RE6 - Heterogeneous Catalyzed Reaction Methanation of CO_2 over a Ru/Al_2O_3 catalyst

Group B20: Oda Bentzen and Jane Bastiansen

Supervisor: Ask Lysne

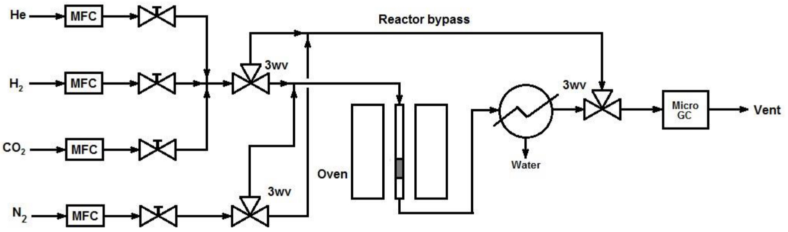
5. oktober 2021

1 Introduction

In this experiment a CO_2 methanation reaction is being carried out at different reaction conditions over a 2 wt% Ru/Al_2O_3 catalyst. The reactor used is a fixed bed quartz reactor in an H_2-rich atmosphere. After going through the reactor, the gases will be analysed using micro gas chromatography (Micro GC). The goal of the experiment is determining the reaction order of CO_2 and the activation energy of the reaction. This will be done by varying the partial pressure of CO_2 and the temperature, respectively.

2 Experimental Procedure

In this experiment, a testing apparatus consisting of three way valves, and gas flows of He, H_2, CO_2, and N_2, managed by mass-flow controllers, was used. Figure 2.1 shows a simplified flow chart of the experiment and the testing apparatus:



Figur 2.1: Simplified flow chart of the experiment and the testing apparatus used. Mass-flow controllers (MFC), three-way valves (3wv) and gas chromatograph (GC).

2.1 Preparation of Reactor

In this experiment, a catalyst testing apparatus was be utilized. The catalyst was Ru/Al_2O_3 (200 mg), containing 2 wt% Ru on a γ-Al_2O_3 support.

The reactor was prepared by placing a small plug of quartz wool in the bottom of the reactor, before the catalyst diluted in SiC (800 mg) was loaded into the column, and isolated with another piece of quartz wool. The oven was then closed, and gas feed and outlet lines were connected. A thermocouple was placed inside the reactor center, to secure accurate monitoring of the temperature. Next gas leakage was checked twice, once by using a detection spray while allowing N_2 flow through, then by using a flammable gas detector as H_2 was passing inside the pipes. Lastly the system was purged by N_2 (100ml /min) for 15 min, first through the reactor, then through the bypass, before the cooling water was turned on.

To distinguish the peak maximum of all four gases, the micro-GC was calibrated. This was carried out by introducing one gas at a time, through the bypass to the micro-GC. The retention time of the gases could then be identified.

2.2 Catalyst Pretreatment

Before starting the reaction, the catalyst (Ru) was reduced to its metallic state by inducing a 50-50 gas flow of H_2 in N_2, as the temperature was raised from 25 °C to 350 °C, at 10 °C per minute.

2.3 Kinetic Experiment

The experiment was divided into 2 parts.

2.3.1 Part 1: Determining Reaction Order

Part 1 consisted of steps 1-3, where the data was used to determine the reaction order of CO_2. The temperature was held steady at 25 °C, while flow composition was changed every 45 min according to the MFC set-points given in B.2.

2.3.2 Part 2: Determining Activation Energy

Part 2 consisted of steps 3-5, where the composition was kept constant, and the temperature varied. The Micro GC continuously analysed the composition of the product gas. The temperature increased by 10 °C every 45 min according to table B.2.

