TECH-LAB: EXPERIMENT 30.

PRODUCTION OF BIOFUELS - INSTRUCTION MANUAL

The purpose of this experiment is to get knowledge on the production and processing of renewable energy sources (biofuels). During the experiment, students will carry out the basic transesterification (methanolysis) of vegetable oil and will measure selected physicochemical parameters of biofuels (density, viscosity, flash point). As a result, students will be able to use the micro-scale apparatus, they will calculate the material and costs balance as well as they are suppose to plan, perform and supervise unit operations. After the experiment the students gain ability to perform qualitative and quantitative evaluation of the industrial process and ability to present results data and to critically analyze the process.

Part 1. Transesterification of vegetable oil.

Equipment	Reagents
vertical reactor with bottom outlet and stirrer (mixer) peristaltic pump graduated cylinder 250 mL graduated cylinder 500 mL beakers: 100mL, 250 mL, 500mL vacuum evaporator + round-bottom flask *set of equipment needed for filtration under reduced pressure*: suction flask (filtering flask) Büchner funnel (suction funnel) conical flask (Erlenmeyer flask) scissors, **Safety measures:** Latex gloves and laboratory goggles	canola oil methanol potassium hydroxide drying agent (silica gel or Na_2SO_4) pH indicator paper (test-paper) filter paper

NOTE:
Students are required to bring their own goggles (it is forbidden to start an exercise without goggles).

You have to do the following sequence of activities:

1. Turn on the cooling water in the reactor condenser, turn on the stirrer, check whether the bottom tap in the reactor is closed.
2. Prepare a solution of 100 cm^3 methanolic KOH at a concentration of 1 M.
3. Pour into a measuring cylinder 250 cm^3 of rapeseed oil and use a peristaltic pump to transfer it into the reactor.
4. Pour 50 cm^3 methanolic solution of KOH (prepared in point #2) into the same graduated cylinder and pump it into the reactor.
5. Carry out transesterification reaction for 30 minutes.

NOTE: At the same time (during realization 5-8 points) use the pycnometer to measure the density of rapeseed oil taken for the reaction. Method of measurement and cleaning of the pycnometer is described in the next section, related to the investigation of physicochemical properties of fuels.

6. Turn off stirrer and allow the layers (phases) to separate, remove the bottom layer (methanol-glycerol) to a **previously weighed** 250 mL flask with joint Φ 29 (a vacuum safe glass should be used).
7. Turn on the stirrer and pump the remaining methanolic KOH solution. Carry out the second step of transestrification for additional 20 minutes.
8. Turn off the stirrer, after separation of layers collect the lower methanol-glycerol layer to the same flask as at point #6, combining it with the previous fraction. **Weigh the total mass of the flask with content** and connect it to a vacuum evaporator. Turn the lower pressure and evaporate methanol (temperature water bath 50°C, time about 15 minutes). Check the weigh of the flask with content and calculate the mass of the resulted residue.
9. Wash the oil layer in the reactor with 50 cm^3 of water containing 5 mL 10% H_2SO_4. After the layers are separated collect the bottom (aqueous) layer. Then, wash organic layer with portions of water (50 cm^3) to obtain a neutral pH: every time intensively stir for several minutes, then turn off the stirrer and pour off the lower layer (aqueous), checking acidity by the use of pH indicator paper. Combine the aqueous layers in a cylinder, and after finishing the perfusion measure their volume.

NOTE: During the implementation of 9-11 points, set the apparatus for measurement of ignition temperature of biofuels obtained by the previous group of students. The method of measurement is given in the next section, related to the investigation of physicochemical parameters of fuels.

10. Assemble a kit for filtration under reduced pressure. If you use Buchner funnel, you will have to prepare appropriate shaped filter paper (you will need pencil, scissors and a Petri shalk, however, if shott funnel is to be used, do not use filtration paper), place it in the funnel and put some amount of drying agent (about 1 cm thick). Filtrate the fatty acid esters through the funnel and drying agent. Wash the precipitate with acetone from a squeeze-bottle two or three times.
11. Wash the reactor with water and detergent (using the same peristaltic pump).
12. Transfer the filtrate obtained in #10 to a weighed round-bottom flask. Weight again, install on vacuum evaporator and evaporate the methanol and acetone (temperature of water bath should be 50 ° C, time about 15 minutes). Reweigh the flask with content and calculate the mass of the resulted mixture. Repeat evaporation until the mass of flask with esters remain constant.
13. Calculate:
    the mass of product
    yield of akaline transesterification
    volume / weight of by-products (assuming d =1kg dm^{-3}).
14. Measure the viscosity.

