Report RE1 - Biodiesel Production in a Batch Reactor

Group B5

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Contents

1 Introduction

In this experiment, biodiesel was produced in a batch reactor. Biodiesel was made from a transesterification reaction of soybean oil (SBO) by methanol, where sodium hydroxide was used as a catalyst. The samples were obtained in intervals, and separated to glycerine and biodiesel in a centrifuge. Furthermore, the biodiesel was analysed using gas chomatography to observe the progress of the transesterification reaction, where SBO goes to fatty methyl esters. The catalyst product selectivity and the conversion over time was observed. The reaction order was determined by comparing the recorded data to three different kinetic models, with reaction orders 0, 1 and 2 found using the integral method.

2 Theory

2.1 Biodiesel

In recent years, biodiesel has gained attention as it can be used to reduce CO_2 emissions. Using biodiesel does not add more carbon to the carbon cycle, as biodiesel is created from organic material already in the carbon cycle. The carbon emissions from fossil fuel increase the amount of carbon in the carbon cycle, as the fuel has been stored in underground reservoirs for millions of years. Biodiesel can be produced from fat, from sources such as colza oil or soy beans. The boiling point and ignition temperature of fat are to high to be used as fuel without processing. One method for making biodiesel from fat is transesterification. Using methanol, the fat is transesterified into fatty methyl esters, which can be used as fuel.[1]

2.2 Reaction Mechanism

Figure 2.1 shows the reaction mechanism of the alkali-catalysed transesterification of vegetable oils. The figure is taken from the lab document.[2] The reaction consists of three reversible steps. First the catalytic base reacts with the alcohol, making an alkoxide and a hydrogenated base. In the next step a nucleophilic attack by the alkoxide at the triglyceride forms an intermediate, generating an alkyl ester and an anion of the diglyceride. In the final step the anion deprotonates the hydrogen base. The di- and monoglycerides are converted into a mixture of alkyl esters and glycerine using the same reaction mechanism.[2]

2.3 Kinetics in Batch Reactors

The mole balance for a batch reactor is:

$$F_{A0} - F_A + G_A = \frac{dN_A}{dt} \tag{2.1}$$

where F_{A0} is the initial flow of substance A in to the system, while F_A is the flow out of the system. G_A is the amount of substance A that has been generated in the reactor. $\frac{dN_A}{dt}$ is how much substance that has been accumulated in the system over a short period of time.

In a batch reactor, the flow into the system is the same as the flow out of the system, so F_{A0}=F_A. G_A can be written like this (where r_A is the reaction rate):

$$G_A = r_A * V = \frac{dN_A}{dt} \tag{2.2}$$

It is desirable to find the reaction rate, and since the volume is constant (V = V_0) the reaction rate is given by:

$$r_A = \frac{dN_A}{V_0 dt} = \frac{dC_A}{dt} \tag{2.3}$$

where C_A is the concentration of the substrate A.

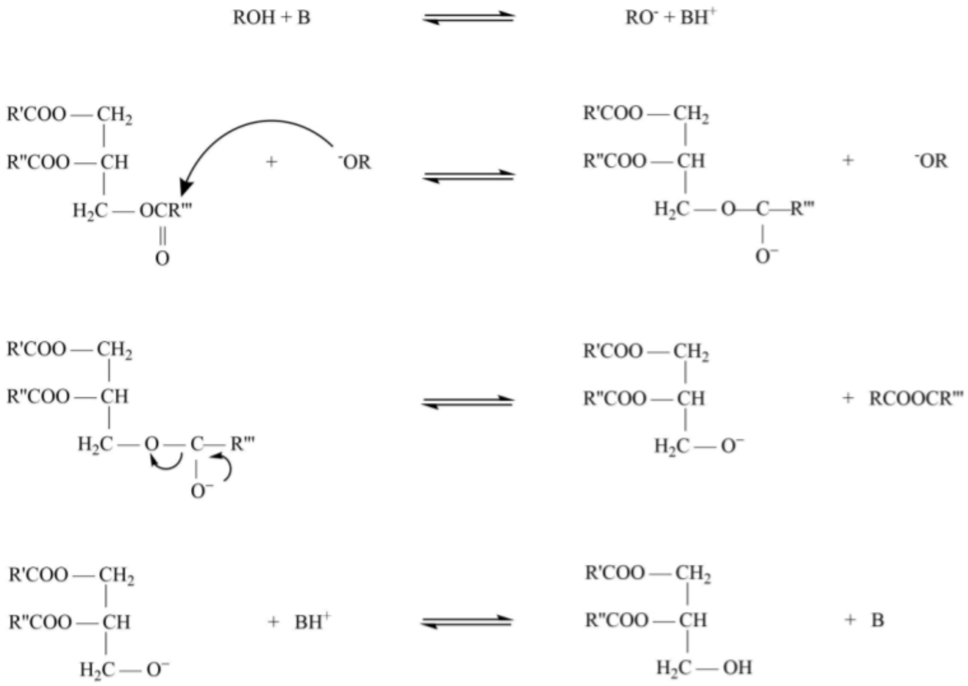

Figure 2.1: The reaction mechanism for the transesterification reaction[2]

2.4 Integral Method

In order to determine the reaction order of a reactor using the integral method, the reaction order is guessed, and the differential equation modeling the system is integrated[3]. The reaction rate of a reaction can be described using a power law, which relates reaction rate to the concentrations of the reactants undergoing the reaction:

$$r = -k \prod_i C_i^{\alpha_i} \tag{2.4}$$

Where k is the rate constant, C_i is the concentration of component i and α_i is the reaction order with respect to component i. Assuming that the reaction order only depends on one component, A, the reaction rate can be expressed by,

$$r = -kC_A^{\alpha} \tag{2.5}$$

Where α is the overall reaction order. Combining equations (2.3) and (2.5) gives,

$$\frac{dC_A}{dt} = -kC_A^{\alpha} \Longrightarrow dC_A = -kC_A^{\alpha} dt \tag{2.6}$$

Integrating equation (2.6) with $C_A = C_{A0}$ at $t = 0$, for reaction orders 0, 1 and 2, a relation between the concentration of component A and the time can be found:

$$C_A = C_{A0} - kt, \qquad \alpha = 0 \tag{2.7}$$

$$\ln \frac{C_{A0}}{C_A} = kt, \qquad \alpha = 1 \tag{2.8}$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt, \qquad \alpha = 2 \tag{2.9}$$

The reaction order of a reaction can be determined from experimental data by plotting the expressions in equations (2.7), (2.8) and (2.9), and checking which plot fits best with a linear curve.

3 Experimental Procedure

3.1 Apparatus

Figure 3.1 shows the setup of the reactor used during the experiment. The picture was collected from the lab document[2].

