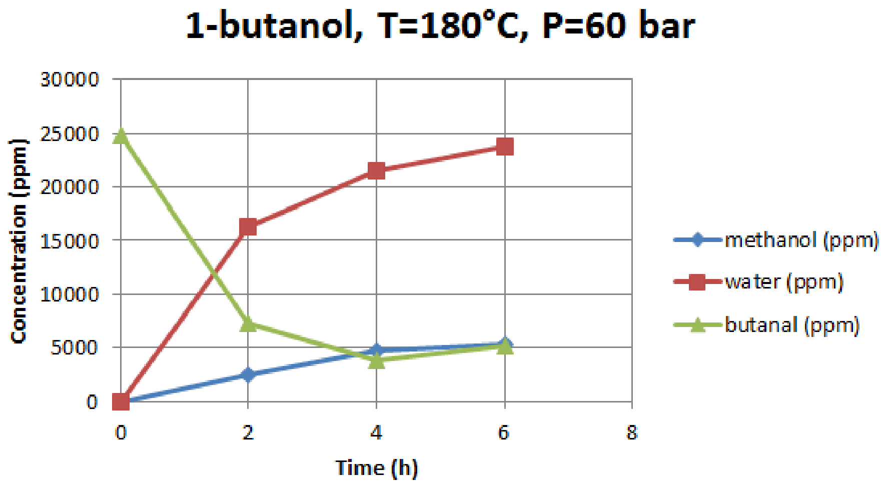
The rate of water formation is much higher in comparison to methanol synthesis rate. It is clear from the bar charts, that the range of water formation was between 21 000 ppm and 24 000 ppm, while the methanol range was between 4400 ppm and 5400 ppm. The highest water concentrations were observed for experiment performed at 200^{o}C.

Figures 55 - 58 present data about the concentrations (ppm) of methanol, water, butanal and 2-butanone in experiments with 2-butanol and 1-butanol at a temperature range from 180^{o}C to 220^{o}C during the reaction time of 6 hours. The same amount of $CuO/ZnO/Al_2O_3$ of 20 g was used for all experiments. It is possible to make more detailed investigation of the influence of temperature on the methanol synthesis and formation of by-products based on these graphs (*vide infra*).



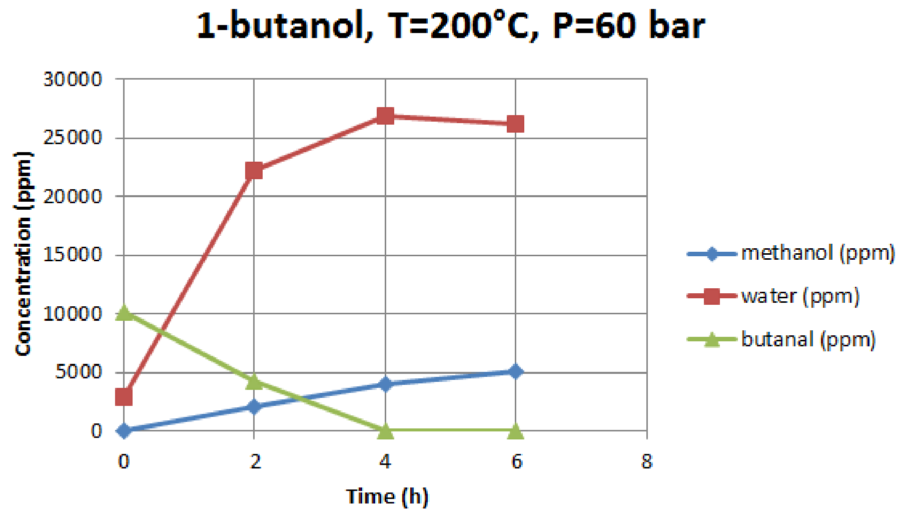
2-butanol, T=180°C, P=60 bar				
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)	2-butanol (ppm)
0	0	10847	27798	942336
2	0	18652	20721	919102
4	4683	24527	14762	915414
6	7141	25229	14576	918734

Figure 55 – Concentrations of methanol and by-products during the reaction time for experiment in 2-butanol at T=180°C and P=60 bar.



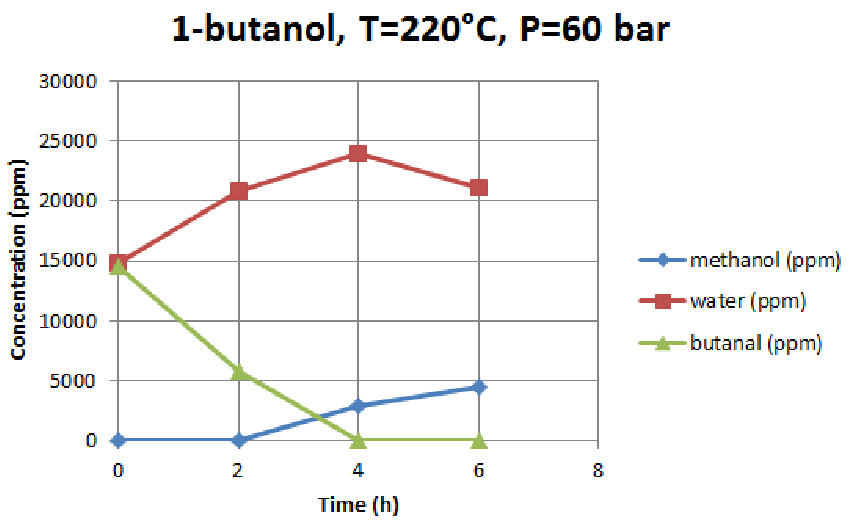
1-butanol, T=180°C, P=60 bar				
Time (h)	methanol (ppm)	water (ppm)	butanal (ppm)	1-butanol
0	0	0	24781	957045
2	2520	16207	7306	953413
4	4820	21473	3924	950688
6	5320	23813	5239	942515

Figure 56 – Concentrations of methanol and by-products during the reaction time for experiment in 1-butanol at T=180°C and P=60 bar.



1-butanol, T=200°C, P=60 bar				
Time (h)	methanol (ppm)	water (ppm)	butanal (ppm)	1-butanol
0	0	2942	10125	947057
2	2020	22253	4300	952868
4	4020	26935	0	943787
6	5120	26155	0	932617

Figure 57 – Concentrations of methanol and by-products during the reaction time for experiment in 1-butanol at T=200°C and P=60 bar.



1-butanol, T=220°C, P=60 bar				
Time (h)	methanol (ppm)	water (ppm)	butanal (ppm)	1-butanol
0	0	14841	14540	909279
2	0	20888	5803	898744
4	2920	24009	0	898472
6	4420	21083	0	891298

Figure 58 – Concentrations of methanol and by-products during the reaction time for experiment in 1-butanol at T=220°C and P=60 bar.

First of all, it is possible to note the formation of butanal and 2-butanone respectively for the experiments with 1-butanol and 2-butanol. Butanal and 2-butanone are the products of catalytic dehydrogenation of the corresponding alcohols based on the Equation 6.1.

$$C_4H_8OH \rightleftarrows C_4H_8O + H_2 \tag{6.1}$$

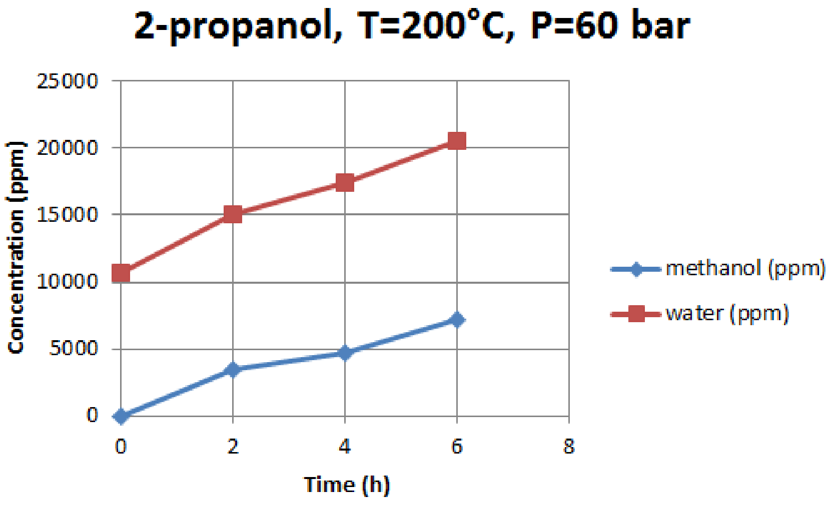
The hydrogen formed in reaction (6.1) was likely the cause of the observed pressure increase in the reactor prior to feeding the reaction gas. The concentrations of the aforementioned by-products were the highest in the initial samples (after heating of the alcohol to the targeted temperature) and varied from 10 000 ppm to 28 000 ppm. After addition of the feed gas, the concentrations of butanal and 2-butanone decreased significantly during the reaction. This might be occurred due to the increased hydrogen pressure leading to the dehydrogenation reactions proceeding to the reverse direction (formation of the corresponding alcohol from hydrogen and 2-butanone / butanal). It can be clearly seen from the graphs, that the concentration of 2-butanone and butanal appeared to approach an equilibrium during the last two hours of the experiments (between third and fourth samples). Additionally, it is possible to note, that the initial concentrations of butanal were significantly lower for experiments with 1-butanol in temperature range of 200 - 220°C. Furthermore, it seems that butanal was not detected at all during the last two hours in both experiments (Figure 59 and 60). This could be connected with analysis inaccuracy, but it is apparent that butanal was largely removed from the reaction mixture at increased reaction times.

Regarding methanol synthesis, it is possible to observe an almost linear increase of the methanol concentration during the experiments. In the experiments with 1-butanol performed at temperatures of 180°C and 200°C, a decrease in the rate of methanol formation was noted in the last 2 hours of the reaction time. This might be connected to the methanol synthesis reaction approaching equilibrium. However, no stagnation in the methanol formation was observed. Consequently, it is possible to conclude that methanol synthesis equilibrium was not reached during the reaction time.

Regarding the formation of water, it is possible to note, that water is formed as a by-product of the methanol synthesis reaction from CO_2 and H_2 (Eq. 2.2). Furthermore, the reverse water-gas shift reaction (Eq. 2.3), which is catalyzed by the methanol synthesis catalyst, has a significant contribution to the overall water formation. Generally, the concentration of water showed an increasing trend with reaction time. However, for some experiments formation of water slowed down after 4 hours of reaction time. In experiments with 1-butanol at T=200ºC and T=220ºC, water concentration even decreased at this stage of reaction. This could be explained by the reverse water-gas shift reaction reaching equilibrium and changing direction, producing carbon dioxide and hydrogen from carbon monoxide and water.

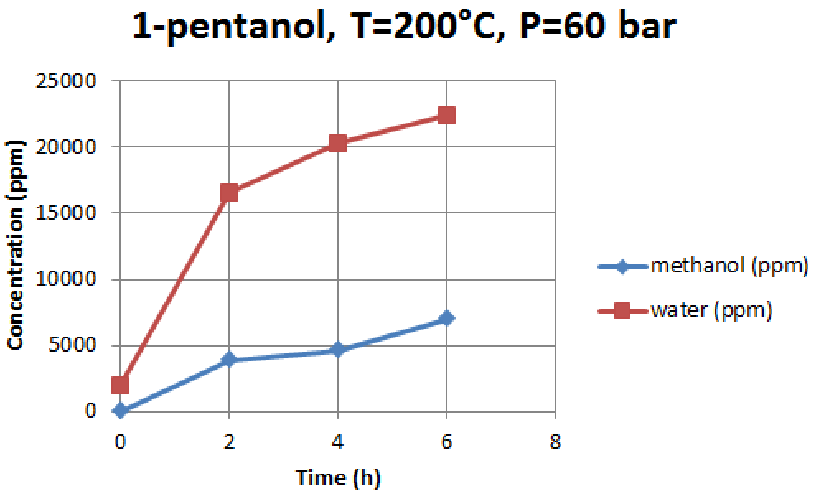
2-propanol and 1-pentanol were also tested as alternative alcohol solvents at T=200ºC and constant pressure of the feed gas at 60 bars. Figures 59 and 60 depict the concentration data from these experiments. It can be clearly seen, that concentration of methanol and water were increasing continuously during the reaction time (equilibrium was not reached). Similarly to previous experiments, formation of water was many times more intensive than formation of methanol which was detected at concentrations of 7223 ppm and 6945 ppm at the end of the reaction time, respectively, for experiments in 2-propanol and 1-pentanol. When comparing the obtained results with the experiments in 1-butanol and 2-butanol, it is possible to conclude that 2-propanol showed the best performance regarding methanol synthesis.