3 Results and Discussion

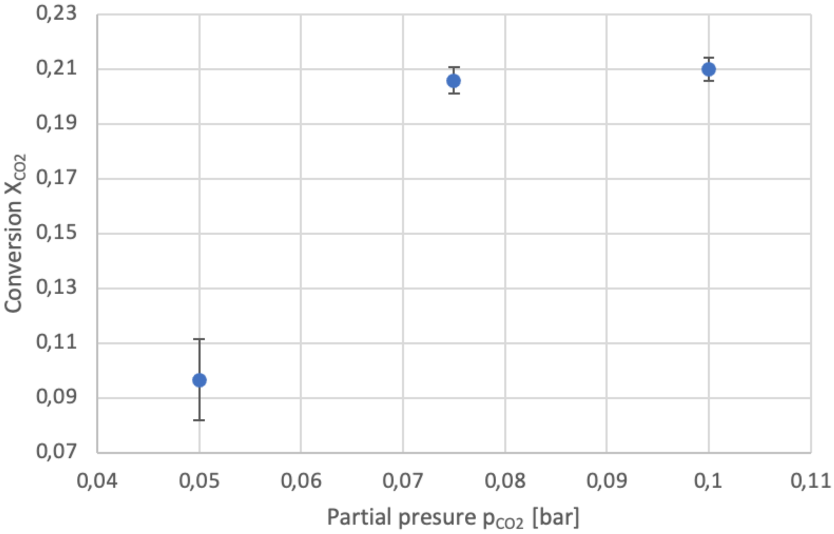
Prior to the experiment, the peak position of the four gases were localized by micro GC. The values for retention time are given in table 3.1.

Tabell 3.1: Retention time of each component

Component	Time [s]
CO_2	310.2
H_2	34.8
N_2	65.8
He	30.5

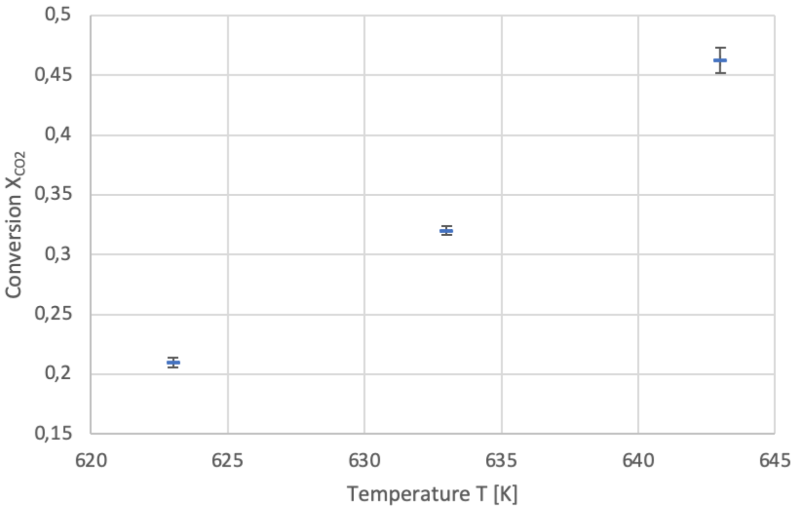
Firstly, the calibration was used to find the relative response factor, RRF_i. The calibration plot is shown in figure B.1. Then the peak integration of CO_2 and of the internal standard N_2 were found with the micro-GC. These results were used to calculate the conversion of CO_2 (X_{CO_2}), the rate of consumption ($-r_{CO_2}$), the reaction order (α), and the activation energy (E_A). The raw data and the calculated values are shown in table A.2 and the calculations are given in appendix B. The results are presented graphically in figures 3.1-3.4.

In figure 3.1, the conversion of CO_2 is plotted against the partial pressure of CO_2 for steps 1-3. The plotted values for X are the averages of the last three measurements for each step. From the plot, it can be seen that the conversion increases when the pressure increases. This result is as expected because increasing the pressure of gaseous reactants, means that there will be more collisions, and therefore the reaction rate increases. Thus, the reaction is faster and the conversion is higher. The error bars show the standard deviation. These show the dispersion of the data points from the mean value. It can be seen that overall the dispersion is low, although the first step has a little higher deviation than the others. This suggests that the system had more or less reached steady state at the time the measurements where taken.