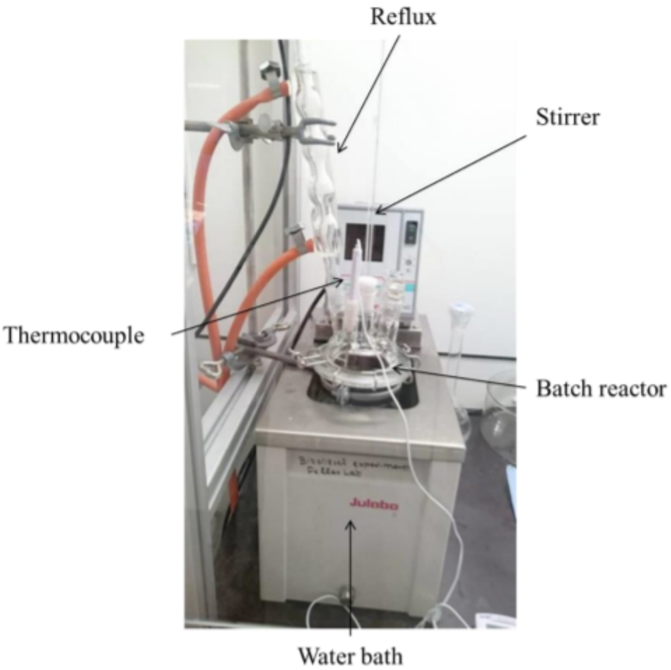

Figure 3.1: The set up for the experiment[2]

3.2 Execution

The experiment consisted of two main parts: The preparation of biodiesel, and the analysis of the product.

3.2.1 Preparation of Biodiesel

- Made sure that the equipment was clean and dry. Tap water contamination in the reactor would have caused the conversion of SBO to decrease. When water is present in the formation of biodiesel, it hydrolyses the triglycerides into diglycerides and fatty acids, which lowers the yield of the reaction. In the presence of bases, the fatty acids are converted into soap molecules. Which leads to impurities in the biodiesel. If there is a lot of soap, it can cause the formation of a gel-like substance, which makes it difficult to separate the biodiesel from the by-products. In a continuous reactor, the soap might cause plugging.[4]

- 280 mL of SBO was measured out, and poured into the batch reactor. SBO was first added, and then the stirring rod, before the lid of the reactor was fastened. The thermometer was placed in one neck, and a reflux condenser was placed over another neck. The last two necks were sealed with stoppers.
- The reactor was stirred at 285 rpm. The water level was approximately 1 cm above the surface level of reactor solution before the heat of the water bath was turned on.
- 71 mL MeOH was measured out in a 150 mL Erlenmeyer flask. 1.65 g of NaOH was weighed out and added to the beaker. This took some time, due to some of the NaOH sticking to the weighing dish. When all the NaOH was in the Erlenmeyer flask, it was covered with parafilm. The solution was then stirred with a magnetic stirrer. Methanol is used instead of ethanol because of the physical and chemical advantages of methanol. Since the alcohol chain is the shortest one possible, it provides better conversion under the same reaction time when reacting with triglycerides. It also easily dissolves in NaOH.[5]
- When the pellets in the Erlenmeyer flask had dissolved completely, and the temperatures in both the batch reactor and the Erlenmeyer flask reached 50 °C, the methoxide solution was added using a funnel, and the timer was started.
- An ice bath was prepared.
- After 3 minutes, 5 mL samples was extracted into a centrifuge tube. The centrifuge tube was shaken slightly, and placed in the ice bath to slow down the chemical reaction. In total 12 samples were collected this way, at the time intervals shown in Table 3.1. The pipette tube was changed between each sample to prevent contamination. The time and temperature was monitored and recorded for each sample. Some of the samples got air bubbles in the pipette, and especially sample 6 was less than 5 mL, due to air bubbles in the pipette.
- When all the samples were collected, the outside of the centrifuge tubes were dried off. The tubes were placed in the centrifuge. The centrifuge was run for 10 min at 4000 rpm.

3.2.2 Product Analysis

- By using a pipette, approximately 250 mg of the top layer of each sample were weighed out in small glass vials. For samples 8 and 11 there was spillage outside the vial. Therefore, the measured weight of the sample is too high.
- 5 mL IST were added to all of the samples.
- 1 mL of the sample solutions in the glass vials were transferred to GC vials using pipettes. A GC analysis was performed by the Kishore, the teaching assistant for the experiment.

Table 3.1 shows the time when each sample was extracted, the temperature in the reactor when the sample was extracted, and the weight of the sample used in the product analysis. Before the methoxide solution were added, when the time = 0, the temperature in the batch reactor was below 50℃.

Table 3.1: Time for each sample, temperature of the samples and the weight of the samples

Sample	Time [min]	Temperature [°C]	Weight [mg]
1	3	51.6	259.8
2	4	51.7	248.2
3	5	51.8	253.8
4	6	51.3	257.4
5	7	51.4	252.8
6	8	50.8	267.4
7	9	50.7	252.9
8	12	50.2	249.4
9	15	50.0	253.2
10	18	49.9	252.5
11	22	49.7	263.3
12	28	50.2	246.9

4 Results and Discussion

Using the expressions derived in Section 2.4, the concentration of SBO in the samples was plotted as a function of time. The plots including a linear regression line are shown in Figure 4.1, Figure 4.2 and Figure 4.3, for the 0th, 1st and 2nd order respectively. Each plot also includes the R^2-value, which indicates how well the linear regression line fits the data. The data points for samples 6, 8 and 11 have been excluded from the linear regression. This is because the values deviates from the others by a lot, this is most likely due to measuring errors during the product analysis step. For sample 6, the most likely cause of the deviancy was that the amount of IST solution added during the product analysis was too small, causing the actual concentration of IST in the sample to be less than what was assumed in the calculations. For samples 8 and 11, the deviation was most likely caused by spillage outside the vials during the weighing of the samples, therefore the measured weights of the samples were too high.

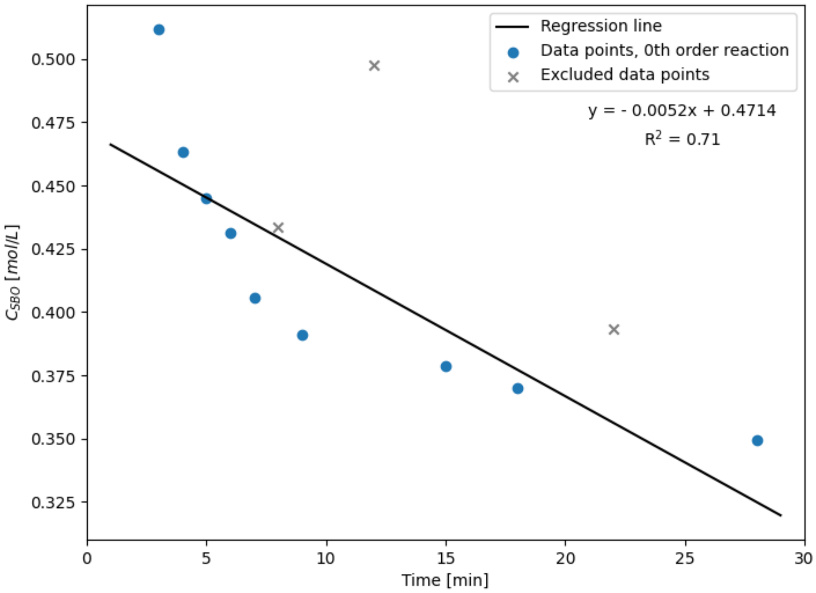

Figure 4.1: Concentration of SBO, C_{SBO}, plotted as a function of time.

