Felles Lab – RE1

BIODIESEL PRODUCTION IN A BATCH REACTOR

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Introduction

Biodiesel is obtained through a transesterification reaction of soybean oil (SBO) by methanol, using sodium hydroxide as a catalyst. The reaction is taking place in a batch reactor. Samples are collected in intervals, then separated in a centrifuge to glycerine and biodiesel. The biodiesel is analysed by gas chromatography (GC), to investigate the progress of the transesterification reaction from SBO to fatty methyl esters (FAME).

The conversion over time should be monitored for all the samples and plotted. The catalyst product selectivity and the reaction order by use of the integral method should also be investigated.

Theory

Biodiesel production is gaining increasing attention as it in principle can reduce CO2 emissions significantly, along with many other environmental advantages [1]. The most common way to obtain biodiesel is the transesterification reaction of vegetable oils in the presence of a low molecular weight alcohol and a catalyst. The transesterification reaction involves the exchange of organic groups R1, R2, R3 belonging to a glyceride, with the organic group of an alcohol R, as is shown in Fig. 1.
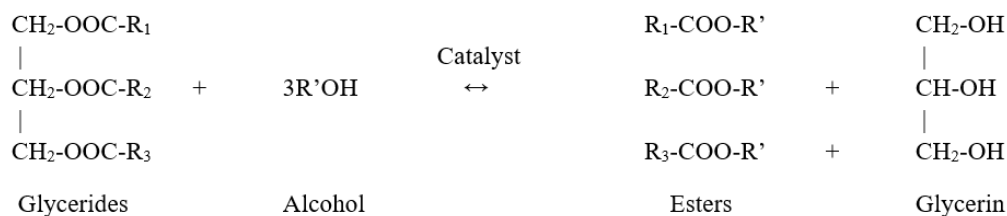
$$
\begin{array}{llllll}
CH_2\text{-}OOC\text{-}R_1 & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\
| & & \text{Catalyst} & & & | \\
CH_2\text{-}OOC\text{-}R_2 & + & 3R'OH \quad \leftrightarrow & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\
| & & & & & | \\
CH_2\text{-}OOC\text{-}R_3 & & & R_3\text{-}COO\text{-}R' & + & CH_2\text{-}OH \\
\\
\text{Glycerides} & & \text{Alcohol} & \text{Esters} & & \text{Glycerin}
\end{array}
$$

Figure 1. The transesterification reaction. R1, R2, R3 is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R= CH3) [2]

The overall process is usually a sequence of three consecutive steps, which are reversible reactions. In the first step, diglyceride is obtained from triglycerides, then monoglyceride from diglyceride, and lastly glycerine is formed from monoglycerides (Fig. 2). In all these reactions, fatty acid methyl esters (FAME) are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product, as shown by Noureddini et al. [3], and will be used in this exercise. The transesterification reaction at this ratio has been described by a second-order mechanism [3, 4].
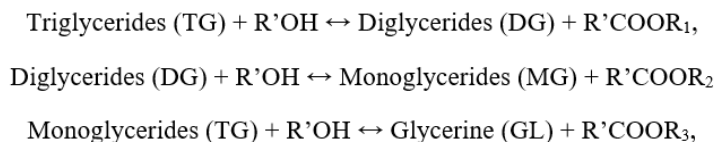
$$Triglycerides\ (TG) + R'OH \leftrightarrow Diglycerides\ (DG) + R'COOR_1,$$

$$Diglycerides\ (DG) + R'OH \leftrightarrow Monoglycerides\ (MG) + R'COOR_2$$

$$Monoglycerides\ (TG) + R'OH \leftrightarrow Glycerine\ (GL) + R'COOR_3,$$

Figure 2. The three consecutive and reversible steps of the transesterification reaction [2].

The reaction product is an immiscible two-phase mixture of biodiesel including excess methanol and glycerine. During separation (e.g. centrifugation), the hydrophilic and denser glycerine migrates to the bottom of the mixture creating a separate layer, while the less dense biodiesel stays on top together with the unconverted oil.

Reaction mechanism

The mechanism of the base-catalysed transesterification of vegetable oils is shown in Fig. 3. The first step is the reaction of the base with the alcohol, producing an alkoxide and a protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which an alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst and reacts with a second molecule of alcohol, starting a new catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerine.

