

leXsolar-BioFuel Large



Teacher's Manual

Layout diagram leXsolar-BioFuel Large
 Item-No.1702
 Bestückungsplan leXsolar-BioFuel Large
 Art.-Nr.1702



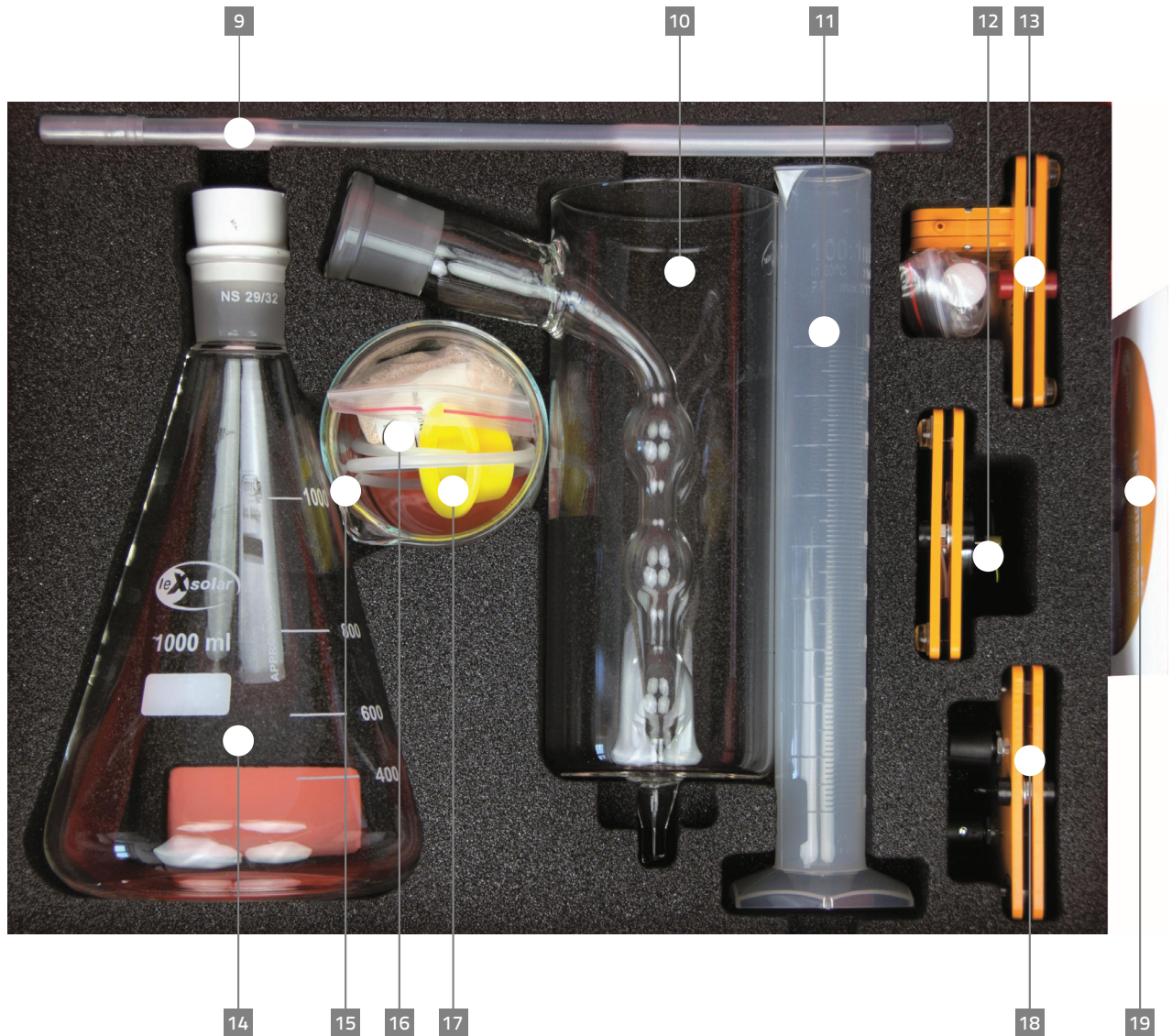
- 1 L2-06-079 Areometer
L2-06-079 Dichtemessspindel
- 2 3xL2-06-085 Pasteur pipette
3xL2-06-085 Pasteurpipette
- 3 L2-06-072 Alcoholmeter
L2-06-072 Alkoholmeter
- 4 L2-06-070 Distilling head
L2-06-070 Destillieraufsatz

