# leXsolar-BioFuel Ready-to-go

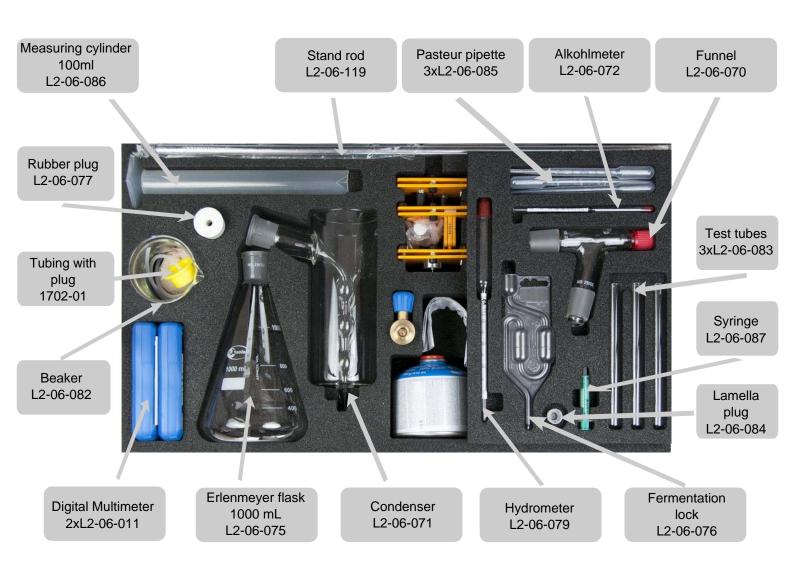


# Teacher's Manual



# Layout diagram leXsolar-BioFuel Ready-to-go

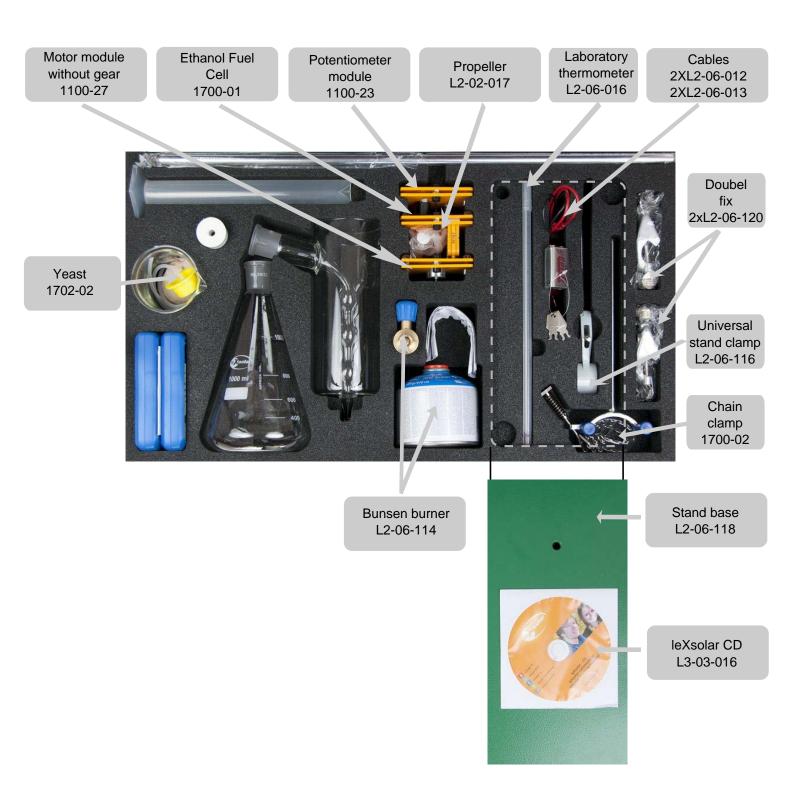
Item-No. 1703





## Layout diagram leXsolar-BioFuel Ready-to-go

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# leXsolar-Bio Fuel Ready-to-go 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

<u>Bio-natural gas</u> (biomethane) – By fermenting (biogenic processes) biomass, fermentation gases are produced (approx. 75 % methane, rest:  $CO_2$ ,  $N_2$ ,  $NH_3$ , ...).

<u>Cellulosic-ethanol</u> – 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"

### <u>History</u>

#### 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.

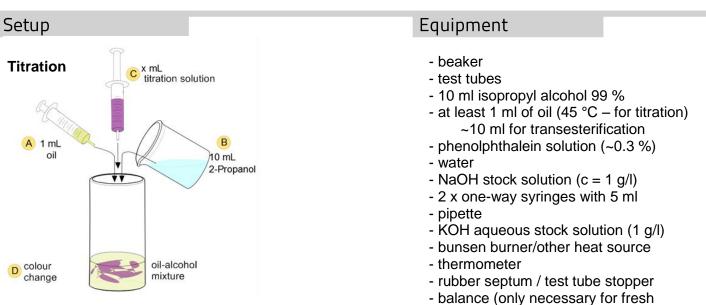


## 1.1 Production of Biodiesel (FAME) from fats & oils

**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 I of water). The phenolphthalein solution is long term stable and should be ordered or produced in advance.