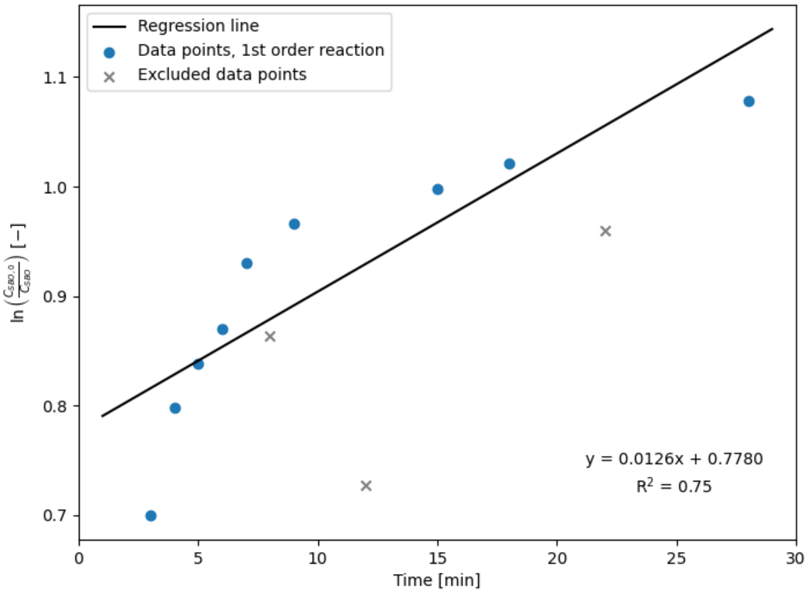

Figure 4.2: $\ln\left(\frac{C_{\mathrm{SBO},0}}{C_{\mathrm{SBO}}}\right)$ plotted as a function of time.

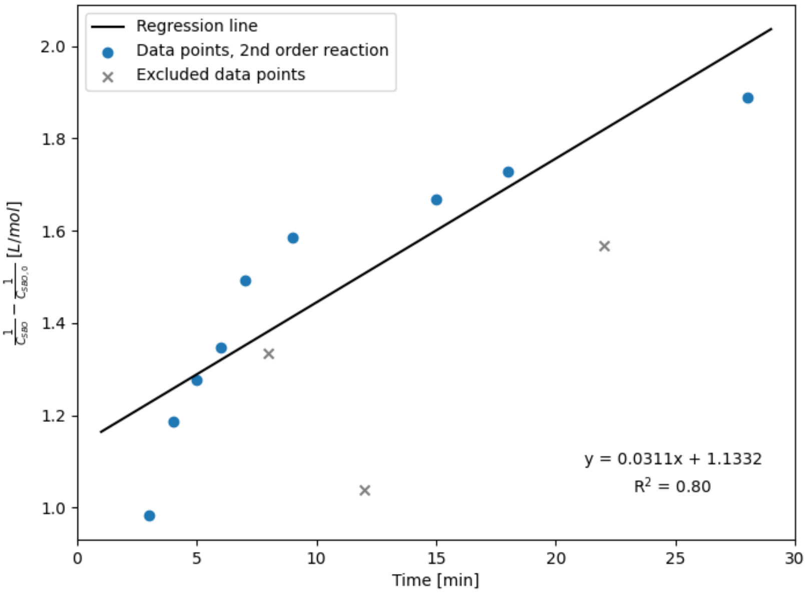

Figure 4.3: $\frac{1}{C_{\mathrm{SBO}}} - \frac{1}{C_{\mathrm{SBO},0}}$ plotted as a function of time.

The literature states that the reaction is a 2nd order reaction.[2] The results of the experiment is in line with this. The R^2-value of the plot of the 2nd order expression is the highest, which indicates that the reaction is a 2nd order reaction.

In Figure 4.4 the conversion of SBO is plotted as a function of time. From the figure, it is clear the the reaction slowed down over time, as the concentration of unreacted SBO decreased.

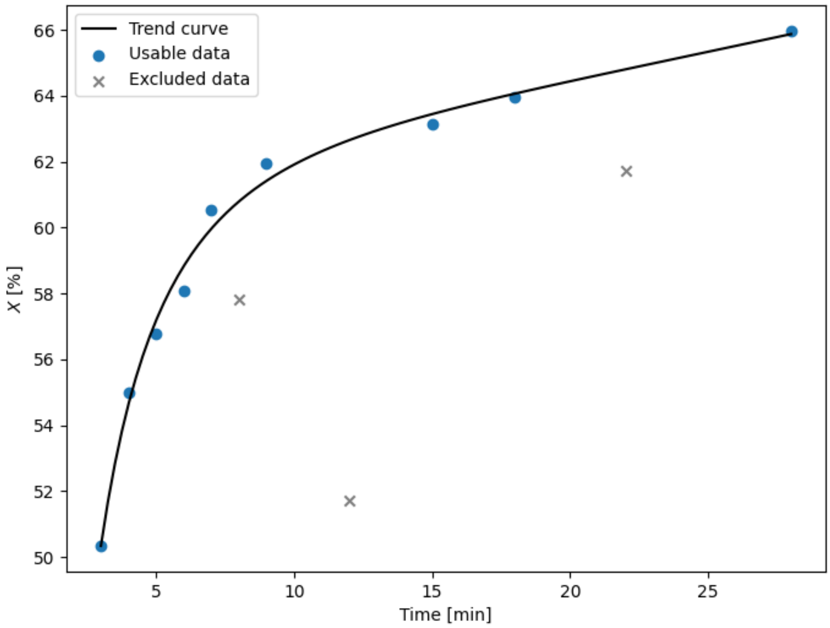

Figure 4.4: The conversion of SBO, X, as a function of time

It was assumed that the reaction stopped when the respective sample was put in the ice bath. In real life, this is not the case. It takes some time to cool down a 50 °C solution, so the reaction would continue after the sample was put in the ice bath. In addition, the last samples were in the ice bath for a much shorter amount of time compared to the first samples. The last sample was only in the ice bath for three minutes. Figure 4.4 shows that the curve did not flat out, as expected from ideal conversion graphs of transesterification. This clearly indicates that the reaction had not stopped for the last samples, which is most likely due to poor cooling.

The added amount of IST was assumed to be constant for each sample. This was not the case, as there were air bubbles in the pipette for some of the measurements. Sample number 6 was abnormal in the graphs, and it was observed to be extra much air bubbles in this sample, so the results clearly gets affected when the IST concentration changes. From the graphs, it is clear that there is some variation in the data points, which is probably due to changes in the IST concentration between each sample. Sample 8 and 11 are also not following the trend in the graphs (can clearly be seen in Figure 4.4), and as earlier mentioned, these samples went through spillage, causing the calculated IST concentration to be wrong. This strengthens the theory about abnormal results when the IST concentration is changed.