Part 2. Analysis of the obtained biofuel.

Equipment	Reagents
Pycnometer with thermometer Thermostat (set at 20°C) Höppler viscometer Stop watch Apparatus for measurement of ignition temperature Optional: Gas chromatograph with MS detector **Safety measures:** Latex gloves and goggles	Fatty acid methyl esters Rapeseed oil (canola oil) Diesel fuel (optionally).

NOTE: students are required to bring their own goggles (it is forbidden to start an exercise without goggles).

A. Measurement of density by pycnometer.

Density measurements are performed at 20°C with a pycnometer (Figure 8).

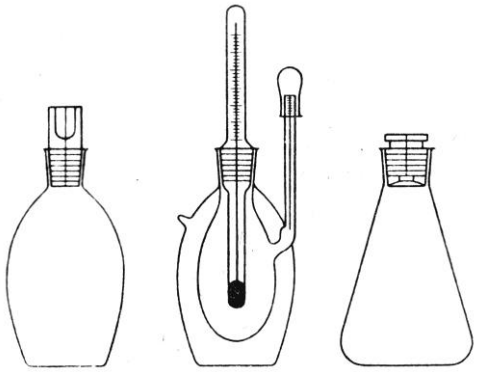


Figure 8. Pycnometers (middle pycnometer with a side tube, vacuum-jacketed and thermometer). Based on Grynberg, Ługowska, Zarzycki *„Technical analysis in the fat industry"* National Technical Publishing House, Warsaw 1954.

Weigh a clean, dry pycnometer (use analytical balance). Record the result ($m_{p1} \pm 0.001$ g). Fill the pycnometer with distilled water at 20°C, remove all excess of water from the surface and weight, note the result ($m_{p1} \pm 0.001$ g). Calculate the volume of the pycnometer ($V_{pycnometer}$, [cm^3]) using the value of the water density at 20°C (0.99823 g/cm^3). Pour out the water, wash the pycnometer with acetone, dry and reweigh (m_{p2}), fill with biofuel at a temperature of 20°C and weigh, record the mass ($m_b \pm 0.001$ g). Calculate the density of the biofuel: $\rho_b^{20} = (m_b - m_{p2}) / V_{pycnometer}$ [g/cm^3]. Present results in the table:

	measurement 1	measurement 2
m_{p1}		
m_{p2}		
m_w		
$V_{pycnometer}$		
m_b		
ρ_b^{20}		

Calculate the average results (arithmetic mean) from at least two determinations. If the results of two determinations differ by more than 0.005 g/cm^3 – the measurement has to be repeated.

B. Determination of dynamic viscosity with the Höppler viscometer

Introduction

Höppler viscometer is an apparatus consisting of a thermostated glass tube filled with analyzed liquid. Determination of viscosity is based on measurement of a time τ during which ball (of known

diameter d and density ρ_K) falls in the liquid and traveling a particular distance l (marked with lines on the glass tube). We assume that the ball falls in a tube with a uniform motion - the gravitation is balanced in by force of resistance R:

$$W = \frac{\pi d^3}{6}(\rho_K - \rho_C)g$$

$$R = \lambda \frac{u^2}{2} \rho_C \frac{\pi d^2}{4}$$

$$W = R$$

In the above equations, u is the velocity of the falling ball and λ is the coefficient of resistance. We assume that the ball movement is laminar, which means that the ball "moves without vortices between the layers of fluid". For this type of movement resistance coefficient is:

$$\lambda = \frac{24\eta}{ud\rho_C}$$

where η is dynamic viscosity of the liquid.

After transformation of the above equations and taking into account the speed $u = \frac{l}{\tau}$, we get:

$$\eta = \frac{d^2 g}{18l}(\rho_K - \rho_C)\tau = K(\rho_K - \rho_C)\tau$$

The parameter K is a ball constant, although it also depends on the distance l.
Scheme of viscometer is shown in Figure 9.