- 5 L2-06-076 Airlock
L2-06-076 Gärspund
- 6 L2-06-084 Grip stopper
L2-06-084 Lamellen Stopfen
- 7 L2-06-087 Syringe 2 ml
L2-06-087 Spritze 2 ml
- 8 3xL2-06-083 Test tubes
3xL2-06-083 Reagenzgläser

Version number
 Versionsnummer

L3-03-142_06.05.2015

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| <p>9 L2-06-016 Laboratory thermometer
L2-06-016 Laborthermometer</p> <p>10 L2-06-071 Condenser
L2-06-071 Kühler</p> <p>11 L2-06-086 Measuring cylinder 100 ml
L2-06-086 Messzylinder 100 ml</p> <p>12 1100-27 Motor module without gear
with L2-02-017 Propeller
1100-27 Motormodul ohne Getriebe
mit L2-02-017 Propeller</p> <p>13 1700-01 Ethanol fuel cell module
1700-01 Ethanol-Brennstoffzellenmodul</p> | <p>14 L2-06-075 Erlenmeyer flask 1000 ml
L2-06-075 Erlenmeyerkolben 1000 ml</p> <p>15 L2-06-082 Beaker 250 ml
L2-06-082 Becherglas 250 ml</p> <p>16 1702-02 Yeast
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Teacher's manual

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Definition BioFuels

BioFuels are fuels/carriers for combustion engines and fuel cells, made out of biomass. These can be gaseous, liquid, or solid (biodiesel, bioethanol, methane, woodchips, etc.). Raw materials for BioFuels are renewable resources, e.g., oil plants such as rapeseed or oil palms, corn like wheat or maize, or high-carbohydrate plants like sugarcane.

Classification

BioFuels are classified under different generations depending on the biomass exploited. The biomass of the plants is either partially (1st generation) or completely (2nd generation) exploited. The production process of BioFuels differs depending on the generation:

1. Generation - plant oils, biodiesel, bioethanol
2. Generation - bio natural gas (biomethane), biomass to liquid fuels

Biodiesel

Biodiesel is a biosynthetic fuel with comparable applications like mineral diesel. In Europe, biodiesel is produced by the transesterification of rapeseed oil with methanol (rapemethylester). The other option, ethanol, is rarely used due to its other applications. Clean biodiesel (named B100) can be used in suitable engines or mixed with mineral diesel in arbitrary mixing ratios due to their chemical similarity. The prefix 'bio' refers to the plant-based origin, in contrast to mineral oil. The carbon neutrality and ecological advantages of biodiesel are highly controversial (keywords: monoculture, "food into the tank", etc.)

→ Experiments "Production of biodiesel and fatty acid composition"

Bioethanol

Bioethanol is produced by fermenting organic materials (corn, potatoes, sugar beets) and subsequently distilling them for better utilization (increasing energy density per volume). Commonly used fuels with ethanol additives are, e.g., premium unleaded fuel (E5), E10 (10 % ethanol, 90 % premium unleaded fuel), E85 (85 % ethanol, 15 % unleaded premium fuel).

→ Experiments "Production of bioethanol"

Additional BioFuels

Bio-natural gas (biomethane) – By fermenting (biogenic processes) biomass, fermentation gases are produced (approx. 75 % methane, rest: CO₂, N₂, NH₃, ...).

Cellulosic-ethanol – This fuel is identical to bioethanol, only that the production starts with cellulose (wood, paper, cardboard). This means chemical or enzyme splitting of cellulose into monosaccharides, which are fermented like in the bioethanol production.

Hint for the teacher: wood splitting products like xylose and arabinose sugars require special yeasts, which ferment the sugar. Secondary experiment is possible. High time consumption due to splitting and yeasts!



Biomass-to-liquid fuels: Conversion of rest biomass (straw, waste, etc.) by different pyrolysis procedures.

Hint for the teacher: secondary experiments are possible: pyrolysis, also called dry distillation. Low effort! Dry distillation of wood inside a test tube. The produced crack gases can directly be ignited. If the initial gases are passed through a cooling tube, additional pyrolysis gases can condensate among other things: unsaturated hydrocarbons, naphthalene, toluol, anthracene, methanol, ammonia, formaldehyde, acetic acid, phenol, etc.