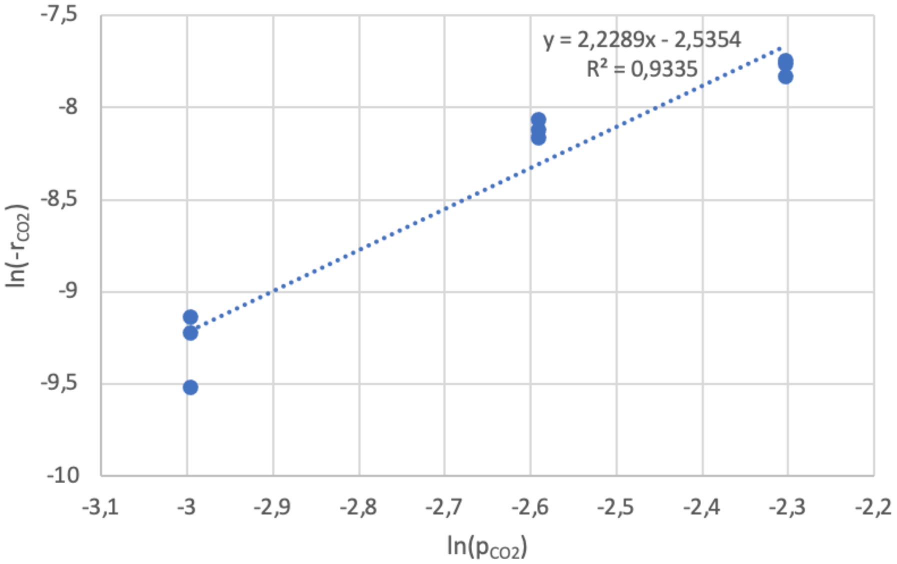
Figur 3.1: The conversion X_{CO_2} as a function of partial pressure p_{CO_2} [bar] for steps 1-3.

In figure 3.2, the conversion of CO_2 is plotted against the increasing temperature for steps 3-5. Also here the values for X are the averages of the last three measurements. This plot shows that the conversion increases when the temperature increases. This result is also as expected because a higher temperature gives a higher reaction rate, which again leads to higher conversion. As in figure 3.1, the error bars are rather small, suggesting that the system had reached steady state.



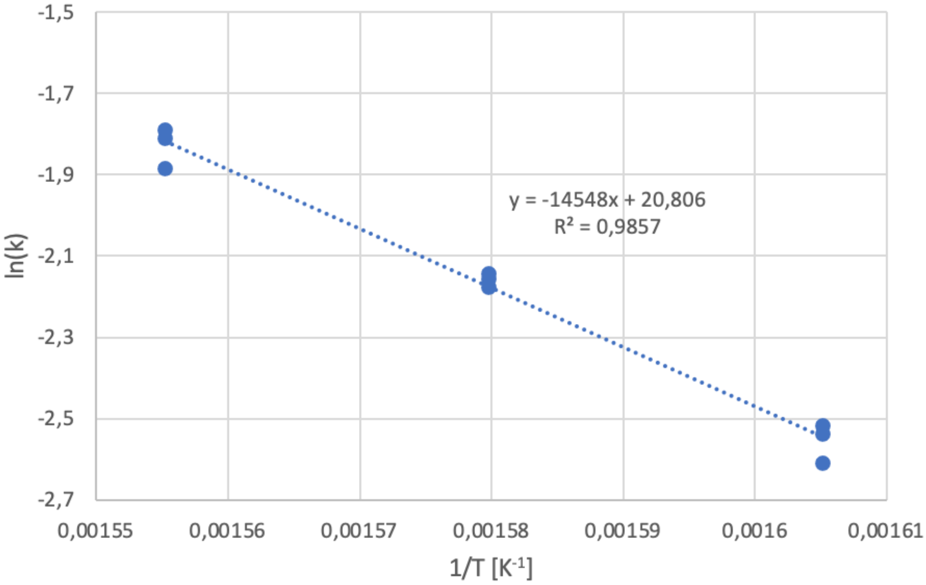
Figur 3.2: The conversion X_{CO_2} as a function of temperature T [K] for steps 3-5.

In figure 3.3, $ln(-r_{CO_2})$ is plotted against $ln(p_{CO2})$ for steps 1-3. The reaction order is found by the slope value, which is 2.23. ln(k) can be found as the intercept value of this graph, which is -2.54. A reaction order of 2 means that the rate of reaction will change as the square of the change in concentration. From step 1 to step 3, the concentration of CO_2 doubled, as the volume fraction went from 5% to 10%. It can be seen from table A.2 that the reaction rate, $-r_{CO2}$, is about four times bigger for step 3 than for step 1. This implies that the calculations for the reaction order are correct.



Figur 3.3: $\ln(-r_{\mathrm{CO}_2})$ as a function of $\ln(p_{\mathrm{CO}_2})$ for steps 1-3.