Commercially, alkaline-catalysed is often preferred over acid-catalysed transesterifications, both due to the higher rate of the alkaline catalyst and the fact that alkaline catalysts are less corrosive to industrial equipment.
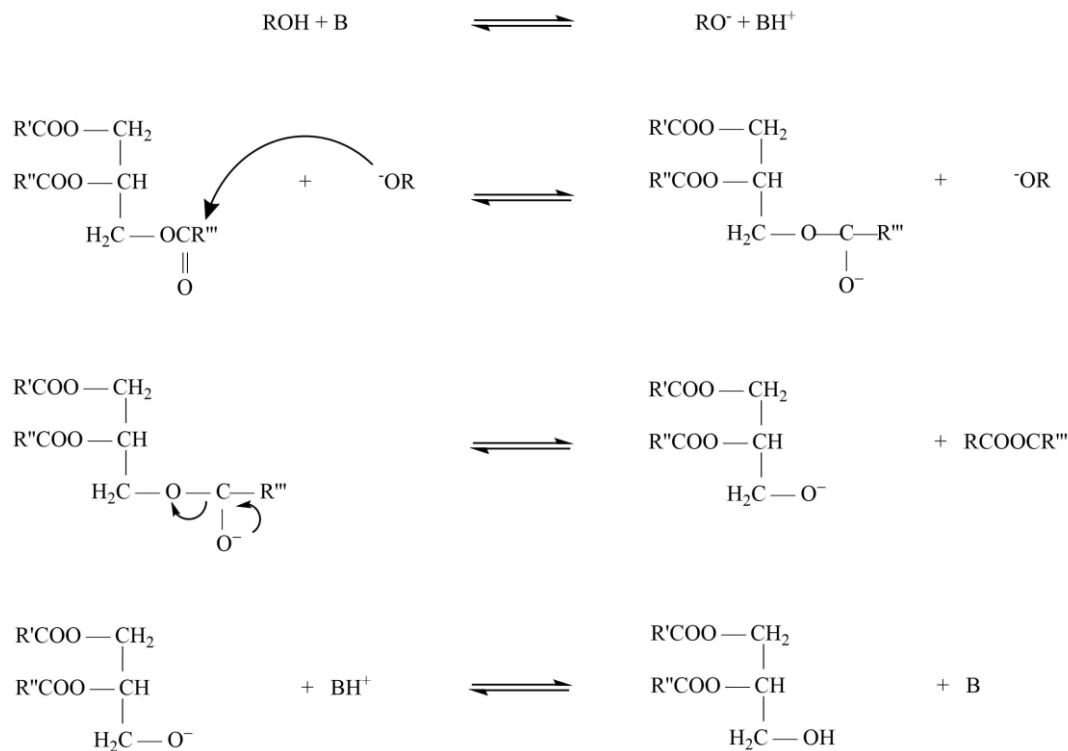
$$ROH + B \rightleftharpoons RO^- + BH^+$$

Figure 3. Mechanism of the alkali-catalysed transesterification of vegetable oils (B=base) [5].

Kinetics

To determine the reaction rate constant the following equation (3.1) can be used in combination with the integral method (see Scott Fogler, Elements of Chemical Reaction Engineering, section 5.2.2):

$$\frac{dC_A}{dt} = r_A \tag{3.1}$$

where C_A is the concentration of A, and r_A is the reaction rate. There are different factors, which influence the reaction rate, such as the influence of the temperature and the catalyst.

Before the lab

The reaction conditions will be given from the supervisor for each group before the lab. See Table 4.

Table 1. Reaction conditions regarding reactor temperature, stirring speed, mole fraction MeOH/SBO and NaOH catalyst weight percentage.

Reaction condition	Value
Temperature [˚C]	A
Stirring speed [rpm]	B
Mole fraction [MeOH/SBO]	C
C_{NaOH} [% w/w]	D

For all groups: $V_{tot} \sim 350mL$

- A work plan must be handed in to the supervisor **two days** before the lab. This work plan must be approved in order to gain access to the lab. If it is not approved, revisions must be made.
- Read the HSE form for the experiment. Write a brief summary of the potential hazards associated with the chemicals used in the lab, and how to handle them.
- Write a plan for the experiment.
- Calculate the amounts of reactants and catalyst from the given reaction conditions.
- Calculate the weight percentage (%w/w) of internal standard (IST) that is injected in the GC if the sample weight is 250 mg. The concentration of the IST solution is 5 mg/mL.

Experimental setup

The production of biodiesel will be performed in a batch reactor, as shown in Figure 4.