Mixture of 1-butanol and hexane (1/1) was tested at T=180ºC and P=60 bar. These conditions were selected as the optimal and were used for all the following experiments. The concentration data of methanol and water is presented in Figure 61. The mixture of alcohol and non-alcohol solvents showed bad performance regarding methanol synthesis (the final concentration of methanol was the lowest in comparison to other experiments), even though water formation was less intensive.



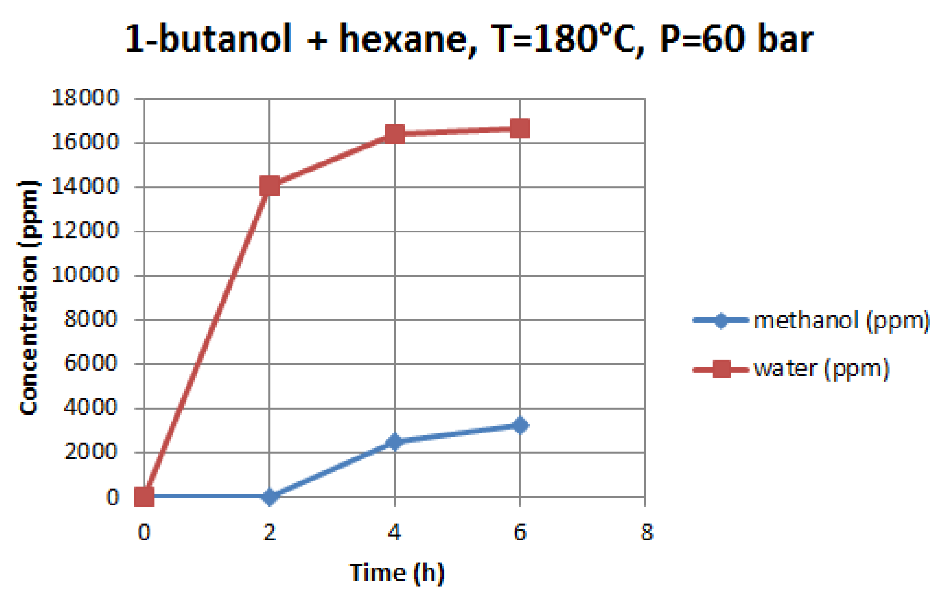
2-propanol, T=200°C, P=60 bar		
Time (h)	methanol (ppm)	water (ppm)
0	0	10664
2	3438	15107
4	4699	17452
6	7223	20537

Figure 59 – Concentrations of methanol and water during the reaction time for experiment in 2-propanol at T=200°C and P=60 bar.



1-pentanol, T=200°C, P=60 bar		
Time (h)	methanol (ppm)	water (ppm)
0	0	1967
2	3779	16597
4	4617	20303
6	6945	22448

Figure 60 – Concentrations of methanol and water during the reaction time for experiment in 1-pentanol at T=200°C and P=60 bar.

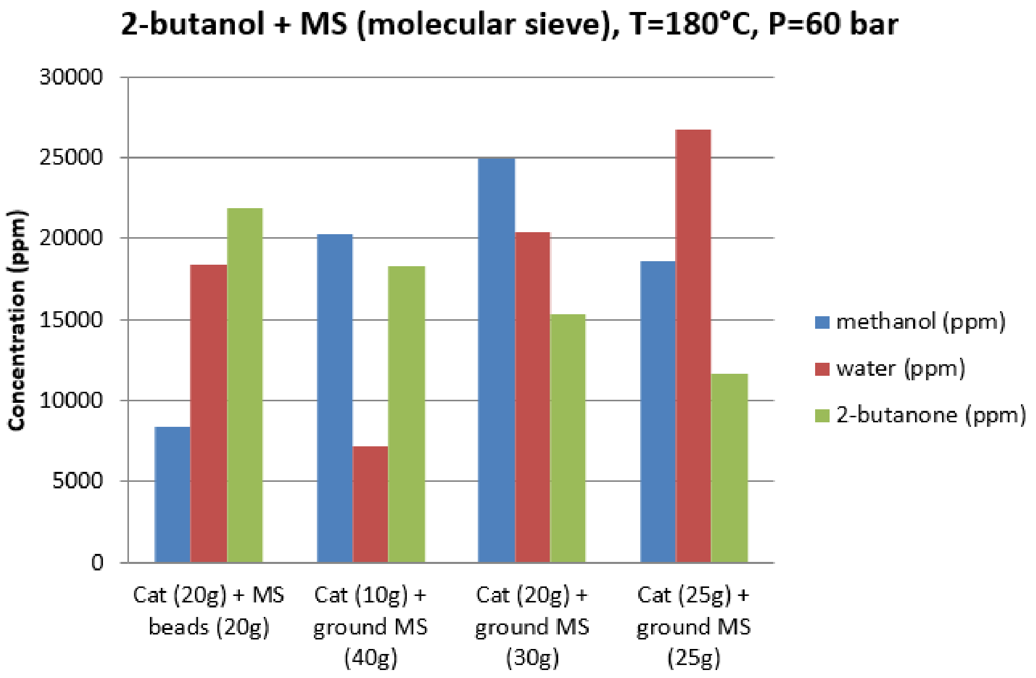


1-butanol + hexane, T=180°C, P=60 bar		
Time (h)	methanol (ppm)	water (ppm)
0	0	0
2	0	14061
4	2520	16402
6	3220	16597

Figure 61 - Concentrations of methanol and water during the reaction time for experiment in 1-butanol and hexane at T=180°C and P=60 bar.

6.3. Effect of in-situ water removal on methanol synthesis

Simultaneous water removal from the reaction mixture was accomplished in a series of experiments by adding different amounts of molecular sieve. The molecular sieve used in the experiments had a pore size of $3 \cdot 10^{-10}$ m, allowing selective adsorption of water while leaving other components in the reaction mixture. Five experiments were conducted with a mixture of molecular sieve and catalyst at different proportions to assess the effect of *in-situ* removal of water from the reaction mixture on methanol synthesis and formation of by-products. 2-butanol and 1-butanol (for which the reaction time was increased to 8 hours) were again used as the alcohol solvents at T=180°C and P=60 bar (optimal conditions). The concentration data of methanol and by-products at the end of the reaction time for experiments in 2-butanol is presented in Figure 62.

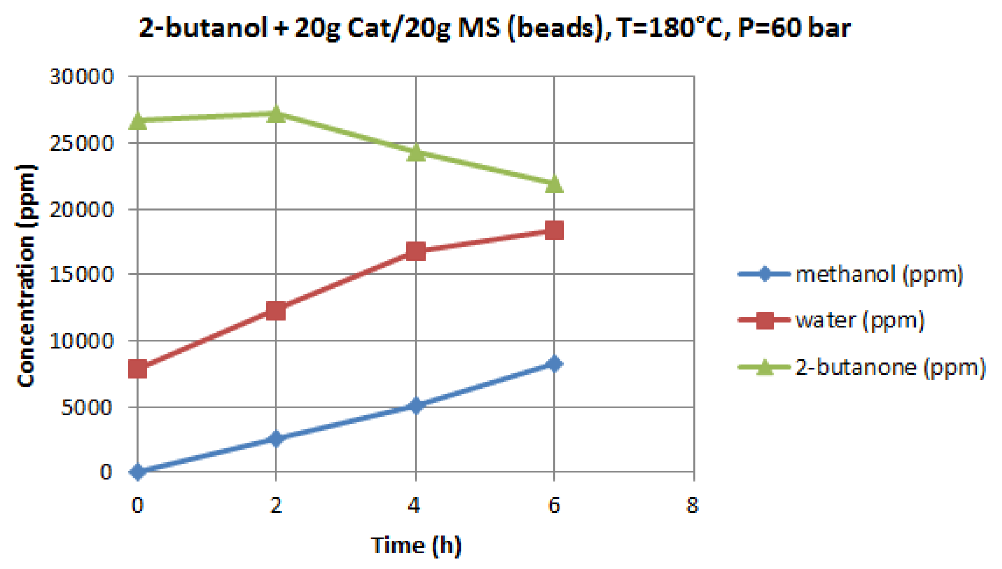


2-butanol + MS (molecular sieve), T=180°C, P=60 bar			
Experiment	methanol (ppm)	water (ppm)	2-butanone (ppm)
Cat (20g) + MS beads (20g)	8324	18389	21932
Cat (10g) + ground MS (40g)	20250	7164	18301
Cat (20g) + ground MS (30g)	24983	20406	15321
Cat (25g) + ground MS (25g)	18611	26720	11690

Figure 62 - Methanol and by-products concentrations (ppm) after 6 hours of the reaction time for experiments with the addition of molecular sieve (MS) in 2-butanol performed at T=180°C and P=60 bar.

As a general observation from Figure 62, it can be noted that addition of molecular sieve did have a positive effect regarding methanol production. The first experiment with the molecular sieve was performed with equal proportions of Cu-based catalyst and molecular sieve in the commercially supplied form (beads with a diameter of 2 mm). When comparing the final concentration of methanol in the experiment with the molecular sieve added in the form of beads (20g) to a reference experiment in 2-butanol performed at the same conditions (Figure 55), it is possible to observe an increase of methanol concentration by approximately 14%. Furthermore, concentration of water decreased by almost 27 % and concentration of 2-butanone increased by approximately 34 %. Subsequently, molecular sieve was decided to be ground and sieved to a particle size of 150-500 µm. In this way, the internal diffusion resistance of the molecular sieve was decreased and the efficiency could be increased.

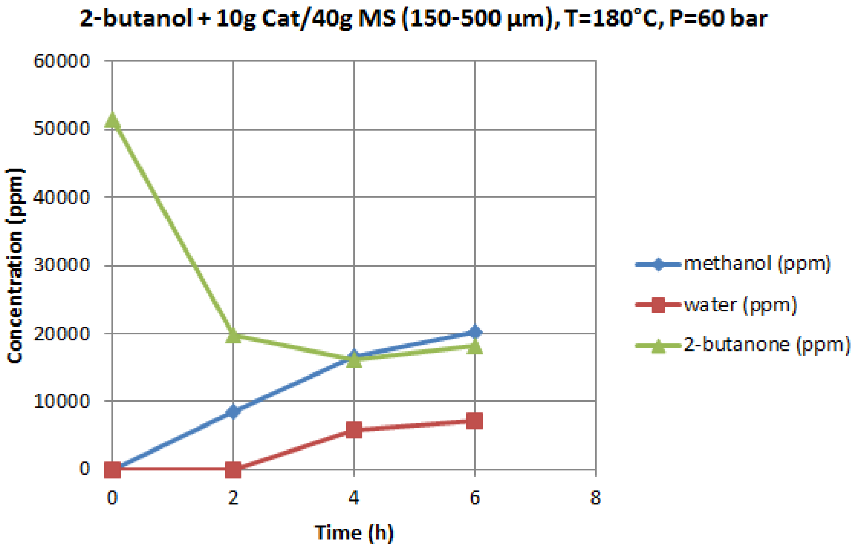
The effect of this was assessed in a series of experiments with 50 g solid phase (mixtures of catalyst and molecular sieve at varied ratios). The addition of ground molecular sieve had a clear effect on methanol production rate, as it can be seen from Figure 62. The final methanol concentrations were in the range of 18 000 ppm and 25 000 ppm, which is significantly higher in comparison to the experiment where molecular sieve was used without preliminary treatment. More detailed concentration data from the experiments with the molecular sieve is presented in Figures 63 – 66.



2-butanol + 20g Cat/20g MS (beads), T=180°C, P=60 bar

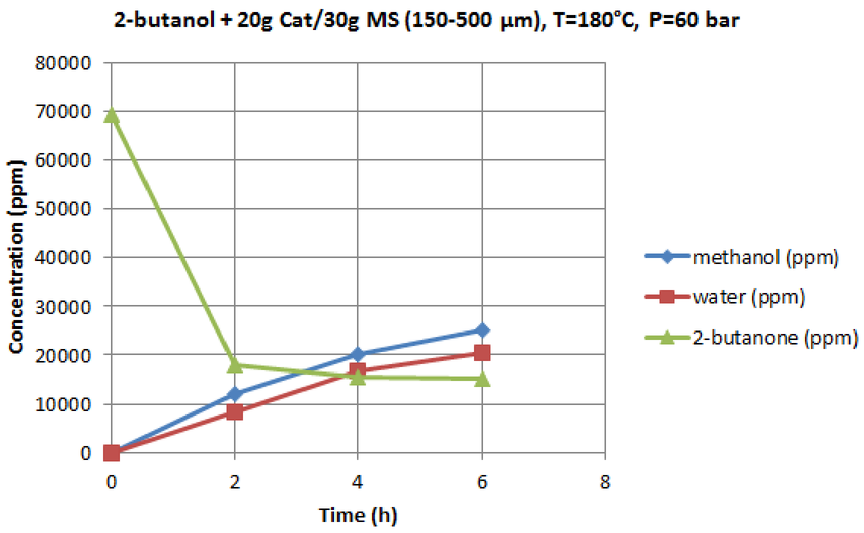
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	7954	26681
2	2589	12338	27332
4	5138	16723	24353
6	8324	18389	21932

Figure 63 – Concentrations of methanol and by-products during reaction time for experiment with 20g Cat / 20g MS (beads) in 2-butanol at T=180°C and P=60 bar.