In figure 3.4, ln(k) is plotted as a function of $\frac{1}{T}$. Here the slope value gives $\frac{-E_A}{R} = -14548$, which gives an activation energy equal to 120.95 $\mathrm{kJ\,mol^{-1}}$. The use of a catalyst means that this value is lower than it would have been without a catalyst. The intercept value gives $\ln(A)$, which is found to be 20.81.



Figur 3.4: lnk as a function of $\frac{1}{T}$ $[K^{-1}]$ for steps 3-5.

In figure 3.3 and 3.4 the R^2-values for the linear regression are 0.93 and 0.99, respectively. This means that the quality of the regression analysis is quite good as the R^2-values are close to 1. This shows that the results are most likely accurate, as there are no large deviations. This also suggests that the assumption of steady state was reasonable, as the data points from the three measurements do not differ a lot.

To calculate the molar flows from the volume flows, and to calculate the partial pressures, ideal gas was assumed, and the ideal gas law was used. At high temperature and low pressure, real gases behave as ideal gases. Therefore this assumption is reasonable, as the temperature in this experiments was 350-370 °C, and the pressure was never higher than 1 atm. In the calibration calculations, ideal gas was also assumed in the calculations of RRF_i. Here the temperature was not as high, only room temperature. However, this is still sufficiently higher than the boiling points of any of the gases, meaning that the assumption was reasonable also for this part.

Another assumption that was made in this experiment is low conversion levels. This is because the CO_2 partial pressure can then be considered constant through the reactor, by assuming differential conditions. This is so that equation B.6 can be used to calculate the rate of consumption. The calculated conversion levels for each step were about 8-48%, as shown in table A.2. To be able to apply differential calculations, the conversion levels should have a maximum of 10%[1], and therefore this assumption does not hold up. Since the overall conversion was too high, the changing CO_2 partial pressure throughout the reactor should ideally have been taken into account, by using an integral reactor model, when calculating $-r_{CO_2}$.

A source of error in this experiment could be that the temperature regulator dwelt at higher temperatures than the ones given for steps 4 and 5. When it was set to 360 °C and 370 °C for step 4 and 5 respectively, the actual temperature in the reactor was consistently at 5-10 degrees higher. This could affect the results, as higher temperature would have given a steeper curve in 3.4, and therefore a greater value for the activation energy.

Trondheim, 5. oktober 2021

Referanser

[1] Leonardo Falbo et al. Kinetics of CO_2 methanation on a ru-based catalyst at process conditions relevant for power-to-gas applications, 2017. URL `https://www.sciencedirect.com/science/article/pii/S0926337317311323?casa_token=E-ENhq-x55QAAAAA:PuFHsRJWdUyP80XlLrSyhhH36-_cpV9KJOyShvU-LSI34YlUVUQUZNrpCLAzUVKuzwi6Z633Uw#tbl0005`.

[2] Ask Lysne. Re6 - kinetics: Heterogeneous catalyzed reaction methanation of CO_2 over a Ru/Al_2O_3 catalyst. URL `https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/RE6_heterogeneous_catalysed_reaction.pdf`.

[3] Gunn Torill Wikdahl. Felleslab 2019 - re6 - kinetics for a heterogenous catalyzed reaction, 2015. Hentet 15.09.21 .