→ Experiments “pyrolysis - dry distillation of matter”

History

Biodiesel

The production of biodiesel by the transesterification of plant-based oils with methanol was described in 1853 by E. Duffy and J. Patrick, several years before the diesel engine was invented. In the context of the world exhibition in 1900, Rudolph Diesel tested the applicability of pure plant oil based fuels in diesel engines. He reported to the *Institution of Mechanical Engineers of Great Britain* about the results: “At the world exhibition in Paris in 1900, a small diesel engine from the manufacturer Otto was shown, which fulfilled the requirements of the French government to run with peanut oil. This engine worked so well that only few people took notice of it. It was constructed to run with mineral oil, but it also ran with plant oil without any modifications.” The results of the Belgian G. Chavanne have been the trigger to utilize biodiesel. On August 31, 1937, Chavanne applied for a patent on the transesterification of plant oils with ethanol and methanol in order to improve their properties as fuels. In 1938, the application of a biodiesel based on palm oil was already successfully tested on a bus route between Brussels and Leuven. In the 1970s, further investigations took place in Brazil and South Africa. In 1983, the production process of biodiesel in fuel quality was internationally published.

Bioethanol

In 1860, Nikolaus August Otto used ethanol as the fuel in a prototype of his combustion engine. The car manufacturer Henry Ford designed his T-model, manufactured since 1908, on the assumption that bioethanol would be the fuel for this people’s car. Ford believed that bioethanol would be the fuel of the future. Due to an insufficient supply situation of gasoline in Germany, the Reichskraftsprit (RKS) was founded in 1925 in order to substitute spirit for gasoline.

In the following centuries, oil became the primary energy source. Only in the 1970s, in the wake of the oil crises, ethanol became interesting again. Starting in Brazil and the United States, the utilization of ethanol made out of sugar cane and corn as fuel as well as other alternative fuels based on renewable resources started to attract support from governmental programs. A global extension of these endeavours arose due to the Kyoto protocol.



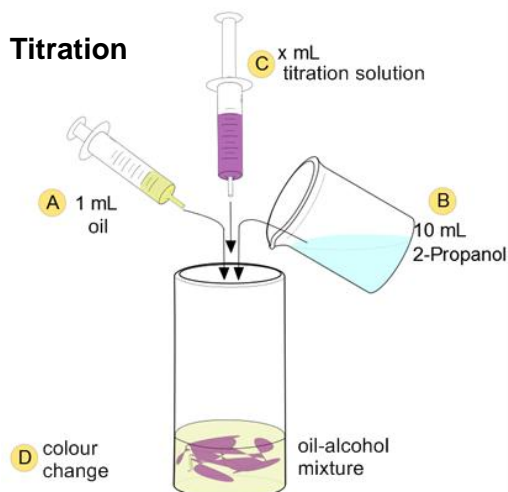
1.1 Production of Biodiesel (FAME) from fats & oils

Hint for the teacher: It is advisable to first start the experiment and then teach the theory because it takes approximately half an hour until the FAME has separated from the glycerol or the water, respectively. For the titration, also an aqueous solution of KOH can be used instead of NaOH (then 1.4 g of KOH to 1 l of water). The phenolphthalein solution is long term stable and should be ordered or produced in advance.

Task

Find out the amount of KOH necessary for the production of FAME by titrating the oil with NaOH stock solution ($c = 1 \text{ g/l}$) and separate the oil into its two components glycerol and biodiesel (FAME).