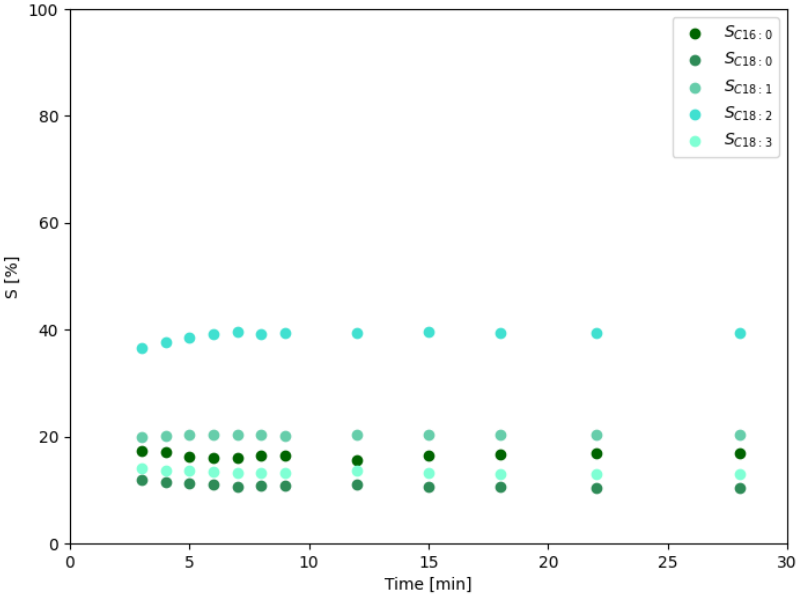

Figure 4.5: The selectivity, S, of the different FAMEs as a function of time

In Figure 4.5 the selectivities of the different FAMEs are plotted as a function of time. The different FAME's selectivities were approximately constant during the experiment, and therefore not changing with time. However, the selectivity was not completely constant in the beginning. The reason for this can be that the temperature changed at the start. The temperature was a bit to high in the beginning, and the batch reactor cooled down a bit before stabilizing at around 8-10 minutes. The temperatures varied from 51.8 °C to 49.7 °C during the experiment, as shown in Table 3.1. The fact that the selectivities were almost constant during the experiment is indicating that the the different fatty acids are equally exposed for nucleophilic attack by the methoxide. Because of this, the difference in selectivity for the different FAME products is due to the composition of the soybean oil.

4.1 Other Sources of Error

There are many possible sources of error in this experiment. To get a better understanding of the error sources, the experiment should have been performed several times, as it would have been easier to see how the mistakes affected the results between the completions. There was not enough time to do the experiment more than once, so these errors are based on this one time the experiment was completed:

One possible source of error is that when the MeOH and NaOH solution was added to the batch reactor, the temperature in both the solution and reactor was too high. They were both above 50 °C. When the MeOH solution was added, it was expected for the temperature to drop, but it increased instead. This shows that the temperature of the solution was too high. During the synthesis of the methoxide solution, the magnetic stirrer was set to 56 °C at one point, so the temperature of the solution might have been at that level.

During the experiment, the mixing might have been non-perfect. The propeller was bent. This indicates that it somehow got broken and did not mix properly. This might have caused some error. Despite of several sources of error, there are still reasonable trends in most of the graphs, indicating that most of the samples were affected equally by the errors. The conversion graph did not reach a plateau as expected, which is most likely due to poor cooling.

5 Conclusion

In this experiment, biodiesel was produced in a transesterification reaction. The reaction took place in a batch reactor in a water bath with a temperature that was approximately constant at 50 °C. Samples were extracted from the reactor at different time intervals. Then, the samples were analyzed by gas chromatography. The conversion of soy bean oil, the selectivity of the different fatty acid methyl esters formed, and the reaction order was investigated. It was discovered that the conversion of soy bean oil slowed down as the reaction went on and the concentration of unreacted soy bean oil decreased. The conversion graph, Figure 4.4, did not flat out like expected. This was due to the last samples not being in the ice bath for long enough, so the reaction did not stop. The selectivity for the different fatty acid methyl esters were different, but approximately constant with time. The reason for the different selectivities is most likely due to the composition of the soy bean oil. The reaction was determined to be a 2nd order reaction, using the integral method, which is in accord with the literature. The error that contributed the most in this experiment was probably insufficient cooling of the samples, which had an impact on the conversion graph. It was observed that there was a lot of variation in the data, which is most likely due to small differences in the amounts of IST added to each sample during the product analysis.

Trondheim, January 9, 2022

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References

[1] Bjørn Pedersen. Biodiesel. `https://snl.no/biodiesel`, Last updated July 2021. Accessed: 2021-10-18.

[2] Kishore Rajedran. Felleslab-re1: Biodiesel production in a batch reactor. `https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/RE1_biodiesel.pdf`, 2021.

[3] H. Scott Fogler. *Elements of Chemical Reaction*. Pearson, Pearson New International Edition, 4. edition, 2014. ISBN 978-1-292-02616-9.

[4] Raj Mosali. Keep water content in methanol to a minimum. `http://biodieselmagazine.com/articles/4235/keep-water-content-in-methanol-to-a-minimum`, Last updated June 2010. Biodiesel Magazine, Accessed: 2021-10-29.

[5] Idris Atadashi Musa. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egyptian Journal of Petroleum*, 25 (1):21–31, 2016. ISSN 1110-0621. doi: https://doi.org/10.1016/j.ejpe.2015.06.007. URL `https://www.sciencedirect.com/science/article/pii/S1110062115000914`.

A Data Tables

A.1 Reaction conditions

Table A.1 shows the assigned reaction conditions:

Table A.1: Reaction conditions

Reaction Condition	Value
Temperature [°C]	50
Stirring speed [rpm]	290
Mole fraction [MeOH/SBO]	6
C_{NaOH} [wt%]	0.5
Total volume [mL]	350

A.2 Physical Data

Table A.2 shows relevant physical data for the compounds used or formed during the experiment[2].

Table A.2: Molar weight and density for the relevant compounds.[2]

Compound	Molar weight [g/mol]	Density [g/mL]
MeOH	32.04	0.792
NaOH	40.00	2.130
SBO	875.1	0.913
IST	270.5	0.853
BIOD	291.5	0.891
C16:0	270.5	-
C18:0	298.5	-
C18:1	296.5	-
C18:2	294.5	-
C18:3	292.5	-

A.3 GC Results

Table A.3 shows the peak areas of the compounds detected during the GC.

A.4 Calculated values

In Table A.4, the calculated weight percentages for each compound detected in the gas chromatography is presented.

Table A.5 shows the calculated weight percentage of biodiesel, the real weight percentages of IST, biodiesel and unreacted SBO and the conversion of SBO for each sample.

In Table A.6 the selectivity of the FAMEs formed during the experiment is presented.

Table A.3: Peak areas from the GC

Sample	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3
1	1426.327	1688.406	1084.945	1799.686	3265.389	1256.009
2	1401.277	1621.583	1038.185	1810.653	3381.625	1222.670
3	1478.956	1700.580	1129.302	2025.072	3828.402	1338.497
4	1507.521	1686.486	1138.521	2090.309	3991.327	1359.561
5	1504.548	1645.487	1105.482	2087.595	4044.577	1331.736
6	1589.384	1685.985	1160.368	2151.044	4139.650	1389.086
7	1607.825	1676.555	1164.341	2154.600	4176.892	1403.787
8	1084.109	1452.969	849.885	1549.721	2991.355	1019.244
9	1638.100	1683.907	1169.851	2231.521	4308.451	1422.149
10	1671.859	1680.251	1172.130	2252.690	4332.816	1426.396
11	1703.151	1677.432	1168.838	2254.158	4353.442	1423.548
12	1717.645	1677.837	1165.373	2255.834	4367.480	1425.500

Table A.4: The calculated weight percentages for each compound detected in the gas chromatography.