A.1 Raw Data and Calculated Results

Tabell A.2: Raw data and calculated values from each step of the experiment

Step	A_{N_2}	A_{CO_2}	$p_{\mathrm{CO_2}}$ [bar]	T [K]	F_{CO_2} [mol/min]	X_{CO_2} [%]	-$r_{\mathrm{CO_2}}$ [mol/ min g]	k
1.1	56069.026	11779.996	0.05	623	$1.783 \cdot 10^{-4}$	7.62	$7.35 \cdot 10^{-5}$	-
1.2	56009.636	11440.618			$1.733 \cdot 10^{-4}$	10.21	$9.85 \cdot 10^{-5}$	-
1.3	56135.353	11344.289			$1.715 \cdot 10^{-4}$	11.14	$1.08 \cdot 10^{-4}$	-
2.1	56921.966	15464.501	0.075	623	$2.305 \cdot 10^{-4}$	20.51	$2.97 \cdot 10^{-4}$	-
2.2	57039.233	15669.937			$2.331 \cdot 10^{-4}$	19.62	$2.85 \cdot 10^{-4}$	-
2.3	57177.551	15311.7540			$2.722 \cdot 10^{-4}$	21.66	$3.14 \cdot 10^{-4}$	-
3.1	57991.333	20963.936	0.10	623	$3.068 \cdot 10^{-4}$	20.52	$3.96 \cdot 10^{-4}$	0.0737
3.2	58281.498	20548.656			$2.992 \cdot 10^{-4}$	22.49	$4.34 \cdot 10^{-4}$	0.0808
3.3	58308.681	20682.976			$3.010 \cdot 10^{-4}$	22.02	$4.25 \cdot 10^{-4}$	0.0791
4.1	60833.183	19037.989	0.10	633	$2.164 \cdot 10^{-4}$	31.21	$6.31 \cdot 10^{-4}$	0.1175
4.2	61250.535	18909.289			$2.579 \cdot 10^{-4}$	32.13	$6.10 \cdot 10^{-4}$	0.1136
4.3	61328.986	18767.110			$2.556 \cdot 10^{-4}$	32.74	$6.22 \cdot 10^{-4}$	0.1158
5.1	65018.871	16657.563	0.10	643	$2.106 \cdot 10^{-4}$	43.68	$8.17 \cdot 10^{-4}$	0.1521
5.2	66114.065	15925.869			$1.981 \cdot 10^{-4}$	47.04	$8.80 \cdot 10^{-4}$	0.1639
5.3	66401.177	15716.061			$1.946 \cdot 10^{-4}$	47.97	$8.97 \cdot 10^{-4}$	0.1670

B Calculations

B.1 Relative Response Factor and CO_2 Conversion

In this experiment, gas chromatography (GC) was used to to find the CO_2 conversion. The response factor, RF_i, for a component i is defined by:

$$RF_i = \frac{A_i}{x_i}, \tag{B.1}$$

where A_i is the peak integration and x_i is the molar fraction of i.

Before analysing, the GC apparatus was calibrated using the internal standard method, with N_2 as the internal standard. Then the amounts of all other components could be determined relative to this standard. The relative response factor, RRF_i was found using equation B.2:

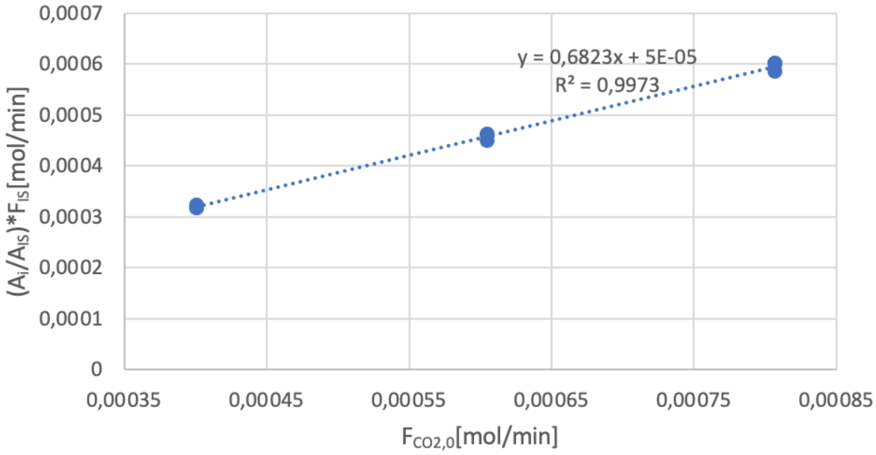
$$\begin{aligned} RRF_i &= \frac{RF_i}{RF_{IS}} \\ &= \frac{A_i}{x_i}\frac{x_{IS}}{A_{IS}}, \end{aligned} \tag{B.2}$$

where RF_{IS}, A_{IS}, and x_{IS} are the response factor, the peak area, and the molar fraction for the internal standard, respectively.

Equation B.2 can be rewritten as equation B.3[2], which was used to calculate the molar flow rate of CO_2:

$$F_i = \frac{A_i}{A_{IS}}\frac{F_{IS}}{RRF_i} \tag{B.3}$$

First, results from the calibration were used to find the relative response factor, RRF_i. By plotting $F_{CO2,0}$ as a function of $\frac{A_i}{A_{IS}} \cdot F_{IS}$, and using linear regression. The plot is shown in figure B.1:



Figur B.1: The calibration curve used to find RRF_i

RRF_i is here the slope value of the function, which equals 0.6823. This value was then used to calculate F_i using B.3.