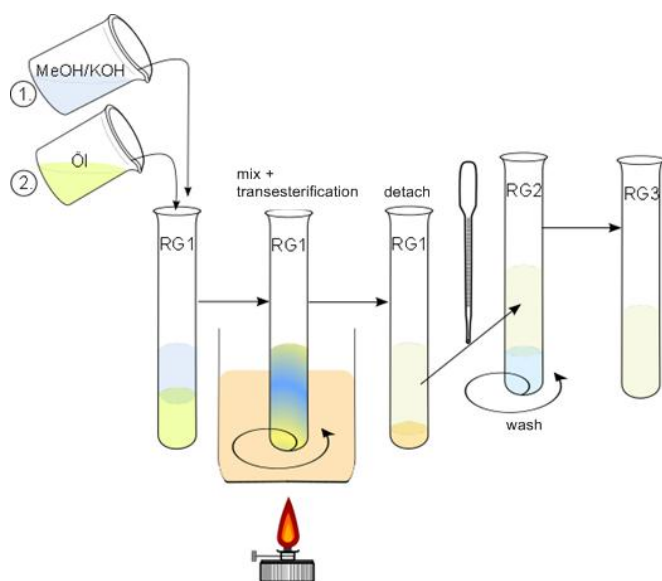
Setup



Equipment

- beaker
- test tubes
- 10 ml isopropyl alcohol 99 %
- at least 1 ml of oil (45 °C – for titration)
~10 ml for transesterification
- phenolphthalein solution (~0.3 %)
- water
- NaOH stock solution ($c = 1 \text{ g/l}$)
- 2 x one-way syringes with 5 ml
- pipette
- KOH aqueous stock solution (1 g/l)
- bunsen burner/other heat source
- thermometer
- rubber septum / test tube stopper
- balance (only necessary for fresh preparation of the KOH solution)

FAME production





1.1 Production of Biodiesel (FAME) from fats & oils

Hint for the teacher: Instead of KOH also NaOH can be used, but is not advisable because the latter makes it nearly impossible to separate the biodiesel from water later on.

The KOH stock solution should be prepared in advance of the experiment and can be kept for a longer time. For the experiment, only a few millilitres of the stock solution are needed depending on the quality of the oil. Use the same syringes only for the same liquids — else, contamination leads to titration errors. Acetone or ethanol can be used instead of isopropyl alcohol. Ethanol, however, hardly mixes with oil and must be well heated or shaken.

Performing

Titration:

1. Measure exactly 1 ml of oil with the one-way syringe/pasteur pipette and add approximately 10 ml isopropyl alcohol to the oil into the beaker.
2. Shortly heat the mixture up to 40 °C. Don't bring it to the boil!
3. Add 3 drops of phenolphthalein to the mixture.
4. Now add the NaOH standard solution by a slight swirling until a permanent pink colour appears in the beaker (at least for 30 seconds). Note the amount used.

Used NaOH standard solution in ml: _____

Hint: At this point, all free fatty acids of the sodium hydroxide solution have been converted into its salts and the pH has increased to 8.5 due to the freely existing OH⁻ ions. The consumption in ml KOH stock solution now has to be converted to the needed amount KOH according to the table/formula. To ensure exact results, the titration may be conducted several times.

As a rule of thumb, the oil quality can be expressed according to its consumption as follows:

- 0 – 3 ml excellent quality; suitable for FAME production
- 3 – 6 ml medium quality; still suitable for FAME production
- > 6 ml low quality; unsuitable for FAME production

Hint for the teacher: If the fat contains too many free carboxylic acids, an increased soap content (the potassium salts of the free carboxylic acids) is formed during transesterification. This leads to an emulsion and makes the separation extremely difficult. The necessary amount of KOH is hard to be exactly maintained when using inaccurate balances. After titration, best is to prepare only one appropriate KOH/MeOH stock solution if all students use the same oil.

5. Using the table, now determine the additional necessary amount of KOH for 1 litre of FAME formation. Determination of the additional necessary amount of NaOH for 1 litre FAME formation

Consumption of stock solution during titration in ml	Additional necessary amount of KOH in g	Total amount of KOH 5 g + X in g	Acid value mg/g oil (density values for the different oils: cf. exp. 1.3 FAME <-> cooking oil, here: 0.92 kg/l)
1.0	1	6	6.5
2.0	2	7	7.6
4.5	4.5	9.5	10.3

6. Fill the necessary amount of methanol and the calculated amount of KOH into the first test tube (TT1) and dissolve it by repeated shaking. It is advisable to calculate the formation for approximately 16 ml of oil due to



1.1 Production of Biodiesel (FAME) from fats & oils

the typical size of a test tube of 20 ml. Then, enough FAME is produced for all following experiments. The calculation of the proportions is conducted according to the following table:

	Formation for 1000 ml of oil	Formation for 16 ml of oil
oil	1000 ml	16 ml
KOH	5 g + X g (e.g. X = 1 g)	0.1 g + X g
methanol	220 ml	3.5 ml

7. Now fill the desired amount of oil for transesterification into test tube 1 (TT1).

8. Heat the mixture in a bain-marie to approx. 50 °C for approx. 20 minutes and shake the test tube from time to time using a stopper.