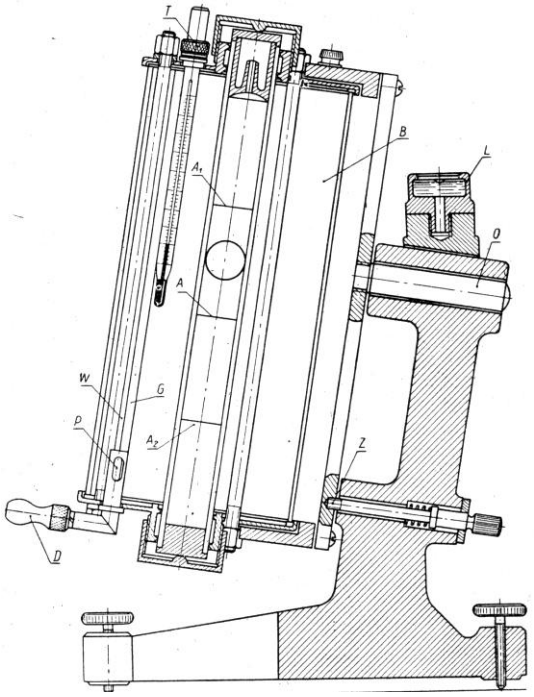


Figure 9.
Höppler viscometer: B – thermostating jacket, O – rotation axis, Z- rotation block, L - spirit level, T – thermometer, A – glass tube with marked levels A_1 i A_2, D and W – inlet and outlet for thermostating water.
(based on: Grynberg, Ługowska, Zarzycki *„Technical analysis in the fat industry"* National Technical Publishing House, Warsaw 1954).

Measurements of viscosity

Check whether the tube is clean and and dry. Close the cap from the bottom, then fill the analyzed liquid to about 25 mm below the upper edge. Then, place a ball into the tube (chose a ball that will be falling during time more than 10 and less than 180 seconds). The characteristic parameters of balls are presented in Table 9. Balls 1 and 2 are made of glass. In order to distinguish them use a meter through which the ball 2 passes and a ball 1 does not pass. Other balls are made of nickel steel.

Tabela 9. Parameters characteristic of viscometer balls.

ball number	ball diameter w 20°C [mm]	ball mass [g]	ball density at 20°C [g/cm^3]	ball constant K [cP·cm^3/g·s]	ball constant K [cP·cm^3/g·s]
1	15,8	4,59950	2,225	0,0098430	0,0097101
2	15,6	4,45620	2,227	0,074828	0,074398
3	15,5	16,05290	8,146	0,13136	0,13111
4	15,0	14,40450	8,146	1,2026	1,2003
5	13,5	9,91410	7,699	10,529	10,522
6	10,0	4,01810	7,674	40,01	40,01

(diameter of the disc included in the set (apparatus) = 15,63 mm)

Level the viscometer, set the temperature, close the tube with upper cap and turn on the circulation of thermostating liquid. After determining the temperature (approximately 20 minutes), turn the apparatus around the axis "O" (see Figure 9) to 180° and measure the time during which the ball falls from level A_1 to A_2 by the use of stop watch. Repeat the measurement several times each time turning the movable part of apparatus around 180°). Based on the obtained results, calculate the average time of falling of the ball (in seconds). *Note*: even small changes of temperature can cause large differences in the time of the ball falling. Pour the biofuel back into the bottle, remove and dry the ball.

Dynamic viscosity (η expressed in cP) of the tested liquid can be calculated from equation:

$$\eta = K\,(\rho_k - \rho_c)\,\tau$$

where η - dynamic viscosity [cP]

τ – time of Ball falling from level A_1 do A_2 [s]

ρ_k – density of ball's material [g cm^{-3}]

ρ_c – density of biofuel at temparature of measurement [g cm^{-3}]

K – ball constant [cP·cm^3/g·s]

Parameters of balls at 20°C are shown in Table 9. The final result is an average (arithmetic mean) of at least three measurements.

Washing the instrument. Any impurities cause a significant reduction in accuracy of measurement, so the instrument must be thoroughly cleaned. After measurement is finished and ball and analyzed liquid are removed, wash the viscometer with acetone and water/soap to completely remove oil or fatty esters. Repeat washing with distilled water and with acetone. Leave the apparatus to dry on air.

C. **Ignition temperature (flash point)[1] measurement in a closed crucible.**

During heating, even below the boiling point, fuel evolve volatile and flammable substances. **Flash point** is the lowest temperature at which the test product heated in a specific way gives vapors sufficient to produce explosive mixtures with air and these mixtures are able to ignite after contact with an external flame. The temperature at which vapors burn itself (after rejecting the flame source) for at least 3 seconds is called **temperature of burning**. Ignition temperature can be determined by the Marcusson method (the open crucible method). Scheme of the Marcusson apparatus is shown in Figure 10. In Pansky-Marcuss apparatus a crucible is place in sand bath. There is a tip of the thermometer in the crucible (it is about 5 mm away from the wall and 2 mm from the bottom of the crucible). The measurement is based on checking the ignition by movable igniter which contains a gas flame.