Then the CO_2 conversion was calculated with equation B.4:

$$X_{CO_2} = \frac{F_{CO_2,0} - F_{CO_2}}{F_{CO_2,0}} \tag{B.4}$$

B.2 Rate of Consumption

The rate of CO_2 consumption, $-r_{CO_2}$, is given by equation B.5:

$$\begin{aligned} -r_{CO_2} &= k p_{CO_2}^{\alpha} p_{H_2}^{b} \\ -r_{CO_2} &= k p_{CO_2}^{\alpha}, \end{aligned} \tag{B.5}$$

where k is the rate constant, p_{CO_2} and p_{H_2} are the partial pressures for their respective reactants, and α and b are the reaction orders for CO_2 and H_2 respectively. The formula can be simplified as shown in equation B.5, because in a H_2-rich atmosphere, the reaction rate is considered independent of H_2 partial pressure (b=0).

Equation B.6 shows an expression for the consumption of CO2 at low conversion levels:

$$-r_{CO_2} = \frac{F_{CO_2,0} X_{CO_2}}{\Delta W}. \tag{B.6}$$

Here $F_{CO_2,0}$ is the feed rate of CO_2, X_{CO_2} is the conversion rate, and ΔW is the catalyst sample mass. This equation was used to find $-r_{CO_2}$ in this experiment.

B.3 Reaction Order

To find the reaction rate and reaction order, equation B.5 is rewritten as equation B.7:

$$ln(-r_{\mathrm{CO}_2}) = lnk + \alpha \cdot ln(p_{\mathrm{CO}_2}) \tag{B.7}$$

Here k and α are the rate constant and the reaction order respectively. These were found by plotting $\ln(-r_{\mathrm{CO}_2})$ with respect to $\ln(p_{CO2})$. The reaction order is then given by the slope value, and the rate constant is the intercept value.

B.4 Activation Energy

The activation energy, E_A, can be found by rewriting the Arrhenius equation to equation B.8:

$$\begin{aligned} k &= Ae^{\frac{-E_A}{RT}} \\ lnk &= lnA - \frac{E_A}{RT} \end{aligned} \tag{B.8}$$

Here A is the constant pre-exponential factor, R is the universal gas constant and T is the temperature of the reactor. By plotting ln$k$ as a function of $\frac{1}{T}$, -$\frac{E_A}{R}$ and ln$A$ were found as the slope value and the intercept value, respectively.

B.5 Flow rates and MFC Input Signal

Figure B.2 shows the calculated MFC setpoints and volume flows, as well as the given volume fractions, total flows, temperatures, and dwell times:

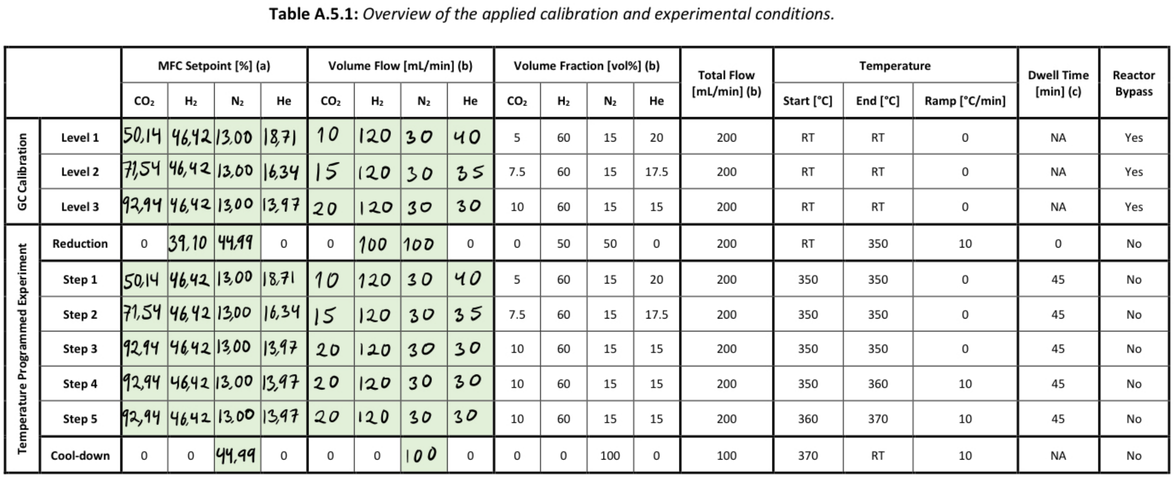


Table A.5.1: *Overview of the applied calibration and experimental conditions.*

		MFC Setpoint [%] (a)				Volume Flow [mL/min] (b)				Volume Fraction [vol%] (b)				Total Flow [mL/min] (b)	Temperature			Dwell Time [min] (c)	Reactor Bypass
		CO_2	H_2	N_2	He	CO_2	H_2	N_2	He	CO_2	H_2	N_2	He		Start [°C]	End [°C]	Ramp [°C/min]		
GC Calibration	Level 1	50,14	46,42	13,00	18,71	10	120	30	40	5	60	15	20	200	RT	RT	0	NA	Yes
	Level 2	71,54	46,42	13,00	16,34	15	120	30	35	7.5	60	15	17.5	200	RT	RT	0	NA	Yes
	Level 3	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	RT	RT	0	NA	Yes
Temperature Programmed Experiment	Reduction	0	39,10	44,99	0	0	100	100	0	0	50	50	0	200	RT	350	10	0	No
	Step 1	50,14	46,42	13,00	18,71	10	120	30	40	5	60	15	20	200	350	350	0	45	No
	Step 2	71,54	46,42	13,00	16,34	15	120	30	35	7.5	60	15	17.5	200	350	350	0	45	No
	Step 3	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	350	350	0	45	No
	Step 4	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	350	360	10	45	No
	Step 5	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	360	370	10	45	No
	Cool-down	0	0	44,99	0	0	0	100	0	0	0	100	0	100	370	RT	10	NA	No

Figur B.2: Completed overview of applied conditions with the required MFC setpoints and volumetric feed flows.

The flow rates and MFC input signals in table B.2 were found by using B.9-B.12.

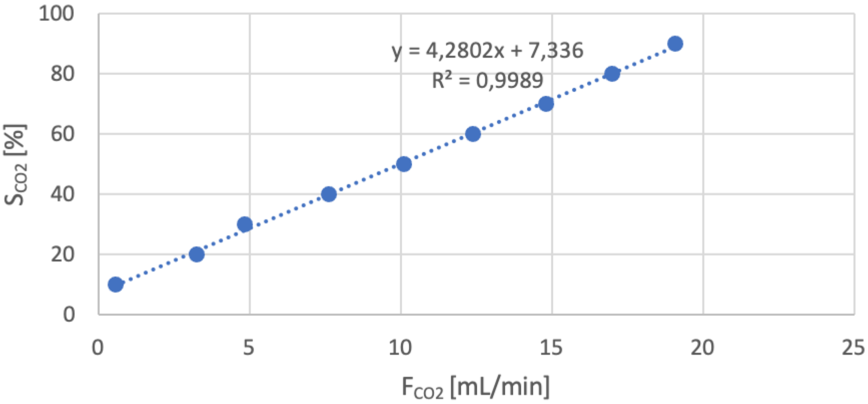
$$S_{\mathrm{CO}_2} = 4.2802 \cdot F_{\mathrm{CO}_2} + 7.336 \tag{B.9}$$

$$S_{\mathrm{H_2}} = 0.3655 \cdot F_{\mathrm{H_2}} + 2.4948 \tag{B.10}$$

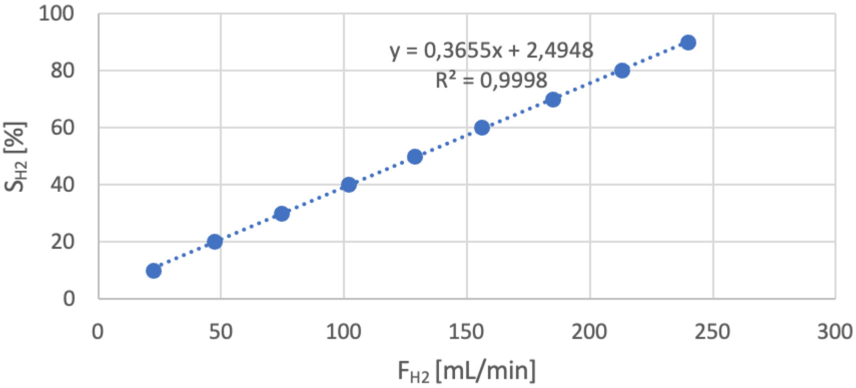
$$S_{\mathrm{N_2}} = 0.4566 \cdot F_{\mathrm{N_2}} - 0.7093 \tag{B.11}$$