9. Let the mixture cool down and wait for phase separation (can take up to one hour).

Hint: The heavier brownish glycerol (density 1.2) settles on the ground, while the yellowish biodiesel (density 0.9) swims on top.

10. Wait for phase separation and pipette the swimming biodiesel carefully into a new test tube (TT2). Add water to the biodiesel in TT2 until the test tube is nearly full. Carefully turn the test tube several times by 180° head first to wash away excess methanol and catalyst rests. It is also possible to shake it carefully.

Hint: If the test tube is shaken too heavily, the separation of the two phases may take very long. To detach the solid parts, it can be helpful to additionally filter the FAME/water mixture if the biodiesel does not get clearer during washing.

Hint for the teacher: If the FAME does not clear despite washing and filtrating or becomes even murky, it can be helpful to add some (solid) sodium sulphate and stir. After waiting for approx. 10 minutes, the solution clears and the sodium sulphate settles on the ground and can be separated.

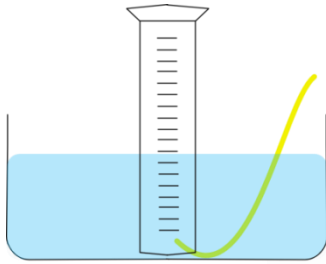


2.3 Relation between reaction speed and temperature

Task

Investigate the relation between reaction speed and temperature!

Setup



Equipment

- measuring cylinder
- thermometer
- hose
- container for bain-marie

Performing

1. Verify the Q_{10} value with the fermentation experiment by measuring the volume of CO_2 created in a certain time interval once at $20\text{ }^\circ\text{C}$ and once at $30\text{ }^\circ\text{C}$ (the formation should already be brought to the correct temperature one hour in advance in order to accelerate the reaction). Therefore, fill the provided measuring cylinder with water and put it upside down in a bain-marie so that no air can enter.
2. Then, thread the hose for the proof of CO_2 from below into the measuring cylinder and measure the volume of CO_2 in a certain time interval.
3. From this, calculate the sugar mass that is converted per minute.

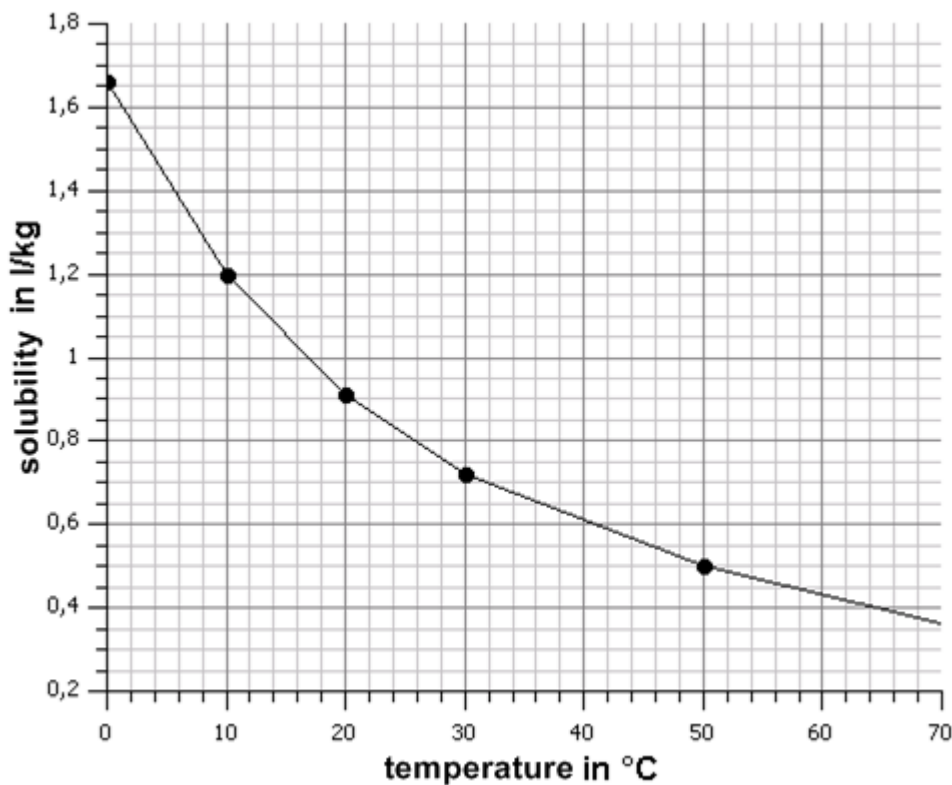
Hint for the teacher: CO_2 dissolves very well in water (cf. previous experiment), which can distort the measured volume in the experiment. Therefore, it is advisable to use warm water as the solubility of carbon dioxide in water decreases with increasing temperature. Alternatively, the volume can also be measured by leading the gas into a gas syringe.