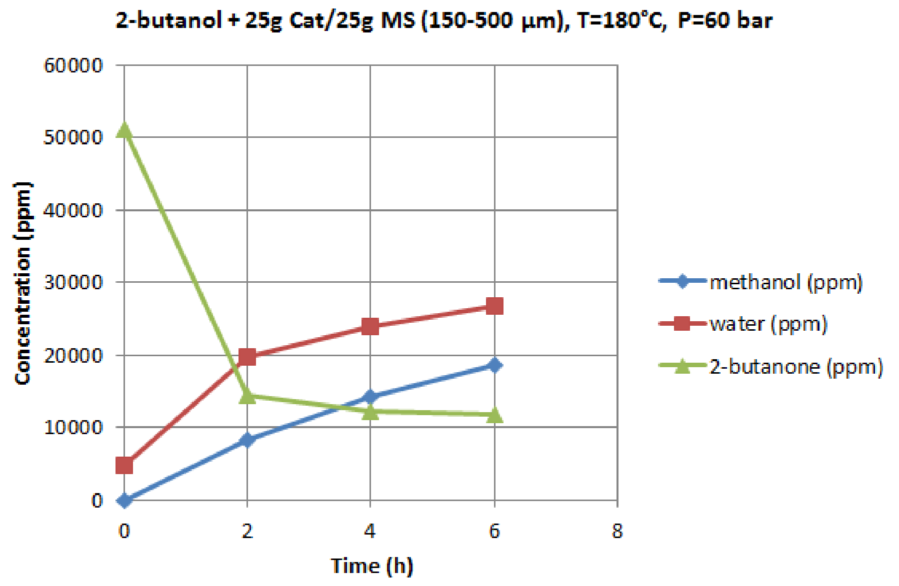
2-butanol + 10g Cat/40g MS (150-500 µm), T=180°C, P=60 bar			
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	0	51634
2	8597	0	19697
4	16699	5761	16066
6	20250	7164	18301

Figure 64 – Concentrations of methanol and by-products during reaction time for experiment with 10g Cat / 40g MS (grinded) in 2-butanol at T=180°C and P=60 bar.



2-butanol + 20g Cat/30g MS (150-500 µm), T=180°C, P=60 bar			
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	0	69326
2	12057	8392	18114
4	20250	16635	15507
6	24983	20406	15321

Figure 65 – Concentrations of methanol and by-products during reaction time for experiment with 20g Cat / 30g MS (grinded) in 2-butanol at T=180°C and P=60 bar.



2-butanol + 25g Cat/25g MS (150-500 µm), T=180°C, P=60 bar			
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	4709	51169
2	8324	19617	14483
4	14241	23826	12155
6	18611	26720	11690

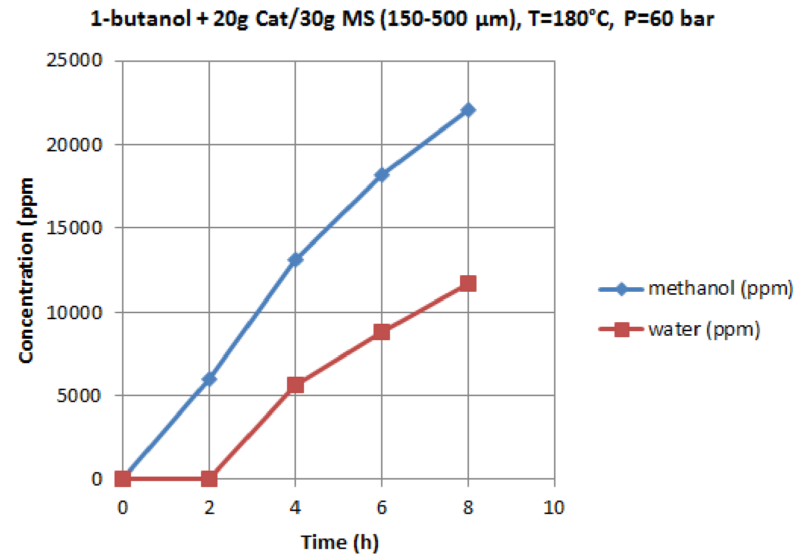
Figure 66 – Concentrations of methanol and by-products during reaction time for experiment with 25g Cat / 25g MS (grinded) in 2-butanol at T=180°C and P=60 bar.

When utilizing the ground molecular sieve, the lowest methanol concentration of 18611 ppm was found in the experiment where 25 g of the catalyst and 25 g of the ground molecular sieve were used. Even for that case, methanol concentration was increased approximately 2.6 times in comparison to a reference experiment in 2-butanol performed at similar conditions (Figure 55). Despite the fact that the molecular sieve was used, water formation seemed to be similar for both experiments in samples collected after 2, 4 and 6 hours of experimental time. However, a doubled decrease in water concentration was observed in the 1st sample in the experiment where the molecular sieve was utilized. In the other two cases, methanol was produced at concentrations of 20250 ppm and 24983 ppm, respectively for the experiments performed with 10g Cat / 40g MS and 20g Cat / 30g MS. In the case where 10g Cat / 40g MS was used, no water was detected in the 1st and 2nd samples. After that, the water concentration started to increase gradually and achieved 7164 ppm in the last sample, which was approximately 3.5 times lower than in the reference experiment in 2-butanol. As for the experiment with 20g Cat / 30g MS, no water was found in the 1st sample. Afterwards, water concentration increased and achieved 20406 ppm at the end of the reaction time.

From the aforementioned observations, it is possible to conclude that increased catalyst mass resulted in more intensive formation of water, which was formed as a by-product of methanol synthesis reaction and as a product of the reverse water-gas shift reaction, and decreased rates of methanol formation. In other words, water formation was catalyzed by the Cu-based methanol synthesis catalyst. The molecular sieve acted as an adsorbent of water, which started to form intensively already during the heating of the reactor to the targeted reaction temperature in some experiment. Interestingly, the best performance regarding methanol synthesis rate was detected in experiments (Figure 64 and 65) where the rate of water formation was lower than the rate of methanol formation. Presumably, the equilibrium of the synthesis reaction was shifted towards the formation of the methanol by selective removal of water from the reaction mixture. This effect is directly connected to a certain adsorption capacity that the molecular sieve possessed.

Another interesting observation was related to more intensive formation of 2-butanone (product of the catalytic dehydrogenation of the corresponding alcohol). The range of 2-butanone formation in the experiments with grinded molecular sieve performed at T=180^{o}C and P=60 bar was between 50 000 ppm and 70 000 ppm at the beginning of the reaction time, which was 2 times higher in comparison with to reference experiments in 2-butanol performed at temperature range of 180^{o}C - 220^{o}C. Presumably, the more intensive rate of endothermic catalytic dehydrogenation of 2-butanol was connected to the water removed simultaneously from the reaction mixture by the molecular sieve.

It is possible to note that optimized reaction environment (optimal concentrations of molecular sieve and catalyst) is needed to produce methanol at significantly increased efficiency. This can apparently be done by lowering the amount of catalyst and increasing the amount of molecular sieve. Additional experiments with varied amounts of the aforementioned solid phases are needed to obtain empirical data and select optimal proportions. However, regarding the conducted experiments, the highest methanol concentration was found in the experiment where 20g Cat / 30g MS were used. For comparison, 1-butanol was also tested with the same amounts of solid phases with increased to 8 hours reaction time. The concentration data of this experiment is presented in Figure 67. From the graph, it can be clearly noted that methanol synthesis equilibrium was not achieved during the 8 hours of reaction time, based on the fact that increasing trend of methanol concentration was observed. If comparing this data with the reference experiment in 1-butanol performed at similar process conditions (Figure 56), it is possible to note that methanol concentration increased approximately 3.4 times after 6 hours of reaction time. Then methanol concentration continued to increase gradually while in the reference experiment in 1-butanol methanol synthesis rate slowed down at this point of the reaction. The rate of water formation was approximately 2 times lower when molecular sieve was utilized. In other words, the ground molecular sieve again had a clear effect on methanol formation by shifting the equilibrium of the reaction towards production of the desirable compound - methanol.

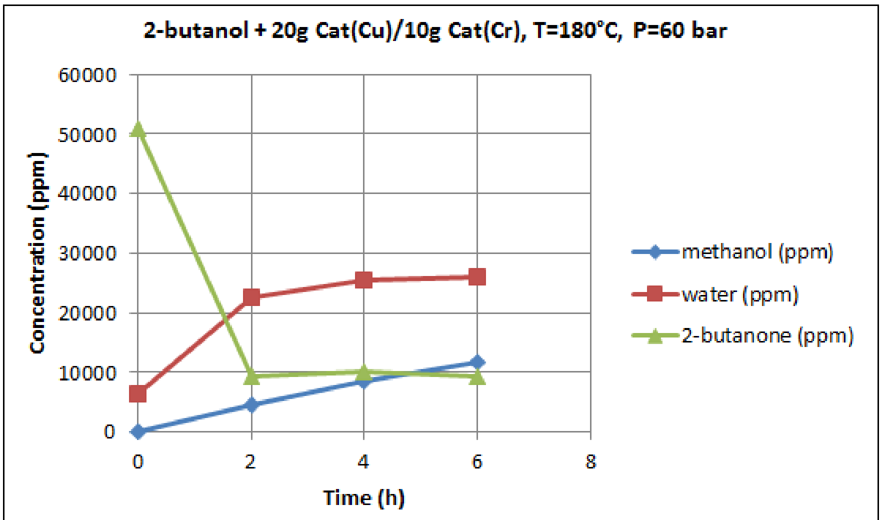


1-butanol + 20g Cat/30g MS (150-500 μm), T=180°C, P=60 bar		
Time	methanol (ppm)	water (ppm)
0	0	0
2	6020	0
4	13122	5673
6	18223	8794
8	22124	11720

Figure 67 - Concentrations of methanol and water during reaction time (8 hours) for experiment with 20g Cat / 30g MS (grinded) in 1-butanol at T=180°C and P=60 bar.

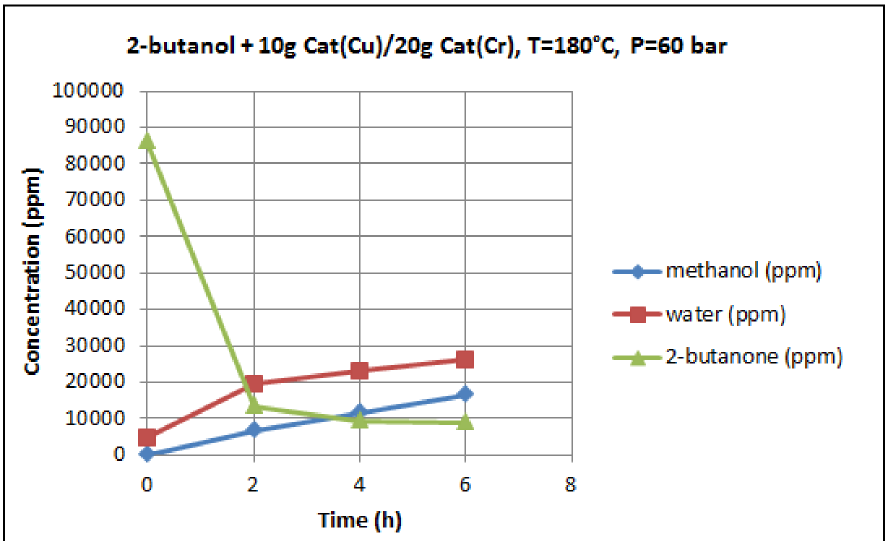
6.4. Effect of catalyst combination on methanol synthesis

The effect of the utilization of promoted catalysts on methanol productivity is well-documented in the Section 3.3 of the literature review. In the current work, a mixture of commercial $CuO/ZnO/Al_2O_3$ and $Cr_2Cu_2O_5$ was tested at different proportions at T=180°C and P=60 bar in 2-butanol to evaluate the effect of catalyst combination on the methanol productivity. The following Figures 68 and 69 provide the concentration data of methanol and by-products during 6 hours of reaction time.