- Five-necked batch reactor (500 ml)
- Electric stirrer for the batch reactor
- Reflux
- Thermocouple
- Water bath
- Erlenmeyer flask
- Stopwatch
- Automatic pipette
- 12 plastic pipette tubes (for each sample)
- Funnel
- 12 Centrifuge tubes (for each sample)
- 12 Glass vials (for each sample)
- Magnet + magnetic stirrer
- Electronic analytical balance scale
- Materials:
    - Soybean oil (SBO)
    - Methanol (MeOH) 99%
    - Sodium hydroxide (NaOH) pellets
    - Methyl heptadecanoate (IST)
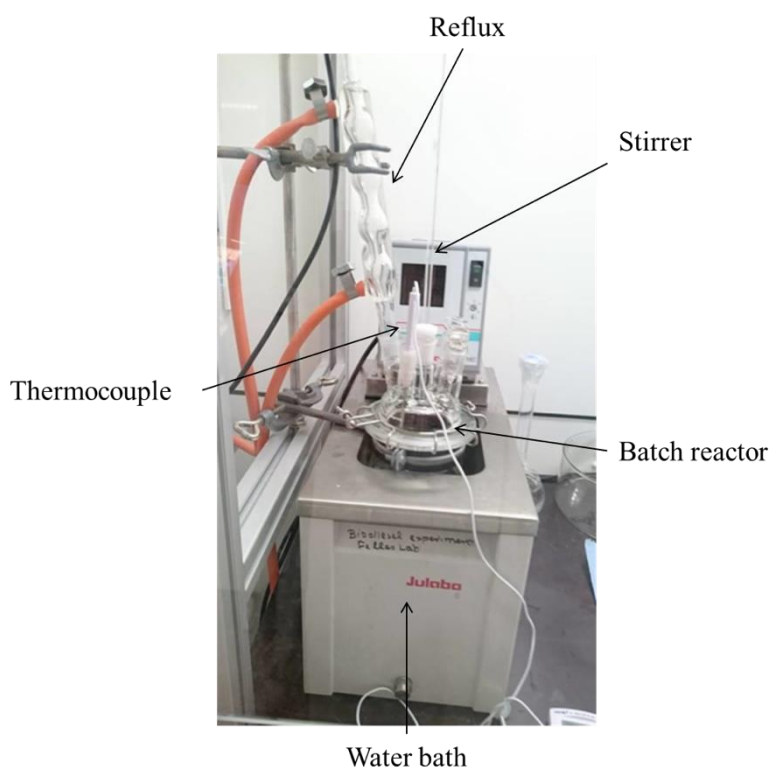   in heptane solution, 5 mg/ml

Figure 4. Setup

Experimental procedure

Biodiesel preparation:

- Measure the given amount of SBO and place it in the batch reactor. It can be advisable to add the SBO and then the stirring rod before fastening the lid of the reactor, to avoid coating the neck of the reactor with oil. Put the thermometer in one neck and put stoppers in the two necks that are not being used. Start stirring the reactor with the stirring speed given by the supervisor.
- Check the water level of the water bath is at the same level as the solution in the reactor, before turning on the heat of the water bath.
- Prepare an ice bath, which will be used to cool the samples after extraction in order to stop the reaction.
- Measure the given amount of MeOH in a beaker. Weigh the given amount of NaOH and add the pellets to the beaker with MeOH - immediately cover the beaker with Parafilm. Stir the solution with a magnetic stirrer.
- Once the temperature of the SBO in the reactor reaches the set point temperature, and the pellets in the MeOH are dissolved, add the methoxide (MeO$^-$) solution to the reactor, using a funnel. Start the stopwatch when all the solution has been added, as this is the start of the reaction.
- Start extracting samples (~5 mL) with the automatic pipette after 3 minutes, being careful not to put the pipette into the stirrer in the bottom of the reactor. See **Table 2** in the appendix for an overview over extraction timing. Remember to change the pipette tube for each sample! Monitor and record the **temperature** as well as **time** for each collected sample.
- Place each sample in numbered centrifuge tubes (1-12), leave the tubes in the ice bath, and shake the cooled tubes slightly to speed up the cooling process.
- After collecting all the samples, wipe off the centrifuge tubes and place them in the centrifuge. Let the centrifuge run for 10 min at 4000 rpm.
- Note: Your glassware should be clean and DRY. When water is present, de-esterification takes place via hydrolysis (and forms soaps, which causes problems such as plugging, gel formation, an increased viscosity that may hamper the product separation), which should be avoided.
- Note: Sodium methoxide solution is a strong base and should be handle with care.