Analysis

Temperature in $^\circ\text{C}$	Solubility in g/kg water	mol/kg water	solubility in l/kg water
0	3.26	0.074	1.66
10	2.28	0.052	1.20
20	1.67	0.038	0.91
30	1.28	0.029	0.72
50	0.82	0.019	0.50
70	0.59	0.013	0.36



2.3 Relation between reaction speed and temperature



Calculation of sugar translated per minute (in the case of glucose):

Example: during 1 minute, 100 ml CO₂ are created, thus 100 ml/min

Calculating the mass using the classical ideal gas law: $pV = nRT$

$$P = 101325 \text{ Pa}, R = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}, T = 293 \text{ K (20 °C)}$$

$$m(\text{CO}_2) = \frac{pV}{RT} * M(\text{CO}_2)$$

$$m(\text{CO}_2) = (101325 \text{ Pa} * 0.0001 \text{ m}^3) / (8.314 \text{ J}/(\text{K} * \text{mol}) * 44 \text{ g/mol}) = 0.176 \text{ g}$$

$$m(\text{sugar translation}) = \frac{0.176 \text{ g} * 180 \text{ g}}{88 \text{ g}} = 0.36 \text{ g}$$

$$n(\text{sugar}) = \frac{m}{M} = 0.36 \frac{\text{g}}{180.18 \frac{\text{g}}{\text{mol}}} = 0.002 \text{ mol} = 2 \text{ mmol}$$

0.36 g or 2 mmol glucose are translated per minute, respectively. This corresponds to 0.03 mmol/s.

Calculation equivalent for 30 °C. According to the Q₁₀ value, the reaction proceeds 2 – 4 times faster with every 10 K incrementation.

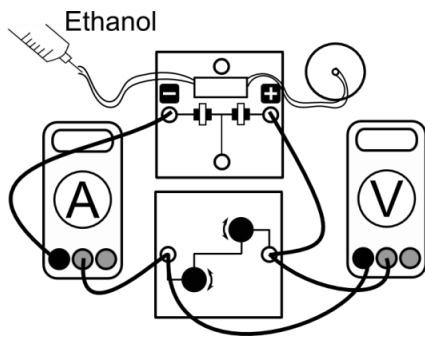


4.4 Concentration dependence of the power and the characteristic curve

Task

Check the dependence of the power and the characteristic curve on the concentration.

Setup



Equipment

- motor module
- fuel cell
- 2 hoses
- syringe
- ethanol
- ammeter
- voltmeter

Performing

1. Set up the circuit as given.
2. Dissolve ethanol to 10 % and 20 %.
3. Lead ethanol with different concentrations into the fuel cell. Start with the lower concentrated ethanol, because when starting with higher concentrated ethanol, the fuel cell would saturate and therefore lead to wrong measurement values.
4. Draw both characteristic curves and the voltage-power-diagram into each one diagram and explain the observed trend!

Hint: The cell should be flushed with water before changing the concentration.