Sample	wt% C16:0	wt% C17:0	wt% C18:0	wt% C18:1	wt% C18:2	wt% C18:3
1	13.557	16.048	10.312	17.106	31.038	11.938
2	13.376	15.479	9.910	17.284	32.280	11.671
3	12.860	14.787	9.819	17.608	33.288	11.638
4	12.804	14.324	9.670	17.754	33.900	11.547
5	12.838	14.041	9.433	17.813	34.512	11.363
6	13.119	13.916	9.578	17.754	34.168	11.465
7	13.196	13.760	9.556	17.684	34.282	11.522
8	12.117	16.239	9.499	17.321	33.433	11.392
9	13.153	13.521	9.393	17.918	34.595	11.419
10	13.336	13.403	9.350	17.970	34.563	11.378
11	13.538	13.334	9.291	17.918	34.604	11.315
12	13.622	13.306	9.242	17.890	34.636	11.305

Table A.5: The calculated weight percentage of biodiesel, the real weight percentages of IST, biodiesel and unreacted SBO and the conversion of SBO for each sample.

Sample	$wt\%_{\mathrm{BIOD}}$	$wt\%_{\mathrm{C17:0}_R}$	wt% $wt\%_{\mathrm{BIOD_R}}$	$wt\%_{\mathrm{SBO_{unc}}}$	X
1	83.952	8.778	45.920	45.302	50.339
2	84.521	9.151	49.967	40.883	54.999
3	85.213	8.967	51.676	39.357	56.766
4	85.676	8.853	52.950	38.197	58.093
5	85.959	8.999	55.095	35.906	60.544
6	86.084	8.550	52.890	38.560	57.835
7	86.240	8.996	56.381	34.623	61.954
8	83.761	9.111	46.993	43.896	51.703
9	86.479	8.986	57.476	33.538	63.150
10	86.597	9.009	58.206	32.785	63.969
11	86.666	8.672	56.364	34.964	61.716
12	86.694	9.195	59.907	30.899	65.972

Table A.6: The selectivity of the FAMEs formed during the experiment.

Sample	$S_{C16:0}$	$S_{C18:0}$	$S_{C18:1}$	$S_{C18:2}$	$S_{C18:3}$
1	17.370	11.971	19.992	36.522	14.145
2	17.026	11.429	20.068	37.737	13.739
3	16.246	11.240	20.292	38.625	13.597
4	16.091	11.010	20.352	39.127	13.420
5	16.372	10.705	20.352	39.701	13.162
6	16.080	10.850	20.250	39.239	13.258
7	16.403	10.806	20.132	39.295	13.298
8	16.469	11.067	20.317	39.487	13.548
9	15.581	10.593	20.344	39.547	13.144
10	16.574	10.528	20.371	39.450	13.077
11	16.808	10.451	20.292	39.458	12.992
12	16.905	10.392	20.252	39.478	12.974

B Calculations Done Before the Lab

B.1 Amount of Reactants and Catalyst

The molar fraction in Table A.1 gives,

$$\frac{n_{\text{MeOH}}}{n_{\text{SBO}}} = 6 \tag{B.1}$$

Where n_i is the number of moles of component i. Equation (B.1) can be rearranged into this expression:

$$n_{\text{MeOH}} = 6 \cdot n_{\text{SBO}} \tag{B.2}$$

The total volume is given in Table A.1, and can be expressed as,

$$V_{\text{tot}} = V_{\text{MeOH}} + V_{\text{SBO}} \tag{B.3}$$

Where V_{MeOH} and V_{SBO} are the added volumes of MeOH and SBO, respectively. The relationship between the volume and the number of moles of any compound, i, can be expressed using,

$$V_i = \frac{n_i \cdot M_i}{\rho_i} \tag{B.4}$$

Where M_i is the molar weight of the compound, and ρ_i is the density of the compound.

Inserting equations (B.2) and (B.4) into equation (B.3), inserting the values in Table A.2 and solving for n_{SBO}, gives:

$$n_{\text{SBO}} = \frac{V_{\text{tot}}}{6 \cdot \frac{M_{\text{MeOH}}}{\rho_{\text{MeOH}}} + \frac{M_{\text{SBO}}}{\rho_{\text{SBO}}}} = \frac{350}{6 \cdot \frac{32.04}{0.792} + \frac{875.1}{0.913}}\,\text{mol} = 0.2914\,\text{mol}$$

Rearranging equation (B.4), using n_{SBO} and the data from Table A.2, the necessary volume of SBO, $V_{\text{SBO}} = 279.3\,\text{mL}$.

Inserting V_{SBO} and V_{tot} into equation (B.3), the volume of MeOH is determined: $V_{\text{MeOH}} = 70.7\,\text{mL}$.

The amount of NaOH catalyst in the solution should be 0.5 wt%, which gives the following relation:

$$m_{\text{NaOH}} = 0.005 \cdot m_{\text{tot}} \tag{B.5}$$

Where m_{NaOH} is the mass of NaOH and m_{tot} is the total mass of the solution.

The total mass is the sum of the mass of SBO, MeOH and NaOH. The mass of SBO and MeOH can be calculated using,

$$m_i = \rho_i \cdot V_i \tag{B.6}$$

The total volume of the solution can then be expressed as:

$$m_{\text{tot}} = m_{\text{SBO}} + m_{\text{MeOH}} + m_{\text{NaOH}} = \rho_{\text{SBO}} \cdot V_{\text{SBO}} + \rho_{\text{MeOH}} \cdot V_{MeOH} + m_{\text{NaOH}} \tag{B.7}$$

Inserting equation (B.5) into equation (B.7), the total mass of the solution becomes:

$$m_{\text{tot}} = \frac{0.913 \cdot 297.3 + 0.792 \cdot 70.7}{0.995}\,\text{g} = 329.1\,\text{g}$$

Inserting m_{tot} into equation (B.5), the required mass of NaOH is determined: $m_{\text{NaOH}} = 1.65\,\text{g}$.

The calculated amounts of the reactants required in the experiment is shown in Table B.1.

Table B.1: The calculated amounts of the reactants required in the experiment.

Compound	Number of moles [mol]	Mass [g]	Volume [mL]
MeOH	1.7484	56.01	70.7
NaOH	-	1.65	-
SBO	0.2914	255.0	279.3

B.2 Weight Percentage of IST

The weight percentage of IST in the samples can be calculated using:

$$wt\%_{\text{IST}} = \frac{m_{\text{IST}}}{m_{\text{tot}}} = \frac{V_{\text{IST}} \cdot C_{\text{IST}}}{m_{\text{tot}}} = \frac{5\,\text{mL} \cdot 5\,\text{mg}\,\text{mL}^{-1}}{250\,\text{mg} + 5\,\text{mL} \cdot 5\,\text{mg}\,\text{mL}^{-1}} \cdot 100\,\% = 9.09\,\%$$

C Calculating the Results

C.1 Weight Percentage

To calculate the weight percentage of compound i, $wt\%_i$, the following formula was used:

$$wt\%_i = \frac{A_i}{A_{\text{tot}}} \cdot 100\% \tag{C.1}$$

Where A_i is the measured area of component i during the gas chromatography, and A_{tot} is the sum of all the areas. The weight percentage of biodiesel, $wt\%_{\text{BIOD}}$ was calculated by adding the weight percentages of the compounds analyzed in the GC, except for the IST, C17:0:

$$wt\%_{\text{BIOD}} = \sum_{i=C16:0, i \neq C17:0}^{C18:3} wt\%_i \tag{C.2}$$

The actual weight percentage of IST, $wt\%_{\text{C17:0}_\text{R}}$, in the samples were calculated using:

$$wt\%_{C17:0_{\text{R}}} = \frac{m_{\text{IST}}}{m_{\text{tot}}} = \frac{V_{\text{IST}} \cdot C_{\text{IST}}}{m_{\text{tot}}} = \frac{5\,\text{mL} \cdot 5\,\text{mg}\,\text{mL}^{-1}}{m_{\text{sample}} + 5\,\text{mL} \cdot 5\,\text{mg}\,\text{mL}^{-1}} \cdot 100\,\% \tag{C.3}$$