Analysis of product.
The following steps are for preparation of the sample for GC-analysis:

- Weigh ~ 250 mg of each sample in small glass vials using a pipette. Be careful to extract only the liquid from the upper layer. Remember to write down the weight for each sample.
- Add 5 mL of IST to each sample. Do not extract IST directly from the volumetric flask to avoid contamination of the standard solution!
- Transfer approximately 1 mL of the sample solution to the GC vials.

The GC analysis will be performed by the supervisor; therefore no handling of gases is needed.

After the lab – calculations and report

- Calculate the mass (grams) of the unreacted SBO (SBO$_{unc}$), BIOD and IST in the samples that you prepared for the GC.
- Calculate the concentrations of the initial amount of soybean oil in the reactor (SBO$_{ini}$), BIOD and SBO$_{unc}$.
- Use the integral method to investigate the reaction order - justify your results!
  Average molecular weight (MW) and density of SBO and BIOD are given in the appendix.
- Calculate the conversion (%) for each sample and plot the conversion as a function of time.

- Calculate the selectivity of all the FAME in all your samples.
- Explain why there is difference in selectivity for the individual FAME products.
- Note: Detailed calculations for **one of the samples** must be included in the appendix.
  Tables containing the calculated values for conversion and selectivity must be included in the appendix for all the samples.
    - Even though data is presented as a figure in the report, a table containing the values must still be included in the appendix. The calculations from the work plan should also be included in the appendix.

GC results

The compounds in the sample will be separated in the GC due to different affinity for the column, and this will cause them to leave the column and be detected separately. The duration a given compound spends in the column is called retention time. The detector is a flame-ionizing detector (FID), and as the name implies the compounds are burned and produce ions that are detected, which will create a peak in chromatogram (plot), and the integral (area, pA*s) of the peak is related to the amount of the specific compound.

In order to quantify, the sample is mixed with an IST, in this case IST methyl heptadecanoate (C17:0). Since the exact amount of the IST added to the sample is known, the detected area of the IST can be related to the detected fatty acid methyl esters (FAME) mixture corresponding to the biodiesel products (BIOD). As the number of carbons in the compounds will affect the signal, a response factor (RF) is typically used to relate compounds with different carbon content. Here we can assume the RF to be equal to one, as the FAME and IST has similar carbon content. An example of a chromatogram for this experiment is shown in Figure 5.
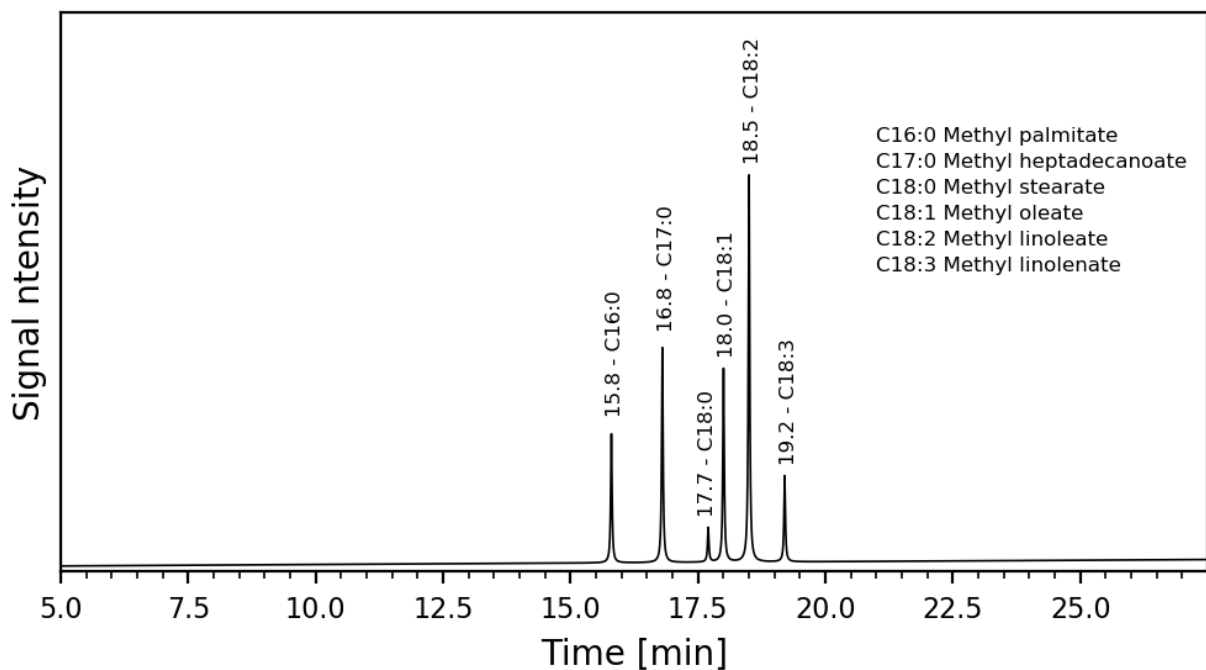

Figure 5. Simulated GC chromatogram of the FAME in this experiment.