$$S_{\mathrm{He}} = 0.4742 \cdot F_{\mathrm{He}} - 0.2538 \tag{B.12}$$

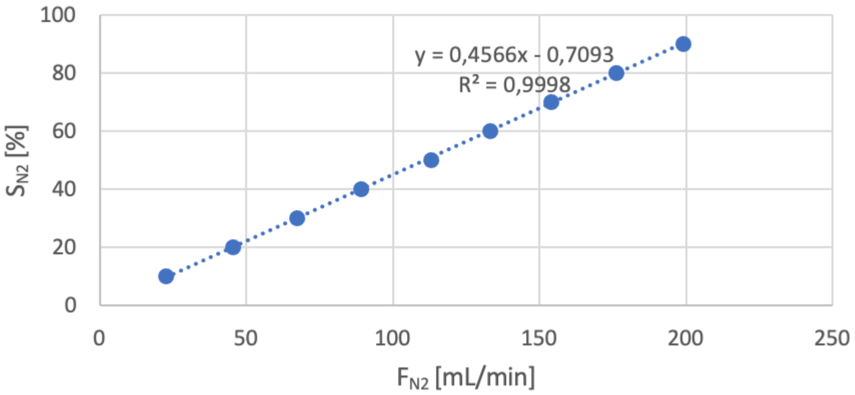
These equations were found by using the given calibration data[2] for each component, and plotting the MFC setpoints, S_i, as a function of the flow rates, F_i, and using linear regression. The calibration curves are shown in figures B.3-B.6:



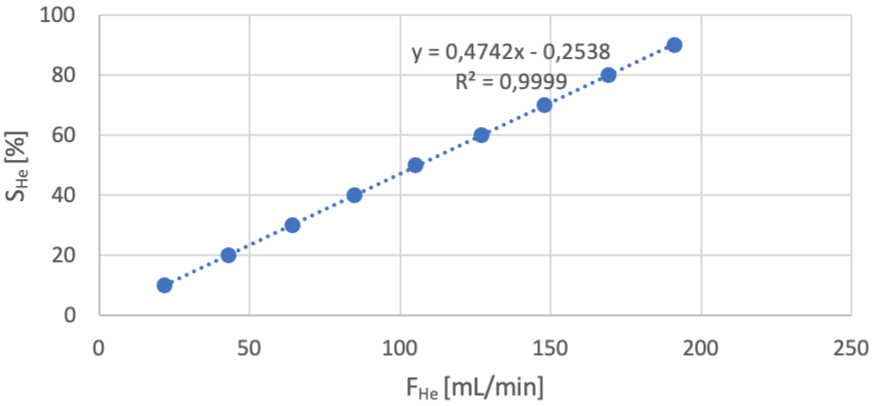
Figur B.3: $S_{\mathrm{CO_2}}$ as a function of $F_{\mathrm{CO_2}}$, plotted with values from calibration data.[2]



Figur B.4: $S_{\mathrm{H_2}}$ as a function of $F_{\mathrm{H_2}}$, plotted with values from calibration data.[2]



Figur B.5: S_{N_2} as a function of F_{N_2}, plotted with values from calibration data.[2]



Figur B.6: S_{He} as a function of F_{He}, plotted with values from calibration data.[2]

B.6 Standard Deviation Error Bars

The error bars showing standard deviations, σ, in figures 3.1 and 3.2 were calculated using equation B.13:

$$\sigma = \sqrt{\frac{\sum |X - \overline{X}|}{n}}, \tag{B.13}$$

where X is the calculated conversions for one step, $\overline{X}$ is the average conversion for said step, and n is the number of data points for each step, here 3.

C Risk Analysis

Lab coat and goggles will be worn at all times during the experiment. Gloves should only be worn when necessary, such as when one is loading the reactor. While insulating the reactor, a dust mask is required, because insulation fibers create a dust that can be irritating if inhaled. There are few risks related to this experiment. The gases being used are non-toxic, and a leak test is done prior to the experiment to minimize the risk of leakage. The experiment is performed with high temperatures, and the oven should therefore not be touched to avoid burns.[3]