Where m_{sample} is the mass of the samples presented in Table 3.1. The following equation was used to calculate the actual weight percentage of biodiesel, $wt\%_{\text{BIOD}_\text{R}}$, in the samples:

$$wt\%_{\text{BIOD}_\text{R}} = wt\%_{C17:0_{\text{R}}} \cdot \frac{wt\%_{\text{BIOD}_{\text{GC}}}}{wt\%_{C17:0_{\text{GC}}}} \tag{C.4}$$

The calculated $wt\%_{\text{BIOD}_\text{R}}$ are presented in Table A.5. The weight percentage of unreacted SBO, $wt\%_{\text{SBO}_{\text{unc}}}$ was calculated using,

$$wt\%_{\text{SBO}_{\text{unc}}} + wt\%_{\text{BIOD}_\text{R}} + wt\%_{\text{C17:0}_\text{R}} = 100\,\% \tag{C.5}$$

C.2 Concentrations

The volume of the samples can be expressed using:

$$V_{\mathrm{sample}} = V_{\mathrm{SBO_{unc}}} + V_{\mathrm{BIOD}} \tag{C.6}$$

The mass of the samples were calculated using:

$$m_{\mathrm{tot}} = m_{\mathrm{IST}} + m_{\mathrm{sample}} \tag{C.7}$$

The volumes of BIOD and unreacted SBO in the samples can be calculated using:

$$V_i = \frac{wt\%_i m_{\mathrm{tot}}}{\rho_i} \tag{C.8}$$

Where i is $\mathrm{SBO_{unc}}$ or $\mathrm{BIOD_R}$, and ρ_i is the associated density. The initial concentration of the soybean oil, $C_{0,\mathrm{SBO}}$, was calculated by assuming pure SBO at the start of the reaction:

$$C_{0,\mathrm{SBO}} = \frac{m_{\mathrm{sample}}}{V_{\mathrm{sample}} M_{\mathrm{SBO}}} \tag{C.9}$$

Where M_{SBO} is the molar weight of SBO. The concentration unreacted SBO in the samples were calculated using,

$$C_{\mathrm{SBO_{unc}}} = \frac{wt\%_{\mathrm{SBO_{unc}}} \cdot m_{\mathrm{tot}}}{V_{\mathrm{sample}} M_{\mathrm{SBO}}} \tag{C.10}$$

C.3 Conversion

The initial molar amount of SBO in the sample were calculated assuming a pure sample of SBO:

$$n_{\mathrm{SBO}} = \frac{m_{\mathrm{sample}}}{M_{\mathrm{SBO}}} \tag{C.11}$$

The molar amount of unreacted SBO were calculated using the following equation:

$$n_{\mathrm{SBO_{unc}}} = \frac{wt\%_{\mathrm{SBO_{unc}}} \mathrm{m_{tot}}}{M_{\mathrm{SBO}}} \tag{C.12}$$

The conversion, X, can then be calculated,

$$X = \frac{n_{SBO} - n_{SBO_{unc}}}{n_{SBO}} \cdot 100\,\% \tag{C.13}$$

C.4 Selectivity

To calculate the selectivities, the molar amount of each FAME is needed, which is dependant of the mass of the FAME in the samples. The data from the GC is not complete, as there were additional peaks in the GC results, which were not included in the analyzed data. This makes it impossible to calculate the weight percentage, and therefore the molar amounts exactly. In addition, the IST solution consisted of more compounds than just IST, causing the total mass of the analyzed sample to be wrong.

The contribution of these errors will be consistent for all the FAMEs in a sample, and will be cancelled out from the division in equation (C.15). By introducing the constant k, which is the product of the actual mass of the GC-sample, and some correctional factor for the weight percentage, the molar amount of each FAME can be calculated from:

$$n_i = \frac{wt\%_i \cdot k}{100\,\% M_\mathrm{i}} \tag{C.14}$$

Furthermore, the selectivity of FAME i was calculated using,

$$S_i = \frac{n_i}{\sum_{\mathrm{FAME}} n_j} \cdot 100\% \tag{C.15}$$

D Example Calculation

D.1 Weight Percentage

To demonstrate the calculations, an example calculation will be made for C16:0 from sample 1. Due to the results being calculated by python, which does not round off values between calculations, some of the expressions does not give the same result as the given answer. The weight percentage was calculated using equation (C.1):

$$wt\%_{C16:0} = \frac{1426.327}{1426.327 + 1688.406 + 1084.945 + 1799.686 + 3265.389 + 1256.009} \cdot 100\,\% = 13.557\,\%$$

The weight percentage of biodiesel was then calculated using equation (C.2):

$$wt\%_{\mathrm{BIOD}} = 13.557\,\% + 10.312\,\% + 17.106\,\% + 31.038\,\% + 11.938\,\% = 83.952\,\%$$

The actual weight percentage of IST in the sample was calculated from equation (C.3):

$$wt\%_{C17:0_\mathrm{R}} = \frac{5\,\mathrm{mL} \cdot 5\,\mathrm{mg\,mL^{-1}}}{259.8\,\mathrm{mg} + 5\,\mathrm{mL} \cdot 5\,\mathrm{mg\,mL^{-1}}} \cdot 100\,\% = 8.778\,\%$$

The actual weight percentage of biodiesel in the sample was calculated from equation (C.4):

$$wt\%_{\mathrm{BIOD_R}} = 8.778\,\% \cdot \frac{83.952\,\%}{16.048\,\%} = 45.920\,\%$$

By rearranging equation (C.5), the weight percentage of unreacted SBO was calculated:

$$wt\%_{\mathrm{SBO_{unc}}} = 100\,\% - 45.920\,\% - 8.778\,\% = 45.302\,\%$$

D.2 Concentrations

The mass of the sample were calculated from equation (C.7):

$$m_{\mathrm{tot}} = 5\,\mathrm{mL} \cdot 5\,\mathrm{mg\,mL^{-1}} + 259.8\,\mathrm{mg} = 284.8\,\mathrm{mg}$$

The volumes of BIOD and unreacted SBO were calculated using equation (C.8):

$$V_{\mathrm{SBO_{unc}}} = \frac{45.302\,\% \cdot 284.8 \cdot 10^{-3}\mathrm{g}}{100\,\% \cdot 0.913\,\mathrm{g\,mL^{-1}}} = 0.141\,\mathrm{mL}$$

$$V_{\mathrm{BIOD_R}} = \frac{45.920\,\% \cdot 284.8 \cdot 10^{-3}\mathrm{g}}{100\,\% \cdot 0.891\,\mathrm{g\,mL^{-1}}} = 0.147\,\mathrm{mL}$$