2-butanol + 20g Cat(Cu)/10g Cat(Cr), T=180°C, P=60 bar			
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	6463	50983
2	4592	22511	9362
4	8506	25404	10107
6	11602	26106	9269

Figure 68 – Concentrations of methanol and by-products during reaction time for experiment with 20g Cat (Cu) / 10g Cat (Cr) in 2-butanol at T=180°C and P=60 bar.



2-butanol + 10g Cat(Cu)/20g Cat(Cr), T=180°C, P=60 bar			
Time (h)	methanol (ppm)	water (ppm)	2-butanone (ppm)
0	0	4907	86086
2	6413	19617	13180
4	11602	22949	9455
6	16608	26194	8990

Figure 69 – Concentrations of methanol and by-products during reaction time for experiment with 10g Cat (Cu) / 20g Cat (Cr) in 2-butanol at T=180°C and P=60 bar.

Copper chromite catalyst is considered as a highly efficient catalyst for hydrogenation and dehydrogenation of organic compounds. This is well matched with the obtained experimental results. As it can be clearly seen from Figures 68 and 69, utilization of copper chromite catalyst in combination with the commercial Cu-based catalyst showed good results regarding methanol synthesis. Methanol concentrations in the final 4th samples were 11 602 ppm and 16 608 ppm, respectively for the experiments where 20g $CuO/ZnO/Al_2O_3$ / 10 g $Cr_2Cu_2O_5$ and 10g $CuO/ZnO/Al_2O_3$ / 20 g $Cr_2Cu_2O_5$ were used. These results were significantly higher than the results obtained in a reference experiment in 2-butanol performed at the similar conditions (Figure 55). It is interesting to note that water formation was approximately the same in both cases and slightly different in comparison to the reference experiment (Figure 55). From this observation, it is possible to conclude that copper chromite did not promote formation of water.

However, as it can be clearly seen from Figures 70 -71, the reaction of alcohol dehydrogenation took place at higher rates while increasing the amount of $Cr_2Cu_2O_5$. Thereby, high concentrations of 2-butanone of 50 983 ppm and 86 086 ppm (higher concentration due to the increased mass of copper chromite catalyst) were detected in the samples of both experiments at the beginning of the reaction time. Afterwards, the concentration of 2-butanone started to decrease during the reaction time similarly as it was observed in all the previous experiments. In conclusion, it is possible to note that the combination of molecular sieve with the commercial copper based catalyst and copper chromite catalyst might potentially result in very good performance regarding methanol synthesis. Nevertheless, optimal proportions of the solid phases must be determined in future investigations.

6.5. Effect of process conditions on the catalyst particle size

Particle size distribution analysis was carried out to evaluate the influence of process conditions on the catalyst particle size. The main purpose of this analysis was to understand whether the selected process conditions and activation procedure negatively affect the catalyst particles superficial changes, such as particle grinding or agglomeration. A significant number of samples were analyzed but no significant changes in the catalyst particle size as well as in the particle size of the molecular sieve were detected. Figures 70 and 71 depict the results from particle size distribution analysis for the experiment in 1-butanol performed at $T=180^oC$ and $P=60$ bar and for the experiment in 2-butanol (where 30 g of molecular sieve was added), respectively, performed at the same process conditions. It can be clearly seen from the Figures 70 and 71 that there were no changes in the particle size by attrition of agglomeration.

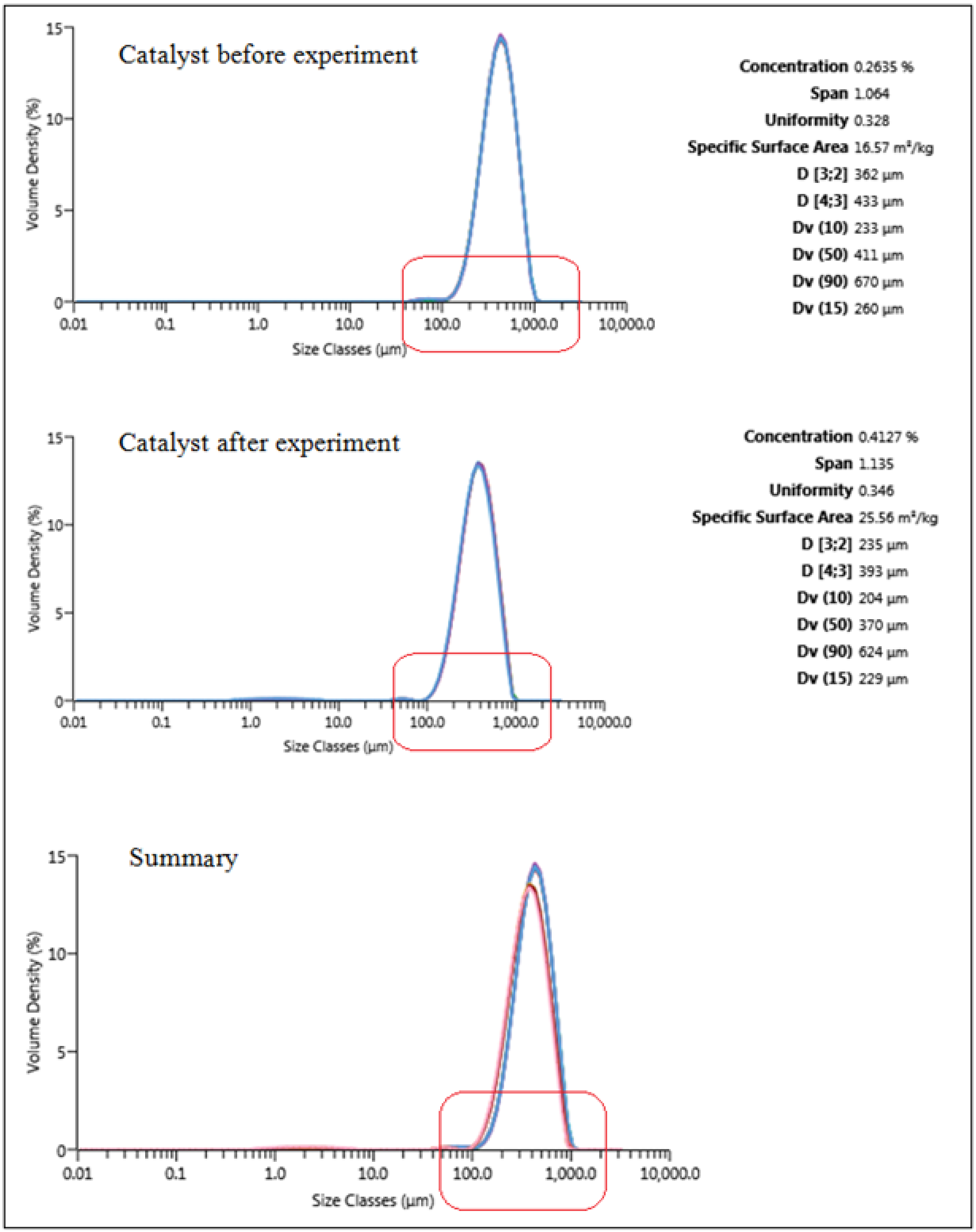


Figure 70 – Results of particle size distribution analysis for experiment in 1-butanol performed at T=180ºC and P=60 bar.

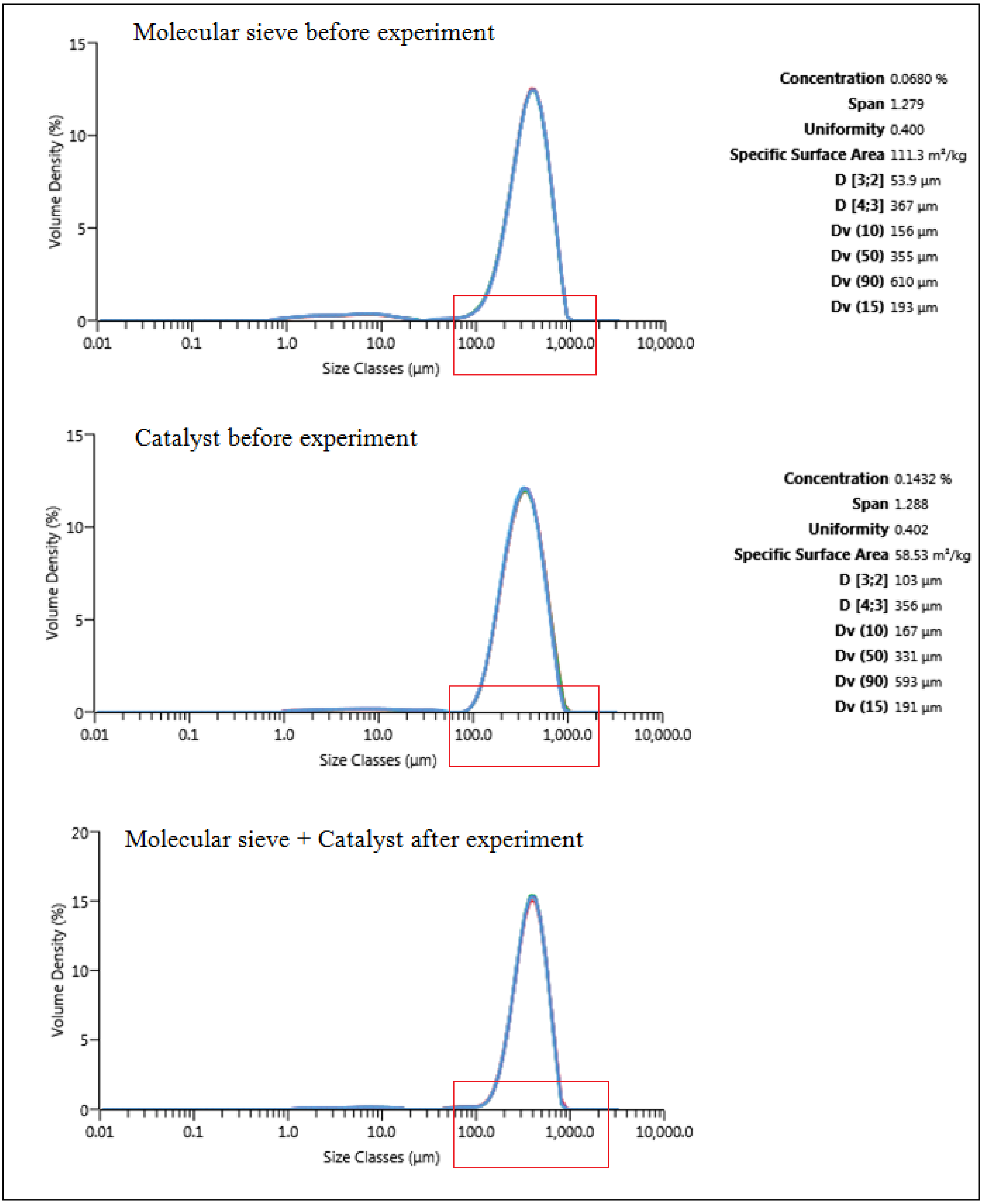


Figure 71 – Results of particle size distribution analysis for experiment in 2-butanol with the addition of molecular sieve performed at T=180°C and P=60 bar.

6.6. Summary of the experimental section

The specific methanol productivity was calculated in order to prepare data for future investigations of the alcohol-promoted methanol synthesis and to quantify the effect of different process conditions, utilization of molecular sieve and modified catalysts on the methanol synthesis. The catalyst and volume specific productivity were used for that purpose. The catalyst specific productivity (CSP) measures the mass of methanol (g) produced per mass of catalyst (kg) per hour. This parameter is commonly used to measure the activity of heterogeneous catalysts. The volume specific productivity (VSP) measures the mass of methanol (g) produced per volume of solvent per hour. This parameter provides more absolute measure of the effectiveness with which methanol is produced. The obtained data can be used for comparative analysis of the results against previous related studies. The results of the calculations of the catalyst and volume specific productivity are presented in Table 3 and Figures 72 and 73, while a calculation example can be found in Appendix II.

Table 3 - Catalyst and volume specific productivity of methanol calculated based on the concentration data obtained in the experiments.

