The energetic potential of bioethanol in Hungary

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Energetický pootenciál bioetanolu v Maďarsku

The basis of the bioethanol production is the agriculture, mostly the corn and wheat growing. With the analysis of their domestic harvest results, the process of the starch formation and the chemical-thermodynamical processes of the alcohol's fermantation, we calculate the annual amount of the producible bioethanol on average and its energy. We determine the specific values of the CO_2 cycle. We examine the energetic possibilities of total substitution of the 2 billion litres of domestic petrol consumption with bioethanol.

Key words: bioethanol, mass balance, CO₂ cycle

Introduction

Hungary similarly as other member states of European Union, requires or significant oil import. Only 10 % of oil processed in refineries is the domestic production. There are 3 million cars in Hungary, and 85 % of them run on petrol. 90 % of these vehicles use the European Standard 95 octain petrol, whose annual consumption is about 2 billion litres (Merétei, 2006). A partial or total substitution of this amount of fossil fuel containing $6,2 \ 10^{16}$ Joule energy for the fuel produced on renewable energy sources is not hopeless. In this essay we present a theoretical energetical calculation starting from the average corn yield of hungary in 2000. As a result of the calculation, we determine the main energetical and mass rates of the petrol substituting bioethanol and the amount of the required arable land.

The mass balance of the theoretical process of bioethanol production

Bioethanol production starts on the wheat and corn field. With the energy radiated by the Sun, the plant creates 1 molecule of starch ($C_6H_{10}O_5$) from 6 molecules of CO_2 in the air and 5 molecules of water (H_2O) accepted from the soil, and creates 6 molecules of oxygen (O_2) as the by product of the process. In reality this extremely difficult chemical and physiological process can be modelled as follows:

$$n (6 \text{CO}_2 + 5 \text{H}_2\text{O}) \rightarrow (\text{C}_6\text{H}_{10}\text{O}_5)_n + n \ 6 \ \text{O}_2.$$
 (1)

The value of n polimerization factor in the formula (if n means amylose) is about 1000, if n means amylopectin it is about 5000. From the point of view of energetics there is no difference between the two polymers. From our point of view the value of n is not important.

To determine the mass rates we have to take into account the mol masses of oxygen $M_0=16$ kg, carbon $M_c=12$ kg, and hydrogen $M_H=1$ kg. Inserting this values into the formula and the result is:

 $6 (12+2.16) \text{ kg} \text{ of } \text{CO}_2+5 (2.1+16) \text{ kg} \text{ of } \text{H}_2\text{O} \rightarrow (6.12+10.1+5.16) \text{ kg} \text{ of starch } +6.2.16 \text{ kg of } \text{O}_2.$

Summing up the chemical processes we find that theoretically from 264 kg of CO_2 in the air and 90 kg water accepted from the soil, 162 kg of starch and 192 kg of oxygen are obtained. Using the solar energy our plants create large quantities of oxygen.

The role of the bioethanol plant is to open up the starch of the corn and wheat grain and to ferment it into alcohol. The fermentation process starts with hydrolysis; accordingly, one molecule of water is added to each molecule of starch. In mildly acid medium with the participation of amylase enzymes and adding some heat, one molecule of grape sugar is obtained from the starch.

$$(C_6H_{10}O_5)_n + n H_2O \rightarrow n C_6H_{12}O_6.$$
 (2)

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Considering the mentioned mol masses and writing them into the formula (2) we get the following:

162 kg of starch + 18 kg of H₂O
$$\rightarrow$$
 180 kg of C₆H₁₂O₆.

The fermentation of these 162 kg of starch is the next step of the chemical process. In the presense of yeast plants the grape sugar transforms into ethanol (C_2H_5OH) while CO_2 and some heat are arising (Kaltschmitt, Hartmann 2001):

$$C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2 CO_2 + 156 kJ.$$
 (3)

After the substitution of the mol masses of carbon, hydrogen and oxygen one arrives at:

180 kg of $C_6H_{12}O_6 \rightarrow 92$ kg of $C_2H_5OH + 88$ kg of CO_2 .

Consequently, from 180 kg of grape sugar, 92 kg of alcohol and 88 kg of CO_2 is obtained. From the 264 kg of CO_2 set by plants we get back 88 kg during the bioethanol production. The technological utilization of the high purity and a great amount of CO_2 is one of the practical goals of the future.

The process of bioethanol production

To make the practical mass balance, we must take into account that the actual sown area of the corn and wheat are both 1,1 million hectares. This is the half of the domestic sown area, which is about the 50 % of the territory of Hungary (KSH 2007). This value is high enough to the result of averagings to be accurate. The average harvest results of the period between 2000-2006 is 4 t/ha of wheat and 6 t/ha of corn. The corn yield ranges from 3,95 t/ha to 7,65 t/ha during the period under survey as a function of the weather. It follows that year has the worst harvest results from the standpoint of corn is typical from the standpoint of wheat. The yield in different regions shows a high quiet dispersion. For example, the average yield of corn ranged from 2,8 to 5,1 t/ha in 2006.

Both grains have 65 % of starch content. It means that corn seems to be a more favourable for the bioethanol production. Further, we deal only with it.

Taking the best ethanol producing technology as the basis, we can count with the 90 % ethanol extraction efficiency in the formula (1), (2), (3). The density of ethanol is 0,789 kg/l.