Calculations

Sum the areas (pA*s) for C16:0, C17:0, C18:0, C18:1, C18:2, C18:3 to obtain the total area, then get the weight percentage of each compound (here an example for C16:0)

$$\%w/w_{C16:0} = \frac{Area_{C16:0}}{Area_{Tot}}$$

Get the weight percentage of biodiesel for each sample

$$\%w/w_{BIOD} = \ \%w/w_{C16:0} + \ \%w/w_{C18:0} + \%w/w_{C18:1} + \ \%w/w_{C18:2} + \ \%w/w_{C18:3}$$

Use the relation below to find the actual weight percentage of BIOD$_R$ ($\%w/w_{BIOD_R}$) in the sample

$$\frac{\%w/w_{BIOD_{GC}}}{\%w/w_{C17:0_{GC}}} = \frac{\%w/w_{BIOD_R}}{\%w/w_{C17:0_R}}$$

where $\%w/w_{C17:0_R}$ is the calculated weight percentage of internal standard solution for each sample.

Calculate the amount of SBO$_{unc}$ in each sample (SBO$_{unc}$ is not detected by the GC)

$$\%w/w_{SBO_{unc}} + \%w/w_{BIOD_R} \ + \ \%w/w_{C17:0_R} \ = \ 100\%$$

Concentrations

All calculations are based on the samples you weigh (approximately 250 mg) after centrifugation. Calculate the mass of BIOD and SBO$_{unc}$ from the weight percentages and known weight of the samples. Find the volume of the samples from the calculated masses and the given densities.

$$V_{sample} = V_{SBO_{unc}} + \ V_{BIOD}$$

1. Calculate the initial concentration of soybean oil (SBO$_{ini}$) (imagine weighing a sample of pure SBO).

2. Plot 0th, 1st and 2nd order using the integral method.

Conversion

Plot conversion as a function of time. n_{SBO} is the amount of moles in the sample if the entire amount was SBO

$$n_{SBO} = \frac{m_{sample}}{M_{SBO}}$$

Conversion can then be calculated as

$$\% \ \text{Conversion} = \frac{n_{SBO} - n_{SBO_{unc}}}{n_{SBO}}$$

Selectivity

Calculate the selectivity of each FAME in the BIOD.

$$\% \ \text{Selectivity} = \frac{n_{FAME,i}}{\sum n_{FAME,i}} \cdot 100\%$$

Plot the selectivity (in mol percentage) as a function of time.

The report

Within one week of performing the experiment a draft can be handed in for feedback– otherwise none is given. The final report must be handed in one week after receiving the feedback, or two weeks after performing the experiment if the draft was not handed in within the deadline.

It is recommended to use BibTeX, Mendeley, EndNote, or other reference managers to handle the references. The report must include an abstract. For more details, see Felles Lab: Short Report Guidelines by Heinz, A Preisig.

References

[1] Gerhard Knothe, Jon Van Gerpen, and Jrgen Krahl. *The Biodiesel handbook*. AOCS Press, Champaign, Illinois, first edition edition, 2005.

[2] J.M. Marchetti, V.U. Miguel, and A.F. Errazu. Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews*, 11(6):1300– 1311, 2007.

[3] H. Noureddini and D. Zhu. Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemists' Society*, 74(11):1457–1463, 1997. [4] Bernard Freedman, Royden O. Butterfield, and Everett H. Pryde. Transesterification kinetics of soybean oil 1. *Journal of the American Oil Chemists'Society*, 63(10):1375–1380, 1986.

[5] Ayhan Demirbas. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31(56):466 – 487, 2005.

Appendix

Table 2. Overview of when to take samples from the batch reactor

Time [min]	Sample
3	1
4	2
5	3
6	4
7	5
8	6
9	7
12	8
15	9
18	10
23	11
28	12

Table 3. Molar weights and densities of the components injected into the GC.

Component	MW [g/mol]	Density [g/mL]
SBO	875.1	0.913
BIOD	291.5	0.891
IST	270.5	0.853

Table 4. Molar weights of the methyl esters.

Methyl esters	C16:0	C18:0	C18:1	C18:2	C18:3
MW [g/mol]	270.46	298.51	296.50	294.48	292.46