Experiment name	CSP [g/kg·h]	VSP [g/l·h]
2-butanol + 20gCat(Cu), T=180°C, P=60 bar	9,59	0,959
2-butanol + 20gCat(Cu), T=200°C, P=60 bar	9,35	0,935
2-butanol + 20gCat(Cu), T=220°C, P=60 bar	8,25	0,825
1-butanol + 20gCat(cu), T=180°C, P=60 bar	7,18	0,718
1-butanol + 20gCat(Cu), T=200°C, P=60 bar	6,91	0,691
1-butanol + 20gCat(Cu), T=220°C, P=60 bar	5,97	0,597
2-propanol + 20gCat(Cu), T=200°C, P=60 bar	9,46	0,946
1-pentanol + 20gCat(Cu), T=200°C, P=60 bar	9,42	0,942
1-butanol + hexane + 20gCat(Cu), T=180°C, P=60 bar	3,93	0,393
2-butanol + 20gCat(Cu) + 20gMS(beads), T=180°C, P=60 bar	11,18	1,12
2-butanol + 10gCat(Cu) + 40gMS(ground), T=180°C, P=60 bar	54,4	2,72
2-butanol + 20gCat(Cu) + 30gMS(ground), T=180°C, P=60 bar	33,56	3,36
2-butanol + 25gCat(Cu) + 25gMS(ground), T=180°C, P=60 bar	20	2,5
1-butanol + 20gCat(cu) + 30gMS(ground), T=180°C, P=60 bar	22,5	2,24
2-butanol + 20gCat(Cu) + 10gCat(Cr), T=180°C, P=60 bar	10,39	1,55
2-butanol + 10gCat(Cu) + 20gCat(Cr), T=180°C, P=60 bar	14,87	2,23

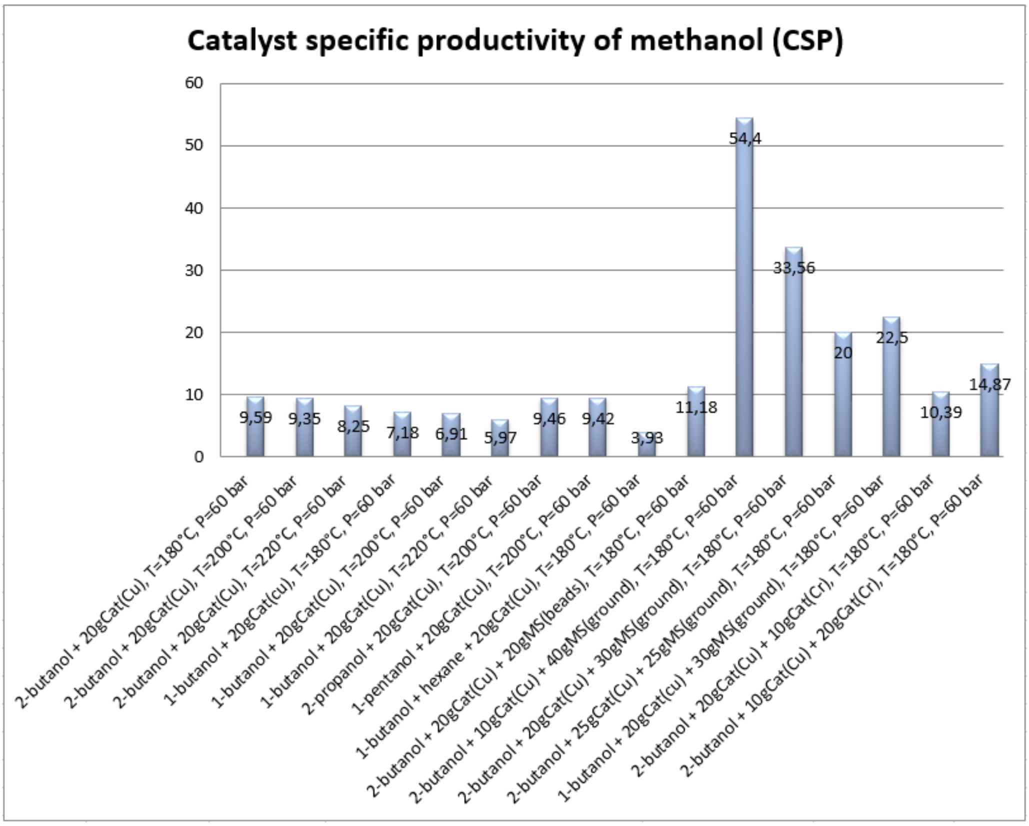


Figure 72 – Catalyst specific productivity of methanol.

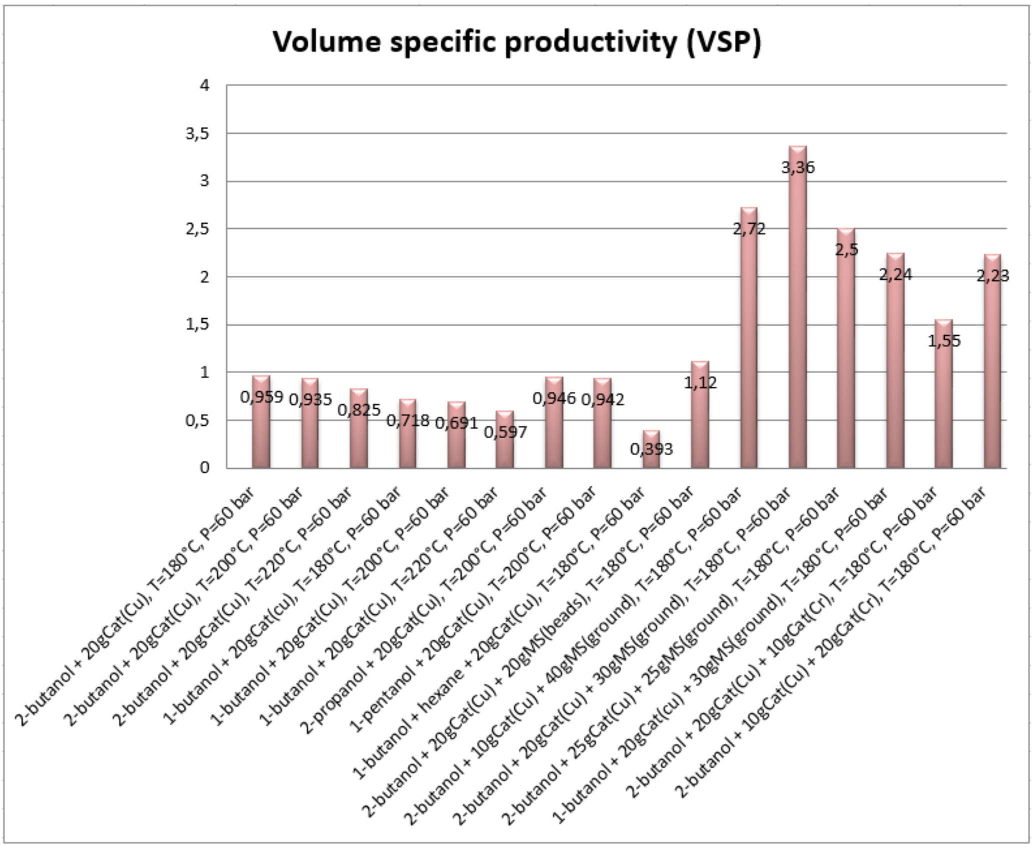


Figure 73 - Volume specific productivity of methanol.

7. Conclusions

The alcohol-promoted liquid-phase methanol synthesis performed in autoclave reactor was studied at a laboratory scale. In the alcohol solvent, methanol synthesis proceeds through an indirect reaction route through the formate ester of the alcohol as an intermediate. Experiments were performed at temperature range of 180-220°C and at total pressure of 60 bar. The reaction gas consisted of CO_2 and H_2 (3:1). Different alcohol solvents, such as 2-butanol, 1-butanol, 2-propanol and 1-pentanol were tested in the methanol synthesis. Conventional $CuO/ZnO/Al_2O_3$ catalyst was used alone and in combination with molecular sieve and $Cr_2Cu_2O_5$ catalyst in different proportions to estimate the effects of simultaneous water removal and utilization of mixed catalysts on the methanol synthesis.

While investigating the effect of temperature on the methanol synthesis, it was found that decreasing temperature of the process was favorable for alcohol-promoted methanol synthesis. The process conditions of T=180°C and P=60 bar was found as the optimal in the regard of methanol synthesis. Typically, methanol formation rate is faster at the higher temperatures of the process due to the increased reaction rate. However, the controversial results obtained in the current research can be explained by the methanol reaction kinetics which depends on the partial pressure of the reaction gas. While increasing temperature of the process, vapor pressure of alcohol solvents was increased. Consequently, partial pressure of the feed gas was decreased. Presumably, this had an effect on the methanol synthesis and its concentrations were higher when the lower process temperature was used.

Catalytic dehydrogenation of alcohols was noticed as a significantly important reaction. The reactions of alcohol dehydrogenation were found to proceed more intensively with the growth of reaction temperature. 2-butanone and butanal were formed from 2-butanol and 1-butanol, respectively, with hydrogen released in the process. The highest concentrations of alcohol dehydrogenation products were found at the beginning of the reaction time. After that, the concentrations of alcohol dehydrogenation products decreased dramatically during the reaction time due to the catalytic dehydrogenation reaction proceeding to the reverse direction.

Water was formed as a by-product of the methanol synthesis reaction from CO_2 and H_2. Furthermore, the reverse water-gas shift reaction was found to be an important role in the overall reaction system. Generally, the concentration of water showed an increasing trend with the reaction time. However, for some experiments, the rate of water formation slowed down or even started to decrease after 4 hours of reaction time. This could be explained if the reverse water-gas shift reaction had reached equilibrium and changed direction producing carbon dioxide (CO_2) and hydrogen (H_2) from carbon monoxide (CO) and water (H_2O).

The limiting effect of water on the methanol synthesis was apparent. This was confirmed in a series of experiments where molecular sieve was used for selective removal of water from the reaction mixture. Addition of ground molecular sieve resulted in significantly increased concentrations of methanol. Interestingly, the best performance regarding methanol synthesis was found in experiments where the rate of water formation during the reaction was lower than the rate of methanol formation. Presumably, the equilibrium of the synthesis reaction shifted towards the formation of methanol by selective removal of water from the reaction mixture, which is known to decrease the activity of catalyst by the inhibition. Remarkably, utilization of molecular sieve also resulted in more intensive reactions of endothermic alcohols dehydrogenation. Utilization of a mixture of commercial copper based catalyst and a copper chromite catalyst also brought positive results with regard to methanol synthesis.

In the alcohol solvents, methanol synthesis proceeds through an indirect reaction route through the formate ester of the alcohol as an intermediate. In cases of 2-butanol, 2-propanol and 1-pentanol the corresponding intermediates are butyl formate, 2-propyl formate and 1-pentyl formate. The aforementioned esters could not be analyzed quantitatively due to the unavailability of the compounds for use as analytical standards. In case of 1-butanol, the intermediate species is 1-butyl formate. This ester was not detected in 1-butanol samples. The reason for that could be that 1-butyl concentration had been too low for detection or the ester had been masked by other components. Furthermore, it could be also explained by methanol formation reaction rate where 1st elementary step of ester formation is rate-limiting (slow), while 2nd elementary step of methanol formation is fast. Hence, analysis was not able to detect the formate intermediate.

Specific methanol productivity was calculated in order to prepare the obtained data for comparative analysis against related studies. A maximal catalyst specific productivity of 54.4 g of methanol per kg of catalyst per hour and volumetric specific productivity of 3.36 g of methanol per liter of solvent per hour were obtained during the experiments. The productivity values are low compared to gas-phase synthesis from CO_2. However, milder process conditions and simple operation of the alcohol-promoted methanol synthesis could prove useful in small-scale methanol production plants. Additional research is required to make a final conclusion about the feasibility of this process.

REFERENCES

1. CO2 Abatement by Methanol Production from flue gas in methanol plant. A. K. Sayah, Sh. Hosseinabadi, M. Farazar. 2010, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, pp. 540-543.

2. Methanol synthesis using captured CO2 as raw material: techno-economical and environmental assessment . Mar Pérez-Fortes, Jan C. Schöneberger, Aikaterini Boulamanti , Evangelos Tzimas. 2015, Aplied Energy, pp. 718-732.

3. Advances in CO2 capture technology. Jose´ D. Figueroa, Timothy Fout, Sean Plasynski, Howard McIlvried. 2007, International journal of greenhouse gas control, pp. 9-20.

4. Broeren, Martijn. Production of bio-methanol. s.l. : International Renewable Energy Agency, 2013.

5. Karen Law, Jeffrey Rosenfeld, Michael Jackson. Methanol as a renewable energy resource. Alexandria : s.n., 2013.

6. Gale, John. Development in renewable methanol production . s.l. : IEAGHG Information paper, 2016.

7. Research Progress on the Indirect Hydrogenation of CO2 to Methanol. Xian-Long Du, Zheng Jiang, Dang Sheng Su, Jian-Qiang Wang. 2016, CHEMSUSCHEM, pp. 322-332.

8. George A. Olah, Alain Goeppert, Surya Prakash. Beyond Oil and Gas: The methanol economy. Los Angeles : WILEY-VCN, 2008.