From 1 ton of corn:

$$\frac{1000}{162} \cdot 0.65 \cdot 92 \cdot 0.9 \cdot \frac{1}{0.789} = 421, \quad \text{[Litres]}$$

bioethanol can be fermented. Considering with the average yield of 6 t/ha, means 2.526 litres/ha of bioethanol. The heating value of bioethanol is 26.870 kJ/kg, so the energy content of the porducible bioethanol is:

$$2.526 \cdot 26.870 \cdot 0,789 = 53,6$$
. [GJ/ha]

The energy content of the annual 2 billion litres of ES-95 octain petrol consumption of Hungary is 6,2.107 GJ if the petrol's heating value is 42.000 kJ/kg and the density is 0,74 kg/litre.

The amount of energy which can be produced is

$$\frac{6.2 \cdot 10^7}{53.6} = 1.16 \cdot 10^6, \qquad [ha]$$

what is a quarter of the total sown area of Hungary. It is not baseless to reckon with this area because of 6 % of fallow land and the overproduction of the last years. In additon, we mention that according to the data of 2006, 95 % of the intervention corn stock of EU was grown and has been stored in Hungary. However, the 5,6 million tons of stock is under using up because of the poor crop of this year.

A bioethanol plant produces accordingly to Fig. 1. Incoming grains are sifted to remove bigger parts (stem of the plant and foreign materials), then the feedstock is passed through a hammer mill, which pulverizes it into fine particles, called meal. Milling prepares grains for the enzymes and water to reach starch quickly and efficiently.

The meal is mixed with water and partly disinfected at a high temperature and pressure (usually $105 \,^{\circ}$ C, 0,7-2,7 bar). It's followed by a held at the high temperature (82-90 $^{\circ}$ C) for 4-8 hours. Then it's mixed with two enzymes. The first enzyme, called alpha-amylase, which breaks down starch into individual molecules during the liquefaction. The second enzyme, called gluco-amylase, breaks down the starches into simpler molecules of sugars. Gluco-amylase can be added to the mash during the cooking period before the fermentation in the period called saccharification or at the beginning of the fermentation.



Fig. 1. The process of bioethanol production. Reference: http://www.vaperma.com

Yeast is now added to the mash and pumped into the fermentation tanks. Fermentation breaks down the sugar molecules into ethanol, carbon dioxide and heat. The mash stays in one fermentation tank for approximately 54 hours. When the fermentation process is complete, the mash is now referred to as beer. The length of the fermentation depends on the yeast fungus, the amount of the enzyme and the temperature.

Beer is pumped into a multi-column distillation system which removes alcohol from the beer by distillation. The beer is not completely liquid, it also contains all the solids from the original feedstock and from the added yeast. Basically, distillation utilizes differences in the evaporating points of ethanol and water. Ethanol has a boiling point at 78 °C, so as long as the temperature of the columns is above that temperature and below 100 °C, the boiling point of water, ethanol in a gaseous form, will rise to the top of the distillation column, where the gas is cooled to below 100 °C. This causes the gas to condense back to the liquid form, and contains a much higher percentage of ethanol than the original beer. This liquid condensate is then passed to the next distillation column in the series, where the process is repeated. By the time the product reaches the final distillation column, 95 % of ethanol. Ethanol after distillation ethanol has the concentration of 100 %, and is suitable for the fuel. Any alcohol used for the fuel needs to be denatured. To render the ethanol unfit for the human consumption, 2-5 % gasoline is added to the ethanol.

Stillage is a valuable raw material energetically and economically. After drying and thickening we get DDGS which is a high protein feed ingredient for animals or can be burned in the furnace as an energy source with 18.600 kJ/kg heating value. To produce 1 ton of bioethanol, 13 GJ of heat is required (Handki, Lakatos 2007), (Weiz 2005), which can be covered by the heating value of the DDGS.

The amplification of the mass balance and the CO₂ cycle

The previous calculations can be demonstrated easily with the CO_2 cycle in Fig. 2. which shows the data of the mass balance referred to 1 litre of bioethanol. The CO_2 balance is zero because the corn plant sets CO_2 from air and gives back to the Nature one third of it during the ethanol production, and two-thirds of it during the ethanol's burning. The oxygen balance is zero too, because the corn plant produces the amount of oxygen earlier, that is required for the ethanol's burning:

$$C_2H_6O + 3 O_2 \rightarrow 2. CO_2 + 3. H_2O + 1.232.880 \text{ kJ}$$
 (4)

After the substitution of the mol mass of C, H₂ and O₂ we get the folloving:

46 kg of bioethanol + 96 kg of $O_2 \rightarrow 88$ kg of CO_2 + 54 kg of H_2O

The carbon dioxide and oxygen cycle are theoretically closed but it doesn't mean that other hydrocarbons can not come into play. Detailed examinations of burning are needed to make clear for example the value of the air excess factor and the amount of the arising aldehydes.



Fig. 2. The mass balance of the CO2 cycle. Reference: http://www.antonuriarte.blogspot.com

To compare petrol with ethanol we examined the burning process of petrol containing only octane (C_8H_{18}) . The density ρ of petrol is 740 kg.m⁻³, the heating value *H* is 42.000 kJ.kg⁻¹. The mol masses of C, H₂ and O₂ are taken into account and the result is:

$$2 C_8 H_{18} + 25 O_2 \rightarrow 16 CO_2 + 18 H_2O$$

$$114 \text{ kg of petrol} + 400 \text{ kg of } O_2 \rightarrow 352 \text{ kg of } CO_2 + 162 \text{ kg of } H_2O$$
(5)

The oxygen requirement of the refuelled $2 \cdot 10^9$ litres of 95 octain petrol in Hungary is $5 \cdot 10^9$ kg and the amount of the arising carbon dioxide is $4, 4 \cdot 10^9$ kg. As opposed to the ethanol's zero oxygen and carbon dioxide balance, billion kilogrammes of oxygen and CO₂ in the case of fossil fuel don't need any explanation.

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