[1] Other names: flash temperature, ignition point, fire point.

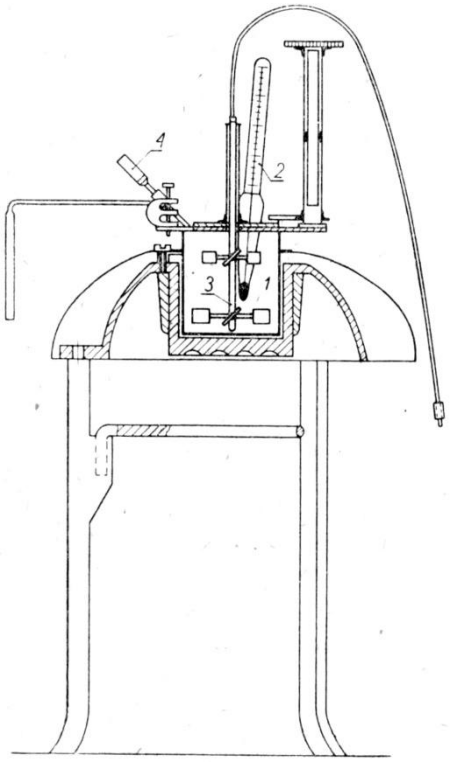


Figure 10.
Pensky Martens Apparatus: 1 – brass crucible placed in a steel vessel, 2-thermometer, 3-stirrer, 4- automatic fuse. Based on Grynberg, Ługowska, Zarzycki *„Technical analysis in the fat industry”* National Technical Publishing House, Warsaw 1954.

Figure 11.
Setaflash Apparatus for the flash point determination in closed crucible: 1 – brass crucible placed in a steel vessel, 2-thermometer, 3-stirrer.

In the experiment you will apply modern Setaflash 30000-03 apparatus (Figure 11). It is a portable device for determining the flash point of fuels, including biodiesel, up to the temperature of 300°C. The crucible is made of aluminum and it is embedded in a heating block. The temperature of heating block is controlled by the use of a digital controller. The temperature of crucible is measured by a platinum resistance thermometer. For safety, a light pulsing diode indicates that the temperature is above 55°C. The device is equipped with a small container of liquid petroleum gas used by burner to initiate ignition. Detection of ignition is automatic (inscription “FLASH” appears on the display). In option AUTO a temperature is set in the 0 to 300°C range. After the set temperature is reached, a clock measures 1 minute when the temperature is lower than 100°C or 2 minutes for temperatures higher than 100°C (the time is necessary to stabilize liquid/vapour equilibria). After this time you can make an attempt approaching ignition by the use of burner flame.

The exact algorithm for performance the measurement is given in the instructions supplied with the apparatus.

NOTE: Running the apparatus is possible only in the presence of the person leading the exercise.

CHECKLIST (Experiment 30: Production of Biofuels)

name of student: A:……..……..……, B: ……..……, C:…….……

Please, mark performed activities as "v" and write the time you started and finished the activity

lp.	What students have to do	student		TIME	
				Start	End
1	Reading of the cards of characteristics	**all**			
2	Cler the pycnometer and determine density of oil.	**B**			
3	Check the reactor, turn the stirrer on.	**A**			
4	Charge the reactor with oil.	**all**			
5	Charge the reactor with 50 mL of methanolic 1M KOH solution.	**A**			
6	Transesterification – first step (about 20 minutes).	**A**			
7	Measure the ignition temperature of biofuels.	**C**			
8	Wash the pycnometer, determine a density of biofuel.	**B**			
9	Turn off the stirrer and separate the layers.	**A**			
10	Pour off the bottom layer methanol-glycerol (to previously weighed round-bottomed flask**)**.	**A**			
11	Put 50 mL methanolic 1M KOH solution.	**A**			
12	Second step the trans-esterification (stir during 20 minutes).	**A**			
13	Turn off the stirrer, separate and pour off the bottom layer.	**A**			
14	Prepare 100 mL water solution of 5% H_2SO_4.	**B**			
15	Evaporate combined glycerolic fractions (from points 10 and 13) on vacuum evaporator.	**B**			
16	Put H_2SO_4 solution (from point 141) to reactor and turn on the stirrer for 5 minutes.	**A**			
17	Turn off the stirrer, separate layers, pour off bottom layer.	**A**			
18	Repeat activities 16-17 (using water instead of H_2SO_4).	**A**			
19	Repeat activities 18 until pH=7 is obtained.	**A,B**			
20	Collect esters in beaker with drying agent.	**A**			
21	Wash the reactor.	**A**			
22	Prepare vacuum filtration kit.	**C**			
23	Filter methyl esters.	**C**			
24	Evaporate methanol from esters (using vacuum evaporator, as you did in point 15)	**C**			
25	Calculate the biofuel mass, yield of process and mass of by-products (assuming d =1kg dm^{-3})	***all***			
27	Turn on cooling water and thermostat connected with viscometer.	**A,B**			
28	Measure dynamic viscosity by the use of Höppler viscometer.	***all***			
29	Turn off thermostat and cooling water.	**A**			
30	Wash the Glass part of viscometer.	***all***			
31	Check the glass and equipment.	***all***			
32	Fill in the results sheet.	***all***			
33	Final inspection of the bench and analytical balance room.	***all***			