9. Peter Biedermann, Thomas Grube, Bernd Höhlein. Methanol as an Energy Carrier. s.l. : Energy Technology, 2006.

10. Johnson Matthey. Reforming (ATR, GHR, SMR) and synthesis (A-SRC, R-SRC, TCC). [Online] http://davyprotech.com/what-we-do/licensed-processes-and-core-technologies/core-technologies/refiningdistillation/specification/#tab-content-2.

11. Methano converter types. Slide share. [Online] https://www.slideshare.net/GerardBHawkins/methanol-converter-types.

12. Martin Bertau, Heribert Offermanns, Ludolf Plass, Friedrich Schmidt, Hans-Jiirgen Wernicke. Methanol: The Basic Chemical and Energy Feedstock of the Future. s.l. : Springer, 2014.

13. CO2 capture ready plants. . Irons R, Sekkapan G, Panesar R, Gibbins J, Lucqiuaud M. 2007, EA Greenhouse Gas R & D Programme.

14. CO2 capture and separation technologies for end-of-pipe applications. A review . Olajire, Abass A. 2010, Elsevier-Energy.

15. Hydrogen Production by Water Electrolysis: A Review of Alkaline Water Electrolysis, PEM WaterElectrolysis and High Temperature Water Electrolysis. Md Mamoon Rashid, Mohammed K. Al Mesfer, Hamid Naseem, Mohd Danish. s.l. : International Journal of Engineering and Advanced Technology, 2015. ISSN: 2249 – 8958.

16. An overview of hydrogen production technologies. J.D. Holladay, J. Hu, D.L. King, Y. Wang. s.l. : Catalysis Today, 2009.

17. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. Suhas G. Jadhava, Prakash D. Vaidyaa, Bhalchandra M. Bhanageb,. s.l. : Chemical Engineering Research and Design, 2014, Vol. 92. 2557–2567.

18. Recycling of carbon dioxide to methanol and derived products – closing the loop. Alain Goeppert, Miklos Czaun, John-Paul Jones, G. K. Surya Prakash and George A. Olah. s.l. : Chem. Soc. Rev, 2014. DOI: 10.1039/c4cs00122b.

19. Methanol synthesis from CO2-rich syngas over a ZrO2 doped CuZnO catalyst. Yang, C., Ma, Z., Zhao, N., Wei, W., Hu, T., Sun, Y. s.l. : Catal. Today, 2006, Vol. 115. 222–227.

20. A Cu/Zn/Al/Zr fibrous catalyst that is an improved CO2 hydrogenation to methanol catalyst. An, X., Li, J., Zuo, Y., Zhang, Q., Wang, D., Wang, J. s.l. : Catal. Lett, 2007. 264–269.

21. Effect of Mg and Mn oxide additions on structural and adsorptive properties of Cu/ZnO/ZrO2 catalysts for the methanol synthesis from CO2. Sloczynski, J., Grabowski, R., Kozlowska, A., Olszewski, P., Lachowska, M., Skrzypek, J., Stoch. s.l. : Appl. Catal., 2003. 129–138.

22. Methanol synthesis from carbon dioxide and hydrogen over Mn-promoted copper/zinc/zirconia catalysts. Lachowska, M., Skrzypek, J. s.l. : React. Kinet. Catal, 2004. 269–273.

23. Reverse topotactic transformation of a Cu–Zn–Al catalyst during wet Pd impregnation: relevance for the performance in methanol synthesis from CO2/H2 mixtures. Melian-Cabrera, I., Granados, M.L., Fierro, J.L.G. s.l. : J. Catal, 2002. 273–284.

24. CO2 hydrogenation to methanol over Cu/ZnO/ZrO2 catalysts prepared via a route of solid-state reaction. Guo, X., Mao, D., Lu, G.,Wang, S.,Wu, G. s.l. : Catal. Commun., 2011. 1095–1098.

25. Synthesis, characterization and activity pattern of Cu–ZnO/ZrO2 catalysts in the hydrogenation of carbon dioxide to methanol. Arena, F., Barbera, K., Italiano, G., Bonura, G., Spadaro, L., Frusteri, R. s.l. : J. Catal., 2007. 185–194.

26. CO2 hydrogenation to methanol over Cu/ZnO/Al2O3 catalysts prepared by a novel gel-network-coprecipitation method. Hong, Z.S., Cao, Y., Deng, J.F., Fan, K.N. s.l. : Catal, 2002. 37–44.

27. Methanol synthesis from CO2 hydrogenation over Cu based catalyst supported on zirconia modified y-Al2O3. Zhang, Y., Fei, J., Yu, Y., Zheng, X. s.l. : Energy Convers Manage, 2006. 3360–3367.

28. Zhang, Y., Fei, J., Yu, Y., Zheng, X. s.l. : Natl. Gas Chem., 2007. 12-15.

29. Wang, J.B., Lee, H.K., Huang, T.J. . s.l. : Catal, 2002. 79–86.

30. Catalytic performance for CO2 conversion to methanol of gallium-promoted copper-based catalysts: influence of metallic precursors. Toyir, J., de la Piscina, P.R., Fierro, J.L.G., Homs, N. s.l. : Appl. Catal, 2001. 255–266.

31. Carbon nanotube-supported Pd–ZnO catalyst for hydrogenation of CO2 to methanol. Liang, X.L., Dong, X., Lin, G.D., Zhang, H.B. s.l. : Appl. Catal., 2009. 315-322.

32. Enhancement of the catalytic performance to methanol synthesis from CO2/H2 by gallium addition to palladium/silica catalysts. Bonivardi, A.L., Chiavassa, D.L., Querini, C.A., Baltanas, M.A. s.l. : Stud. Surf. Sci. Catal, 2000. 3747–3752.

33. CO2 hydrogenation over carbide catalysts. Dubois, J.L., Sayama, K., Arakawa, H. 1992 : Chem. 5–8.

34. Coal Gasification and Its. D. Bell, B. Towler, M. Fan. s.l. : Elsevier, 2010.

35. Recent advances in catalytic hydrogenation of carbon dioxide. Wei Wang, Shengping Wang, Xinbin Ma and Jinlong Gong. s.l. : Chem Soc Rev, 2011. 3703-3727.

36. Frilund, Christian. CO2 HYDROGENATION TO METHANOL. 2016.

37. E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein. s.l. : Nat. Chem., 2011, Vol. 3. 609–614.

38. Z. B. Han, L. C. Rong, J. Wu, L. Zhang, Z. Wang, K. L. Ding. s.l. : Ding, Angew. Chem. Int. Ed, 2012, Vol. 51. 13041–13045.

39. E. Balaraman, Y. Ben-David, D. Milstein. s.l. : Angew. Chem. Int. Ed., 2011, Vol. 50. 11702–11705.

40. C. A. Huff, M. S. Sanford. s.l. : J. Am. Chem. Soc., 2011, Vol. 133. 18122–18125.

41. Y. Chen, S. Choi, L. T. Thompson. s.l. : ACS Catal, 2015, Vol. 5. 1717–1725.

42. S. H. Kim, S. H. Hong. s.l. : ACS Catal, 2014, Vol. 4. 3630–3636.

43. A two-stage catalyst bed concept for conversion of carbon dioxide into methanol. Rahimpour, M.R. s.l. : Elsevier, 2007, Vol. 89. 556-566.

44. Optimal design of an industrial scale dual-type reactor for direct dimethyl ether DME) production from syngas. Reza Vakili, Reza Eslamloueyan. s.l. : Chemical Engineering and Processing, 2012, Vol. 62. 78-88.

45. Direct dimethyl ether (DME) synthesis through a thermally coupled heat exchanger reactor. R. Vakili, E. Pourazadi, P. Setoodeh, R. Eslamloueyan, M.R. Rahimpour. s.l. : Applied Energy, 2011, Vol. 88. 1211-1223.

46. CAMERE Process for methanol synthesis from CO2 hydrogenation. Oh-Shim Joo, Kwang-Deog Jung and Yonsoo, Jung. s.l. : Elsevier, 2004. 67-72.

47. New process of low-temperature methanol synthesis from CO/CO2/H2 based on dual-catalysis. ZENG Jianqing, TSUBAKI Noritatsu ,FUJIMOTO Kaoru. Tokyo : SCIENCE IN CHINA, 2002, Vol. 45. 106-112.

48. Liquid phase methanol (LPMEOH) Project. Tijm, Peter J.A. San Francisco : Conference materials, 1999.

49. Efficient conversion of carbon dioxide to methanol using copper catalyst by a new low-temperature hydrogenation process. Liu, Y., Zhang, Y., Wang, T., Tsubaki, N. s.l. : Chem. Lett, 2007, Vol. 36. 1182–1183.

50. Low-temperature methanol synthesis from carbon dioxide and hydrogen via formic ester. Fan, L., Sakaiya, Y., Fujimoto, K. s.l. : Appl. Catal., 1999. 11—13.

51. Methanol synthesis from CO2and H2 in multi-tubular fixed-bed reactor and multi-tubular reactor filled with monoliths. Sofiane Arab, Jean-Marc Commenge, Jean-Franc¸ois Portha, Laurent FalkLaboratoire. s.l. : chemical engineering research and design, 2014. 1-11.

52. R. P. W. J. Struis, S. Stucki and M. Wiedorn. s.l. : J. Membr. Sci, 1996, Vol. 113. 93-100.

53. An experimental study of CO2 hydrogenation into methanol involving a zeolite membrane reactor. Fausto Gallucci, Luca Paturzo, Angelo Basile. s.l. : Elsevier-Chemical Engineering and Processing, 2004, Vol. 43. 1029–1036.

54. Yuan, G. Chen and Q. s.l. : Separation and purification technology, 2004, Vol. 34. 227-237.

55. Current Progress on Zeolite Membrane Reactor for CO2 Hydrogenation. I.G.B.N. Makertiharta1, P.T. Dharmawijaya and I.G. Wenten. Bondung : AIP, 2016. 1-5.

56. Industrial Applications of Reactive distillation- recent trends. Rameshwar S. Hiwale, Yogesh S. Mahajan, Nitin V. Bhate, Sanjay M. Mahajani. s.l. : Chemical Reactor Engineering, 2004, Vol. 2. 2-51.

57. Dimethyl ether: A review of technologies and production challenges. Zoha Azizia, Mohsen Rezaeimaneshb, Tahere Tohidiana, Mohammad Reza Rahimpoura. s.l. : Elsevier- Chemical engineering and processing, 2014, Vol. 82. 150–172.

58. Use of catalytic distillation reactor for methanol synthesis. US 20020177741 A1 2002.

Appendix I: Analysis of liquid samples

Figure A-1 shows the chromatogram obtained for the mixed solution containing equal parts of methanol, 2-butanol, 2-butanone and water. Obtained compounds retention times were used for the identification of these compounds in the actual samples. Similar method was used for the clarification of the retention time of the corresponding compounds expected in the experiments where 1-butanol, 2-propanol and 1-pentanol were used as alcohol solvents.

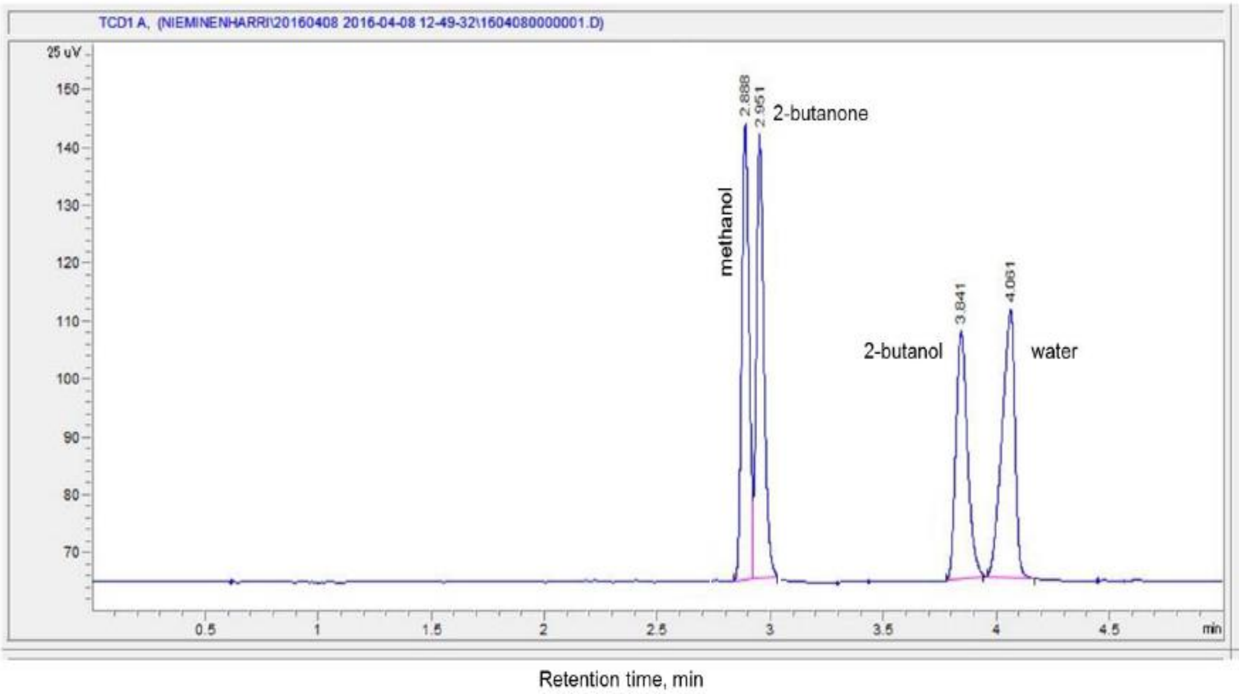


Figure A-1 – Chromatogram used for the identification of the retention time of the targeted compounds in the samples.