The volume of the sample was calculated using (C.6):

$$V_{\text{sample}} = 0.141\,\text{mL} + 0.147\,\text{mL} = 0.288\,\text{mL}$$

The initial concentration of SBO was calculated from equation (C.9):

$$C_{0,\text{SBO}} = \frac{259.8 \cdot 10^{-3}\,\text{g}}{0.288 \cdot 10^{-3}\,\text{L} \cdot 875.1\,\text{g}\,\text{mol}^{-1}} = 1.031\,\text{mol}\,\text{L}^{-1}$$

The concentration of unreacted SBO were calculated from equation (C.10):

$$C_{\text{SBO}_{\text{unc}}} = \frac{45.302\,\% \cdot 284.8 \cdot 10^{-3}\,\text{g}}{100\,\% \cdot 0.288 \cdot 10^{-3}\,\text{L} \cdot 875.1\,\text{g}\,\text{mol}^{-1}} = 0.512\,\text{mol}\,\text{L}^{-1}$$

D.3 Conversion

The initial molar amount of SBO in the sample were calculated from equation (C.11):

$$n_{\text{SBO}} = \frac{259.8 \cdot 10^{-3}\,\text{g}}{875.1\,\text{g}\,\text{mol}^{-1}} = 2.9688 \cdot 10^{-4}\,\text{mol}$$

The molar amount of unreacted SBO were calculated using equation (C.12):

$$n_{\text{SBO}_{\text{unc}}} = \frac{45.302\,\% \cdot 284.8 \cdot 10^{-3}\,\text{g}}{100\,\% \cdot 875.1\,\text{g}\,\text{mol}^{-1}} = 1.4743 \cdot 10^{-4}\,\text{mol}$$

Then, the conversion was calculated from equation (C.13):

$$X = \frac{2.9688 \cdot 10^{-4}\,\text{mol} - 1.4743 \cdot 10^{-4}\,\text{mol}}{2.9688 \cdot 10^{-4}\,\text{mol}} \cdot 100\,\% = 50.339\,\%$$

D.4 Selectivity

To calculate the molar amount of C16:0, equation (C.14) was used:

$$n_{C16:0} = \frac{13.557\,\% \cdot k}{100\,\% \cdot 270.5\,\text{g}\,\text{mol}^{-1}} = 5.0127 \cdot 10^{-4}\,\text{mol}\,\text{g}^{-1} \cdot k$$

The molar amount of the other FAMEs were calculated using the same formula. Then, the selectivity could be calculated from equation(C.15):

$$S_{C16:0} = \frac{5.0127 \cdot 10^{-4}\,\text{mol}\,\text{g}^{-1} \cdot k}{(5.0127 + 3.4546 + 5.7693 + 10.5398 + 4.0821) \cdot 10^{-4}\,\text{mol}\,\text{g}^{-1} \cdot k} \cdot 100\% = 17.370\,\%$$

E Health, Safety and Environment

Lab coat and glasses are always mandatory in the lab, and were used throughout the entire experiment. There were some additional hazards associated with the chemicals used in this experiment, which made some extra safety precautions necessary.

Methanol was used during the experiment. It can be toxic if it is swallowed, inhaled or in contact with the skin. Therefore protective gloves were worn while handling methanol. Methanol is also highly flammable, and causes damage to the organs. For these reasons, it was handled carefully, and kept away from heat.

NaOH is corrosive on skin and eyes, so gloves were necessary while measuring out the necessary amounts.

The IST was dissolved in heptane. Heptane is flammable, can cause skin irritation and can be deadly if swallowed. It is also poisonous to aqueous environments. The heptane solution was handled with care. The solution was kept under a fume hood at all times, and handled with gloves.

The COVID-19 restrictions has been repealed, so it was not necessary to do much due to infection control. However, as a precaution, the lab space and equipment used during the experiment was cleaned and wiped with disinfectant before leaving the lab.