EXPERIMENT No 30 (Production of Biofuels)

Results sheet

names: date:……

TRANSESTERIFICATION

substrates

vegetable oil: ……g, KOH: ……g, methanol: ……mL

products

	glycerol fraction [g]	oil fraction [g]
tare		
gross weight (before evaporation)		
gross weight (after evaporation)		
net weight (solvent)		
net weight (residue)		

Measurement of oil and biofuel density

temperature of measurement:……

		measurement 1	measurement 2
Clean, dry pycnometer	m_{p1}	g	g
pycnometer with water	m_w	g	g
Volume of pycnometer	$V_{piknometru}$	cm^3	cm^3
Clean, dry pycnometer	m_{p2}	g	g
picnometer with biofuel	m_b	g	g
Pycnometer with oil	m_o	g	g
Oil density	ρ_o^{20}	g/cm^3	g/cm^3
Biofuel density	ρ_b^{20}	g/cm^3	g/cm^3

Measurement of oil and biofuel viscosity

Temperature of measurement:……

ball constant:

time of ball falling

1)……. sec.

2)……. sec.

3)……. sec.

Measurements of biofuel ignition temperature

reference substance:……

ignition temperature of reference substance:

1)……. °C,

2)……. °C,

3)……. °C,

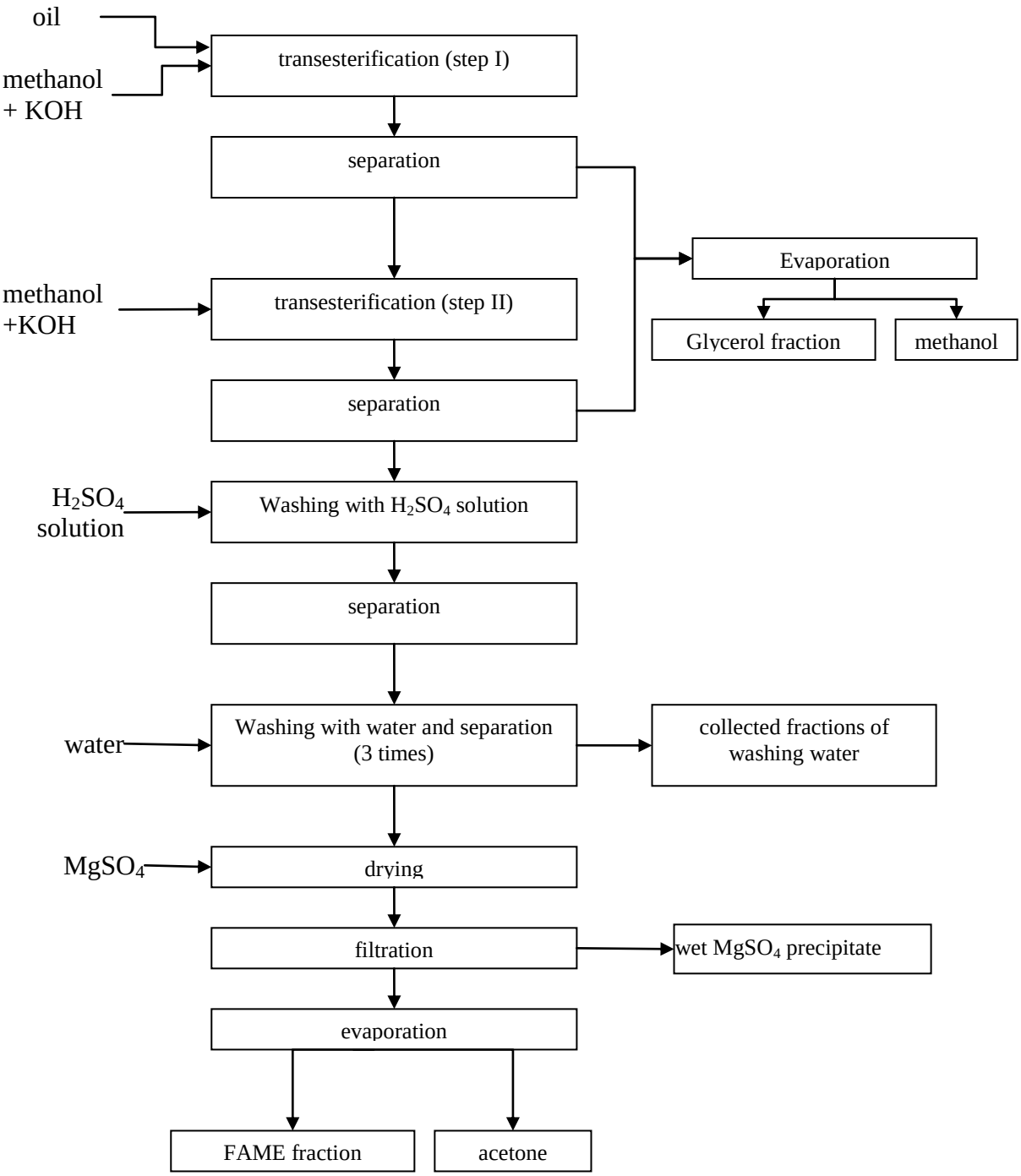
signature of the instructor:

Material balance of process (to draw a Sankey diagram = process flow diagram).*

Lp.	Substance	Entering [g]	Leaving[g]
1	oil		x
2	KOH		x
3	methanol		x
4	glycerol fraction before evaporation	x	
5	glycerol fraction after evaporation	x	
6	evaporated methanol	x	
8	H_2SO_4 solution		x
9	water used for washing the oil fractuon		x
10	combined aqueous layers		
11	drying agent		x
12	precipitate after filtration	x	
13	acetone to wash the precipitate		x
14	oil fraction before evaporation	x	
15	oil fraction after evaporation	x	
16	evaporated solvents	x	
		Σ =	Σ = without points 4,14

* Sankey Diagram should include all relevant stages of the process (see process flow sheet), and it should be drawn on graph paper and have a scale (the legend).

The yield of transesterification:



Block process flow sheet for transesterification.

Description of exercise should include:

1. Aim of experiment.
2. Description of experiment, including:
a. scheme of the apparatus,
b. description of performed activities as well as reaction conditions and parameters,
c. results sheet signed by instructor.
3. Results, including:
a. equations,
b. calculations of the results,
c. Sankey Diagram prepared on the basis of flow diagram and mass balance (according to the rules on www website),
d. Gantt chart (according to the rules described below).
4. Discussion of the results.
a. yield of reaction,
b. sources of errors,
c. comparison of physicochemical parameters and the literature data.
5. Conclusions - you should discuss:
a. advantages and disadvantages of method of synthesis,
b. economic aspect of the process (suggest the way of regenerating unused reagents),
c. toxicological aspects (see: cards of characteristics),
d. discuss the environmental aspects of the process and try to suggest how to improve some of them,
e. Express your opinion whether the aim of the exercise has been achieved.

How to prepare the Gantt's chart

The Gantt's Chart is a two-dimensional diagram applied for a visual description of the project.

From correctly-made chart we can quickly read the structure of the project, the tasks (activities) and the time of their performance (start and end time, and the order of tasks performed). Gantt Chart can be made by hand (on graph paper) or by the use of computer. It is always necessary to unambiguously determine the time intervals. To prepare Ganntt's Chart you have to use the checklist sheet on which you noticed the start time and end time of each activity.

activity name	start	end
A	8:30	8:45
B	8:35	8:45
…	….	….
…	….	….
N	12:25	12:50
O	12:50	13:00

On the axis of ordinates, please put the name of the activity and on the axis of abscissae put time scale (eg hours with division into minutes, quarters, etc.):