Table A-1 provides the data of retention time for each compound. As it was discussed in Section 5.2.4, two different columns - Zebron ZB-WAXplus and HP-1MS - were used, respectively, for the analysis of samples when 2-butanol (2-propanol and 1-pentanol) and 1-butanol were used as the alcohol solvents. Thus, different retention times can be observed for water due to the fact that different chromatography methods were used.

Table A-1 – Retention time of the analyzed compounds

Compound name	Retention time [min]
Methanol	2.9
Water (for 2-butanol)	4
Water (for other solvents)	2.7
2-butanol	3.9
2-butanone	3
1-butanol	5.8
1-butyl formate	6.8
butanal	4.9
2-propanol	3.9
1-pentanol	7.8

Figure A-2 and A-3 provide the examples of the chromatograms from the analysis of liquid samples obtained from the experiments in 1-butanol and 2-butanol.

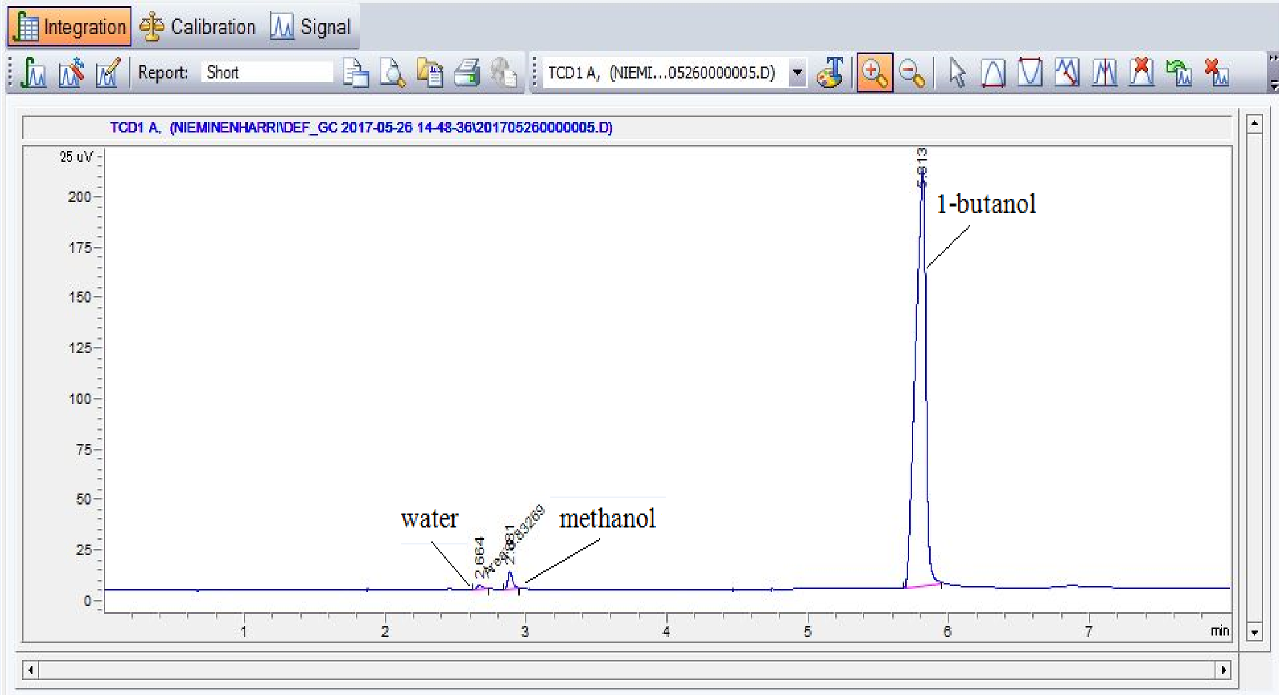


Figure A-2 – Spikes of 1-butanol, methanol and water obtained by gas chromatography analysis of the 5th liquid sample from experiment with 1-butanol, 20g Cat(Cu) and 30g MS (grinded) performed at T=180°C and P=60 bar.

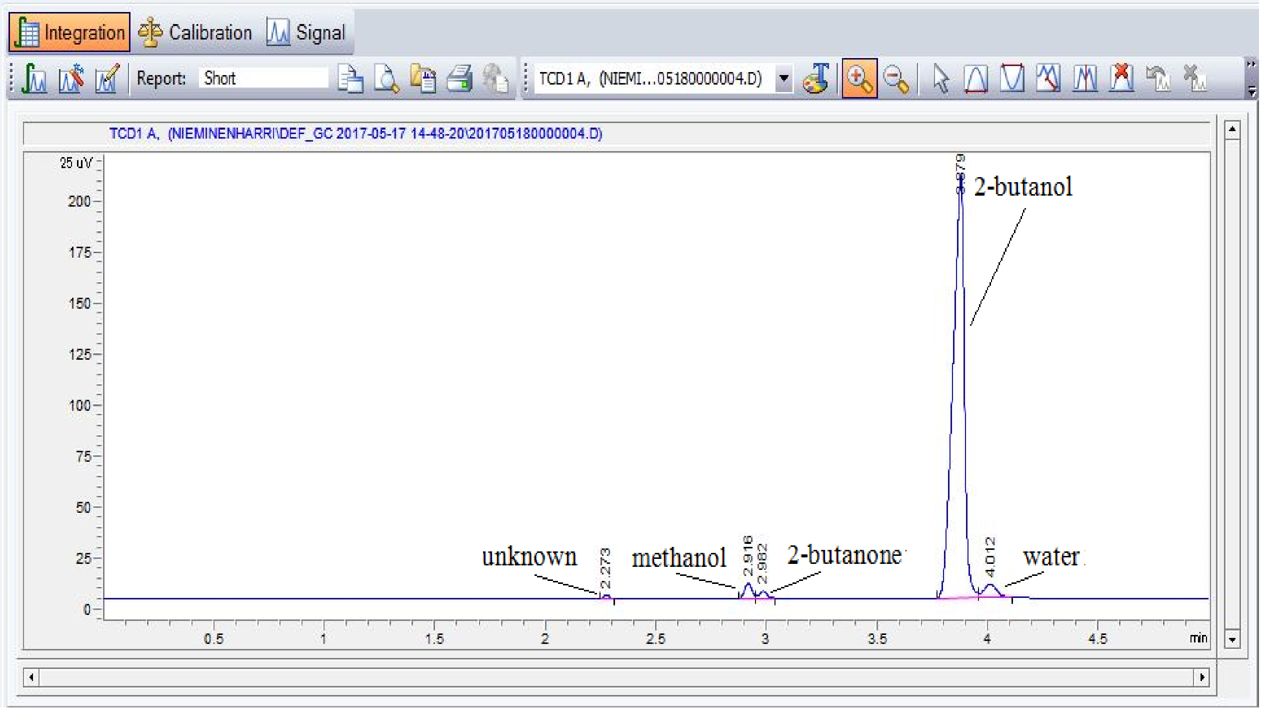


Figure A-3 – Spikes of 2-butanol, methanol, water and 2-butanone obtained by gas chromatography analysis of the 4th liquid sample from experiment with 2-butanol, 10g Cat(Cu) and 20g Cat(Cr) performed at T=180°C and P=60 bar.

Mixed standard solutions in the relevant concentration range for each compound (low concentrations of the expected reaction products and high concentrations of the alcohol solvents) were prepared to create a calibration curves. Calibration curves were used than to obtain equations for the calculations of the concentrations based on the data obtained from the gas chromatography analysis (x - peak area was the main parameter in these calculations). Figures A-4, A-5 and A-6 show the calibration curves and equations used for concentration calculations based on the analysis data from experiments where 1-butanol, 2-butanol, 2-propanol and 1-pentanol were used as alcohol solvents, respectively.

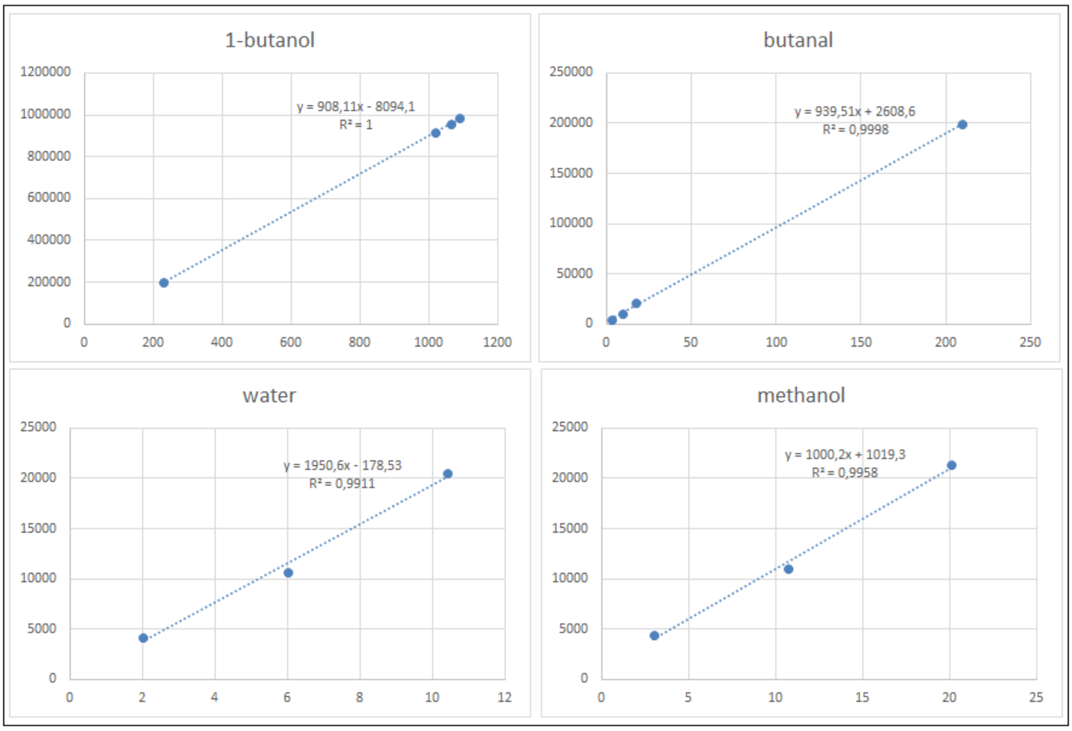


Figure A-4 – Gas chromatography calibration curves and equations for the concentrations calculations of the expected compounds in samples of 1-butanol experiments.