F Python Code

Below is the code used to do all calculate and plot the results from the experiment.

```
import numpy as np
import matplotlib.pyplot as plt

# Define "constants"
V_ist = 5   # [mL]
C_ist = 5   # [mg/mL]
m_ist = V_ist * C_ist
m_sample = np.array([259.8, 248.2, 253.8, 257.4, 252.8, 267.4,
                     252.9, 249.4, 253.2, 252.5, 263.3, 246.9])  # [mg]
rho_IST = 0.853   # [g/mL]
rho_BIOD = 0.891   # [g/mL]
rho_SBO = 0.913   # [g/mL]
Mw_BIOD = 291.5   # [g/mol]
Mw_SBO = 875.1   # [g/mol]
Mw_16 = 270.46   # [g/mol]
Mw_18_0 = 298.51   # [g/mol]
Mw_18_1 = 296.50   # [g/mol]
Mw_18_2 = 294.48   # [g/mol]
Mw_18_3 = 292.46   # [g/mol]
times = np.array([3, 4, 5, 6, 7, 8, 9, 12, 15, 18, 22, 28])  # [min]


# Function to calculate Rsquared
def Rsquared(x, y, f_regression):
    y_avg = np.average(y)
    SStot = np.sum((y - y_avg) ** 2)
    SSres = np.sum((y - f_regression(x)) ** 2)
    return 1 - (SSres / SStot)


A_C_16, A_C_17, A_C_18_0, A_C_18_1, A_C_18_2, A_C_18_3 = \
    np.loadtxt("Datafiles/GC_data.txt", usecols=(1, 2, 3, 4, 5, 6), skiprows=1, unpack=True)
# Calculating the weight percentages using equation (C.1)
A_tot = A_C_16 + A_C_17 + A_C_18_0 + A_C_18_1 + A_C_18_2 + A_C_18_3
wt_C_16 = (A_C_16 / A_tot) * 100
wt_C_17 = (A_C_17 / A_tot) * 100
wt_C_18_0 = (A_C_18_0 / A_tot) * 100
wt_C_18_1 = (A_C_18_1 / A_tot) * 100
wt_C_18_2 = (A_C_18_2 / A_tot) * 100
wt_C_18_3 = (A_C_18_3 / A_tot) * 100

# Calculating the weight percentage of biodiesel, eq. (C.2)
wt_BIOD = wt_C_16 + wt_C_18_0 + wt_C_18_1 + wt_C_18_2 + wt_C_18_3

# Calculating the actual weight percentage of IST, using eq. (C.3)
wt_C_17_real = (V_ist * C_ist) / (m_sample + V_ist * C_ist) * 100

# Calculating the actual weight percentage of BIOD, using eq. (C.4)
wt_BIOD_real = (wt_BIOD / wt_C_17) * wt_C_17_real

# Calculating the actual weight percentage of unreacted SBO, rearranging eq (C.5)
wt_SBO_unreacted = 100 - wt_BIOD_real - wt_C_17_real

# Concentrations
# Finding the total volume of the sample
# Equation (C.7)
```

```
m_tot = (m_ist + m_sample) / 1000  # Converted mg to g
# Equation (C.8)
V_SBO_unreacted = wt_SBO_unreacted / 100 * m_tot / rho_SBO
V_BIOD = wt_BIOD_real / 100 * m_tot / rho_BIOD
# Equation (C.6)
V_sample = (V_SBO_unreacted + V_BIOD) / 1000  # [mL] to [L]

# Finding the mass of SBO_unc
m_SBO_unreacted = (wt_SBO_unreacted / 100) * m_tot

# Finding the initial mass of SBO (assuming pure SBO sample)
m_SBO_initial = m_sample / 1000
# Equation (C.9)
c_SBO_initial = m_SBO_initial / (V_sample * Mw_SBO)
# Equation (C.10)
c_SBO_unreacted = m_SBO_unreacted / (V_sample * Mw_SBO)

# Separating the values that deviate much from the fitted curves
index_of_err = [5, 7, 10]
err_c_SBO_unc = []
err_c_SBO_ini = []
n = 0

x = times
x_err = []
for index in index_of_err:
    err_c_SBO_unc.append(c_SBO_unreacted[index - n])
    err_c_SBO_ini.append(c_SBO_initial[index - n])
    c_SBO_unreacted = np.delete(c_SBO_unreacted, index - n)
    c_SBO_initial = np.delete(c_SBO_initial, index - n)
    x_err.append(x[index - n])
    x = np.delete(x, index - n)
    n += 1
err_c_SBO_unc = np.array(err_c_SBO_unc)
err_c_SBO_ini = np.array(err_c_SBO_ini)

# Plotting the graph for the 0th order reaction
y0 = c_SBO_unreacted
y0_err = err_c_SBO_unc
params0 = np.polyfit(x, y0, 1)
f0 = np.poly1d(params0)
x_values = np.linspace(1, 29, 100)

fig = plt.figure(figsize=[8, 6])
ax = fig.add_subplot()
R20 = Rsquared(x, y0, f0)
plt.scatter(x, y0, label='Data points, 0th order reaction')
plt.scatter(x_err, y0_err, label='Excluded data points', color='grey', marker='x')
plt.plot(x_values, f0(x_values), label="Regression line", color="black")
ax.text(0.83, 0.8, f"y = - {-params0[0]:.4f}x + {params0[1]:.4f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
ax.text(0.83, 0.75, r"R$^2$" + f" = {R20:.2f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
plt.xlim(0, 30)
plt.xlabel('Time [min]')
plt.ylabel(r'$C_{SBO}$ $[mol/L]$')
plt.legend()
plt.savefig('0th_order')
plt.show()
```

```
# Plotting the graph for the 1st order reaction
y1 = np.log(c_SBO_initial / c_SBO_unreacted)
y1_err = np.log(err_c_SBO_ini / err_c_SBO_unc)
params1 = np.polyfit(x, y1, 1)
f1 = np.poly1d(params1)

fig = plt.figure(figsize=[8, 6])
ax = fig.add_subplot()
R21 = Rsquared(x, y1, f1)
plt.scatter(x, y1, label='Data points, 1st order reaction')
plt.scatter(x_err, y1_err, label='Excluded data points', color='grey', marker='x')
plt.plot(x_values, f1(x_values), label="Regression line", color="black")
ax.text(0.83, 0.15, f"y = {params1[0]:.4f}x + {params1[1]:.4f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
ax.text(0.83, 0.10, r"R$^2$" + f" = {R21:.2f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
plt.xlim(0, 30)
plt.xlabel('Time [min]')
plt.ylabel(r'$\ln\left(\frac{C_{SBO,0}}{C_{SBO}}\right)$ $[-]$')
plt.legend()
plt.savefig('1st_order')
plt.show()

# Plotting the graph for the 2nd order reaction
y2 = 1 / c_SBO_unreacted - 1 / c_SBO_initial
y2_err = 1 / err_c_SBO_unc - 1 / err_c_SBO_ini
params2 = np.polyfit(x, y2, 1)
f2 = np.poly1d(params2)

fig = plt.figure(figsize=[8, 6])
ax = fig.add_subplot()
R22 = Rsquared(x, y2, f2)
plt.scatter(x, y2, label='Data points, 2nd order reaction')
plt.scatter(x_err, y2_err, label='Excluded data points', color='grey', marker='x')
plt.plot(x_values, f2(x_values), label="Regression line", color="black")
ax.text(0.83, 0.15, f"y = {params2[0]:.4f}x + {params2[1]:.4f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
ax.text(0.83, 0.10, r"R$^2$" + f" = {R22:.2f}", horizontalalignment='center',
        verticalalignment='center', transform=ax.transAxes, fontsize=10, color='black')
plt.xlim(0, 30)
plt.xlabel('Time [min]')
plt.ylabel(r'$\frac{1}{C_{SBO}} - \frac{1}{C_{SBO,0}}$ $[L/mol]$')
plt.legend()
plt.savefig('2nd_order')
plt.show()

# Finding the conversion:
# Equation (C.11)
n_SBO_intial = m_SBO_initial / Mw_SBO
# Equation (C.12)
n_SBO_unreacted = m_SBO_unreacted / Mw_SBO
# Equation (C.13)
X_SBO = (n_SBO_intial - n_SBO_unreacted) / n_SBO_intial * 100

# Separating the values that deviate much from the fitted curves
index_of_err = [5, 7, 10]
err_X_SBO = []
n = 0
```

```
for index in index_of_err:
    err_X_SBO.append(X_SBO[index - n])
    X_SBO = np.delete(X_SBO, index - n)
    n += 1

params = np.polyfit(np.log(x), X_SBO, 3)
f = np.poly1d(params)
x_values = np.linspace(3,28,100)

fig = plt.figure(figsize=[8, 6])
plt.scatter(x, X_SBO, label='Usable data')
plt.plot(x_values, f(np.log(x_values)), color='black', label='Trend curve')
plt.scatter(x_err, err_X_SBO, color='grey', label='Excluded data', marker='x')
plt.xlabel(r"Time [min]")
plt.ylabel(r"$X$ [$\%$]")
plt.legend()
plt.savefig('Conversion')
plt.show()

# Finding the selectivity
# Equation (C.14)
n_C_16 = wt_C_16 / (Mw_16 * 100)
n_C_18_0 = wt_C_18_0 / (Mw_18_0 * 100)
n_C_18_1 = wt_C_18_1 / (Mw_18_1 * 100)
n_C_18_2 = wt_C_18_2 / (Mw_18_2 * 100)
n_C_18_3 = wt_C_18_3 / (Mw_18_3 * 100)

# Equation (C.15)
n_tot = n_C_16 + n_C_18_0 + n_C_18_1 + n_C_18_2 + n_C_18_3
S_16 = n_C_16 / n_tot * 100
S_18_0 = n_C_18_0 / n_tot * 100
S_18_1 = n_C_18_1 / n_tot * 100
S_18_2 = n_C_18_2 / n_tot * 100
S_18_3 = n_C_18_3 / n_tot * 100

# PLotting the selectivity
fig = plt.figure(figsize=[8, 6])
plt.scatter(times, S_16, label=r'$S_{C16:0}$', color='darkgreen')
plt.scatter(times, S_18_0, label=r'$S_{C18:0}$', color='seagreen')
plt.scatter(times, S_18_1, label=r'$S_{C18:1}$', color='mediumaquamarine')
plt.scatter(times, S_18_2, label=r'$S_{C18:2}$', color='turquoise')
plt.scatter(times, S_18_3, label=r'$S_{C18:3}$', color='aquamarine')
plt.xlabel(r"Time [min]")
plt.ylabel(r"S [%]")
plt.xlim(0, 30)
plt.ylim(0, 100)
plt.legend()
plt.savefig('Selectivity')
plt.show()
```