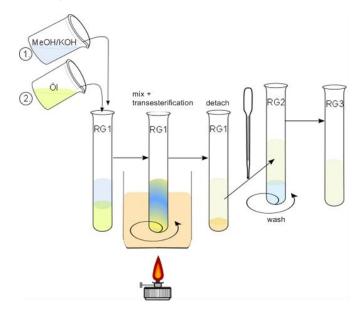
#### Task

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



## preparation of the KOH solution)







## 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<sup>-</sup> 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<br>solution during titration<br>in ml | Additional necessary amount of KOH in g | Total amount of KOH<br>5 g + X in g | Acid value<br>mg/g oil<br>(density values for the<br>different oils: cf. exp. 1.3<br>FAME <-> cooking oil,<br>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                      |
| КОН      | 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.



Task

Investigate the relation between reaction speed and temperature!

| Setup | Equipment   |
|-------|---|
|       | - measuring cylinder<br>- thermometer<br>- hose<br>- container for bain-marie |

## Performing

- Verify the Q<sub>10</sub> value with the fermentation experiment by measuring the volume of CO<sub>2</sub> created in a certain time interval once at 20 °C and once at 30 °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<sub>2</sub> from below into the measuring cylinder and measure the volume of CO<sub>2</sub> in a certain time interval.
- 3. From this, calculate the sugar mass that is converted per minute.

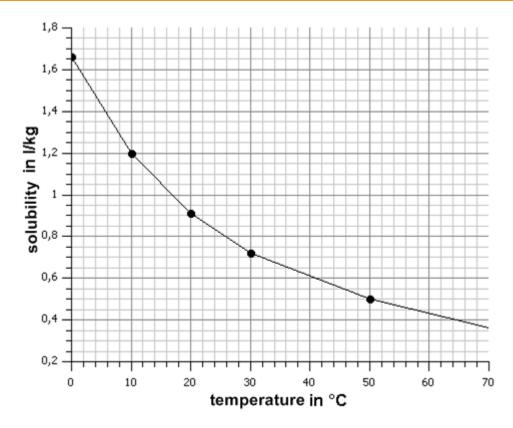
**Hint** for the teacher:  $CO_2$  dissolves very well in water (cf. previous experiment), which can distort the measured volume in the experiment. Therefore, it is advisable to use warm water as the solubility of carbon dioxide in water decreases with increasing temperature. Alternatively, the volume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

## Analysis

| Temperature in °C | Solubility in g/kg water | mol/kg water | solubility in I/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 CO<sub>2</sub> are created, thus 100 ml/min

Calculating the mass using the classical ideal gas law: pV = nRT  $P = 101325 \text{ Pa}, R = 8.314 \frac{J}{K * \text{mol}}, T = 293 \text{ K} (20 °C)$   $m(CO2) = \frac{pV}{RT} * M(CO2)$   $m(CO2) = (101325 \text{ Pa} * 0.0001 \text{ m}^3)/(8.314 \text{ J}/(\text{K} * \text{mol}) * 44 \text{ g/mol} = 0.176 \text{ g}$   $m(sugar translation) = \frac{0.176 \text{ g} * 180 \text{ g}}{88 \text{ g}} = 0.36 \text{ g}$   $n(sugar) = \frac{m}{M} = 0.36 \frac{\text{g}}{180.18 \frac{\text{g}}{\text{mol}}} = 0.002 \text{ mol} = 2 \text{ mmol}$  $0.36 \text{ g or 2 mmol glucose are translated per minute, respectively. This corresponds to 0.03 mmol/s.$ 

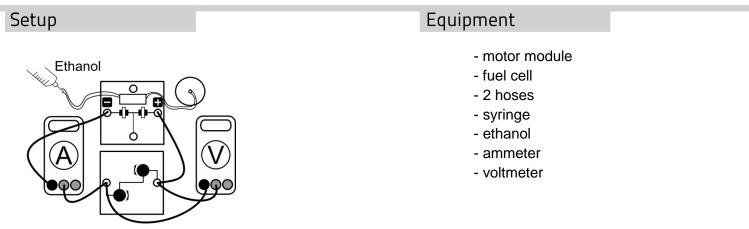
Calculation equivalent for 30 °C. According to the  $Q_{10}$  value, the reaction proceeds 2 – 4 times faster with every 10 K incrementation.



## 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.



## 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.

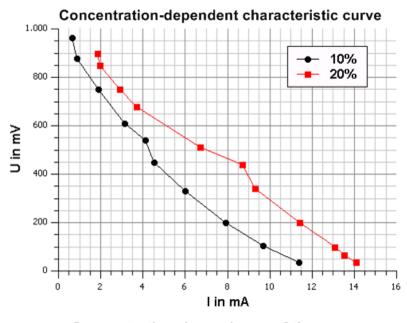
## Analysis

| 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   |

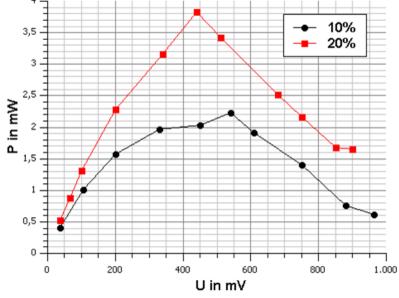




| 10 %    |         | 20 %    |         |         |         |
|---------|---------|---------|---------|---------|---------|
| V in mV | I in mA | P in mW | V in mV | l in mA | P in mW |
| 200     | 7.89    | 1.578   | 200     | 11.40   | 2.280   |
| 104     | 9.67    | 1.006   | 100     | 13.06   | 1.306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









**BioFuel Large** 



#### 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.



# understanding new energies

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