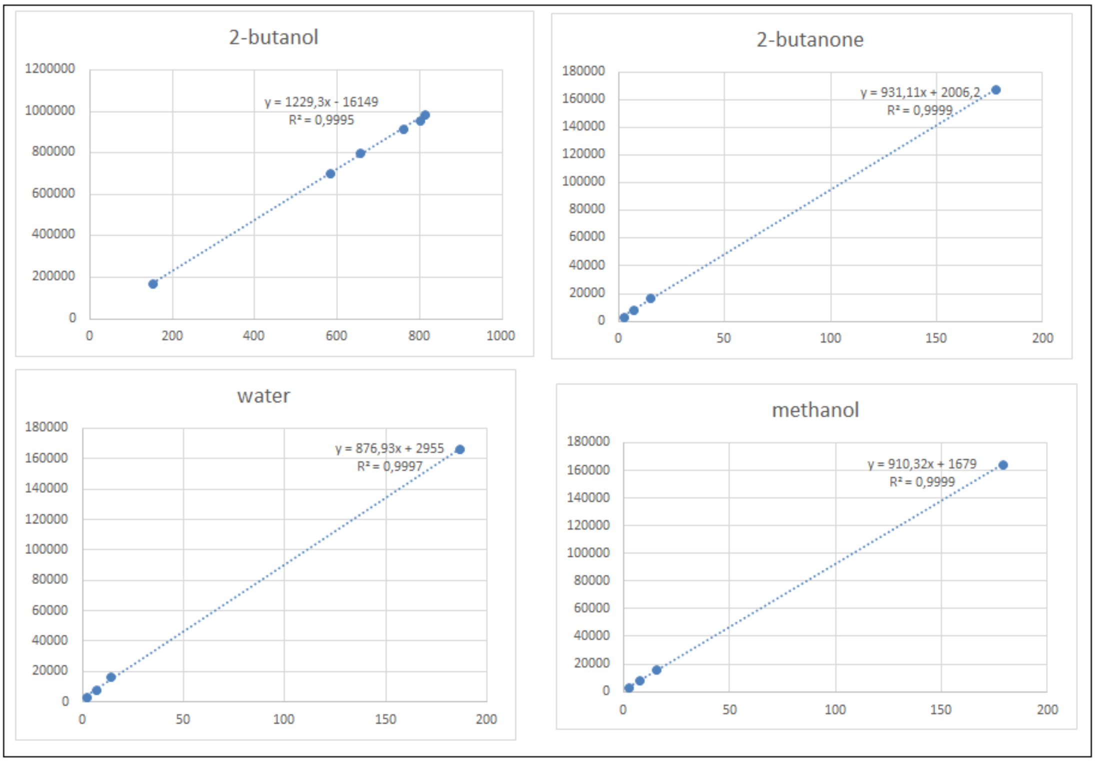


Figure A-5 – – Gas chromatography calibration curves and equations for the concentrations calculations of the expected compounds in samples of 2-butanol experiments.

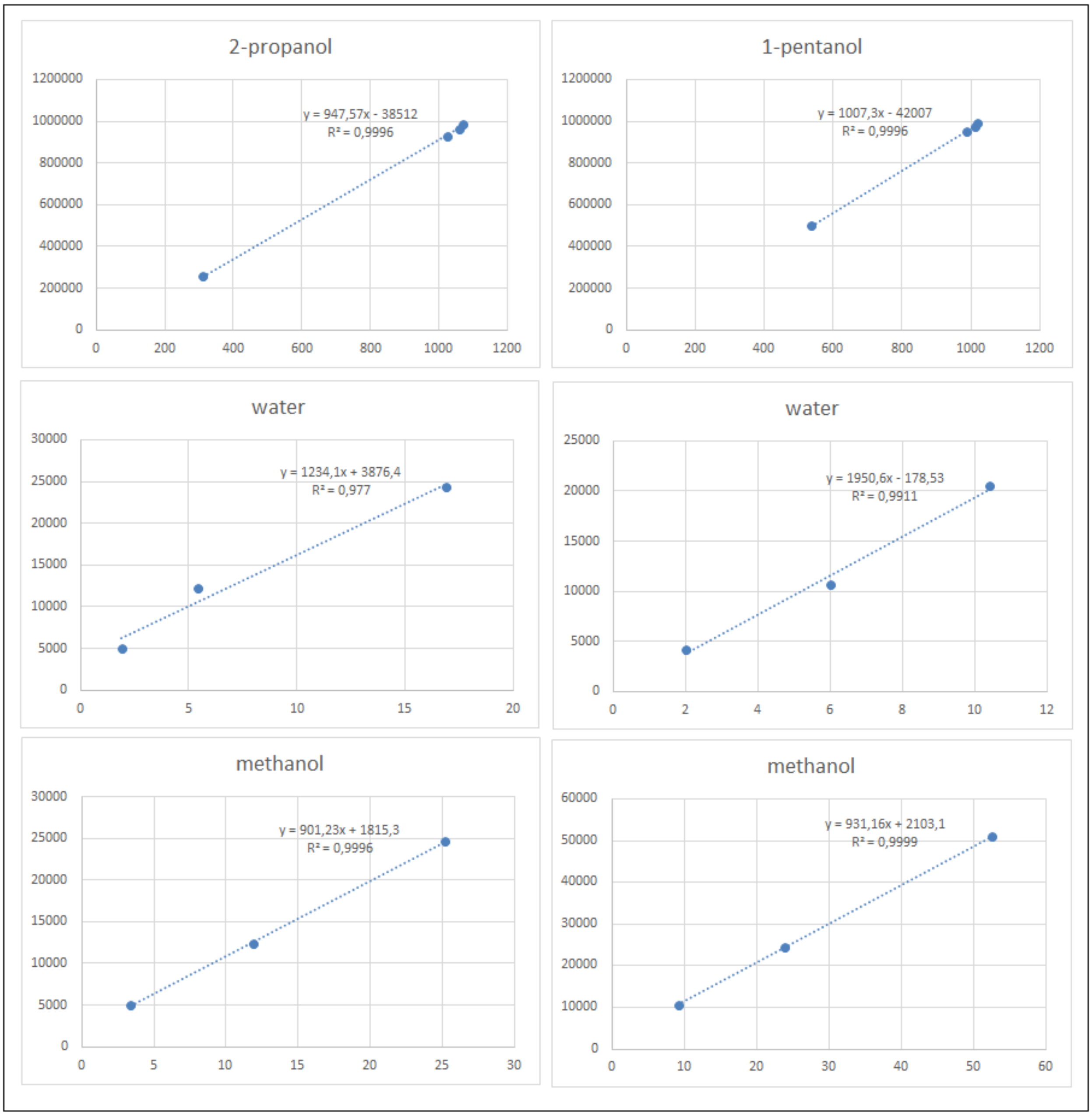


Figure A-6 – Gas chromatography calibration curves and equations for the concentrations calculations of the expected compounds in samples of 2-propanol (left column) and 1-pentanol (right column) experiments.

Appendix II: Calculation examples

Catalyst and volume specific productivity of methanol

Catalyst specific productivity (CSP) measures the mass of methanol (g) produced per mass of catalyst (kg) per hour. Volume specific productivity (VSP) measures the mass of methanol (g) produced per volume of solvent per hour. Catalyst and volume specific productivity of methanol are presented by the following Equations 1 and 2.

$$\mathrm{CSP} = \frac{\mathrm{m_{MeOH}}}{\mathrm{m_{catalyst}} \cdot \mathrm{t}} = \frac{\frac{\mathrm{c_{MeOH}}}{1000} \cdot \mathrm{V_{solvent}} \cdot \rho_{\mathrm{solvent}}}{\mathrm{m_{catalyst}} \cdot \mathrm{t}} \quad \left[\frac{\mathrm{g}}{\mathrm{kg} \cdot \mathrm{h}}\right] \tag{1}$$

$$\mathrm{VSP} = \frac{\mathrm{m_{MeOH}}}{\mathrm{V_{solvent}} \cdot \mathrm{t}} = \frac{\frac{\mathrm{c_{MeOH}}}{1000} \cdot \mathrm{V_{solvent}} \cdot \rho_{\mathrm{solvent}}}{\mathrm{V_{solvent}} \cdot \mathrm{t}} \quad \left[\frac{\mathrm{g}}{\mathrm{l} \cdot \mathrm{h}}\right] \tag{2}$$

Where, $\mathrm{m_{MeOH}}$ – Mass of methanol produced [g]

$\mathrm{m_{catalyst}}$ –Mass of catalyst used [kg]

t – Experimental time [h]

$\mathrm{c_{MeOH}}$ – Methanol concentration [ppm], [mg/kg]

$\mathrm{V_{solvent}}$ – Volume of the solvent [m^3]

ρ_{solvnet} – Density of the solvent [kg/m^3]

It is possible to show the example of calculations of catalyst and volume specific productivity of methanol based on the experiment performed in 2-butanol at T=180°C and P=60 bar during 6 hours with 10 g of $CuO/ZnO/Al_2O_3$ and 20 g of $Cr_2Cu_2O_5$ catalysts. A standard volume of 200 ml of 2-butanol was used. The density of 2-butanol is 806 kg/m^3 at room temperature. Methanol concentration in the final sample was 16 608 ppm.

Calculation example:

$$\mathrm{CSP} = \frac{\mathrm{m_{MeOH}}}{\mathrm{m_{catalyst}} \cdot \mathrm{t}} = \frac{\frac{16608\ \mathrm{mg/kg}}{1000\ \mathrm{mg/g}} \cdot 200 \cdot 10^{-6} \mathrm{m^3} \cdot 806\ \mathrm{kg/m^3}}{0.03\ \mathrm{kg} \cdot 6\ \mathrm{h}} = 14.87 \quad \left[\frac{\mathrm{g}}{\mathrm{kg} \cdot \mathrm{h}}\right]$$

$$\mathrm{VSP} = \frac{\mathrm{m_{MeOH}}}{\mathrm{V_{solvent}} \cdot \mathrm{t}} = \frac{\frac{16608\ \mathrm{mg/kg}}{1000\ \mathrm{mg/g}} \cdot 200 \cdot 10^{-6} \cdot 806\ \mathrm{kg/m^3}}{200 \cdot 10^{-6} \cdot 6} = \ 2231\ \left[\frac{\mathrm{g}}{\mathrm{m^3} \cdot \mathrm{h}}\right] = 2.231\ \left[\frac{\mathrm{g}}{\mathrm{l} \cdot \mathrm{h}}\right]$$

Partial pressure of the feed gas

The partial pressures ($P_{partial}$) of the feed gas (mixture of CO_2 and H_2) were calculated based on the following equation:

$$\mathrm{P_{partial}} = \mathrm{P_{total}} - \mathrm{P_{vapor}} \tag{3}$$

The similar total pressure (P_{total}) of 60 bar was used for all experiments. The vapor pressures (P_{vapor}) of the alcohols were calculated based on the Anotoine equation:

$$\log_{10}\mathrm{P_{vapor}} = \mathrm{A} - \frac{\mathrm{B}}{\mathrm{C} + \mathrm{T}} \tag{4}$$

Where, P – vapor pressure of the alcohol [bar];
T – reaction temperature [K];
A, B and C – constants for Antoine equation.

Table A-II – Antoine's equation specific constants for different alcohols.

Alcohol	A	B	C	Temperature range [K]
1-butanol	4.43	1305	-94.68	419.34 – 562.98
2-butanol	4.2	1094.25	-111.6	422.11 – 535.9
2-propanol	4.58	1221.42	-87.47	395.1 – 508.24
1-pentanol	3.97	1106.11	-134.58	437.79 – 513.79

The examples of calculations of the feed gas partial pressure are presented below.

The experiment in 1-butanol performed at T=180°C:

$$\mathrm{P_{vapor}} = 10^{\left(\mathrm{A}-\frac{\mathrm{B}}{\mathrm{C+T}}\right)} = 10^{\left(4.43-\frac{1305}{-94.68+453.15}\right)} = 6.16\ \mathrm{bar}$$

$$\mathrm{P_{partial}} = \mathrm{P_{total}} - \mathrm{P_{vapor}} = 60 - 6.16 = 53.84 \approx 54\ \mathrm{bar}$$

The experiment in 2-butanol performed at T=180°C:

$$\mathrm{P_{vapor}} = 10^{\left(\mathrm{A}-\frac{\mathrm{B}}{\mathrm{C+T}}\right)} = 10^{\left(4.2-\frac{1094.25}{-111.6+453.15}\right)} = 9.91\ \mathrm{bar}$$

$$\mathrm{P_{partial}} = \mathrm{P_{total}} - \mathrm{P_{vapor}} = 60 - 9.91 = 50.09 \approx 50\ \mathrm{bar}$$

The experiment in 2-propanol performed at T=200°C:

$$\mathrm{P_{vapor}} = 10^{\left(\mathrm{A}-\frac{\mathrm{B}}{\mathrm{C+T}}\right)} = 10^{\left(4.58-\frac{1221.42}{-87.47+473.15}\right)} = 25.89\ \mathrm{bar}$$

$$\mathrm{P_{partial}} = \mathrm{P_{total}} - \mathrm{P_{vapor}} = 60 - 25.89 = 34.11 \approx 34\ \mathrm{bar}$$

The experiment in 1-pentanol performed at T=200°C:

$$\mathrm{P_{vapor}} = 10^{\left(\mathrm{A}-\frac{\mathrm{B}}{\mathrm{C+T}}\right)} = 10^{\left(3.97-\frac{1106.11}{-134.58+473.15}\right)} = 5.05\ \mathrm{bar}$$

$$\mathrm{P_{partial}} = \mathrm{P_{total}} - \mathrm{P_{vapor}} = 60 - 5.05 = 54.95 \approx 55\ \mathrm{bar}$$