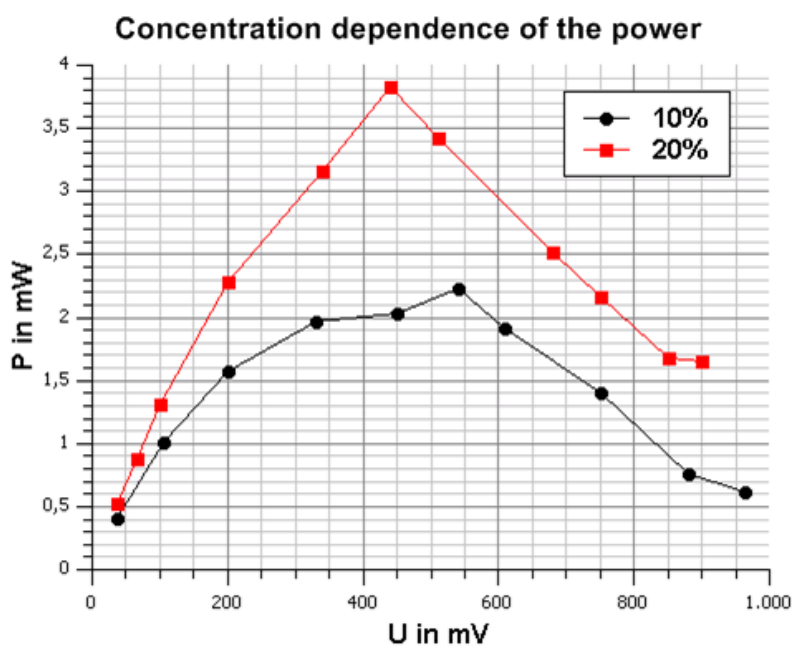
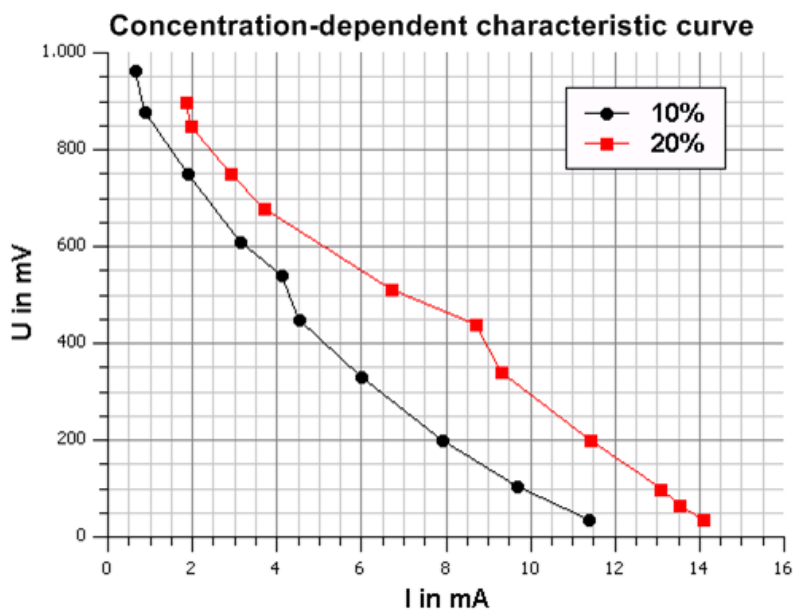
Analysis

10 %			20 %		
V in mV	I in mA	P in mW	V in mV	I in mA	P in mW
964	0.64	0.617	900	1.83	1.647
880	0.86	0.757	850	1.97	1.674
750	1.87	1.403	750	2.89	2.168
610	3.13	1.909	680	3.70	2.516
540	4.12	2.225	510	6.70	3.417
450	4.51	2.030	440	8.70	3.828
330	5.98	1.973	340	9.30	3.162



4.4 Concentration dependence of the power and the characteristic curve

10 %			20 %		
V in mV	I in mA	P in mW	V in mV	I in mA	P in mW
200	7.89	1.578	200	11.40	2.280
104	9.67	1.006	100	13.06	1.306
36	11.38	0.410	65	13.53	0.879
			37	14.09	0.521





4.4 Concentration dependence of the power and the characteristic curve

Explanation:

It is obvious that the power increases with higher concentrations because higher concentrations contain more ethanol molecules and, therefore, lead to an increased electron flow. The position of the power maximum, however, seems to always lie at the same voltage (approx. 450 mV). This knowledge is important for the technical application of the fuel cell: at the same voltage, the 20 % solution has a higher current density than the 10 % solution. This can be explained by the fact that the current density is defined as the amount of charge carriers through a certain cross-section per time unit. At a higher ethanol concentration there exist also more electrons and, therefore, the current density increases.

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