ETHYL AND METHYL ESTERS PRODUCTION FIELD ESTERIFICATION PLANT

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Abstract

Production of biofuels from vegetable oils, which would be able to meet restrictive standards in quality, is a complicated process. It results from building provision determinants to be met, as well as the method of process, which requires necessary equipment. While the production of ethyl esters is less harmful for operators than in case of methyl esters, so far for both alcohols there are many hazardous for them. One way of reduction inconvenience of the construction requirements for work with explosives is to put the installation on the mobile platform that will enable the creation of biofuels away from the urban areas.

For the production of esters from rapeseed oils may be used methanol and ethanol. Depending on alcohol used, the resulting ester will have different properties. Presented material describes the requirements for the buildings where the production of esters can be made. A comparison of properties of methyl and ethyl esters, as well as a description of the transesterification process and the quality of test results obtained in the field esterification plant.

The paper focuses on the renewable energy on the example of biodiesel. Esters, being an alternative to diesel oil, fall into two groups: methyl or ethyl fatty acids esters derived from oils, most often rapeseed oil. Biodiesel is available at petrol stations as 100% ester or mixture with diesel oil.

Keywords: *esters, methanol, ethanol, field esterification plant*

1. Introduction

Pro-ecological policies, which are nowadays a priority for all developed countries, force them to take steps limiting the use of natural resources, reducing toxic exhaust fumes and switching economies to "green energy". Thus windmills, solar collectors, biogas, liquid biofuels or additives enriching traditional fuels have become popular. Poland, like other European Union countries, is obliged to achieve the set goals as far as renewable energy is concerned. Fig. 1 presents these goals for particular countries [1].

The study focuses on the renewable energy on the example of biodiesel. Esters, being an alternative to diesel oil, fall into two groups: methyl or ethyl fatty acids esters derived from oils, most often rapeseed oil [2]. Biodiesel is available at petrol stations as 100% ester (B100) or mixture with diesel oil (B20). Every year more and more engines are fuelled by biofuels, which is illustrated by Fig. 2 [2].

2. A field esterification plant

In order to produce biofuels on a larger scale, for purposes other than fulfilling one's own needs, the premises where the equipment is installed must meet a lot of requirements. Basic regulations which pertain to building systems for the production process of biofuels are as follows:

1. Regulation of the Minister of Agriculture and Food Economy of 7 October 1997 on technical conditions which should be met by agricultural buildings and their location, in regard to general conditions, which should be met by buildings with biofuel production systems.

2. Regulation of the Minster of Economy of 22 December 2005 on general requirements for protective equipment and systems to be used in areas threatened with explosions. The regulation lists requirements which have to be followed so that a building and its surroundings are protected against explosions.
3. Regulation of the Minister of the Interior and Administration of 7 June 2010 on fire protection of buildings, other built constructions and areas. This document contains basic indications as regards fire protection.
4. Standard PN-EN 1127-1:2009 Explosive atmospheres – Explosion prevention and protection. The norm contains a classification of spheres threatened with explosion.

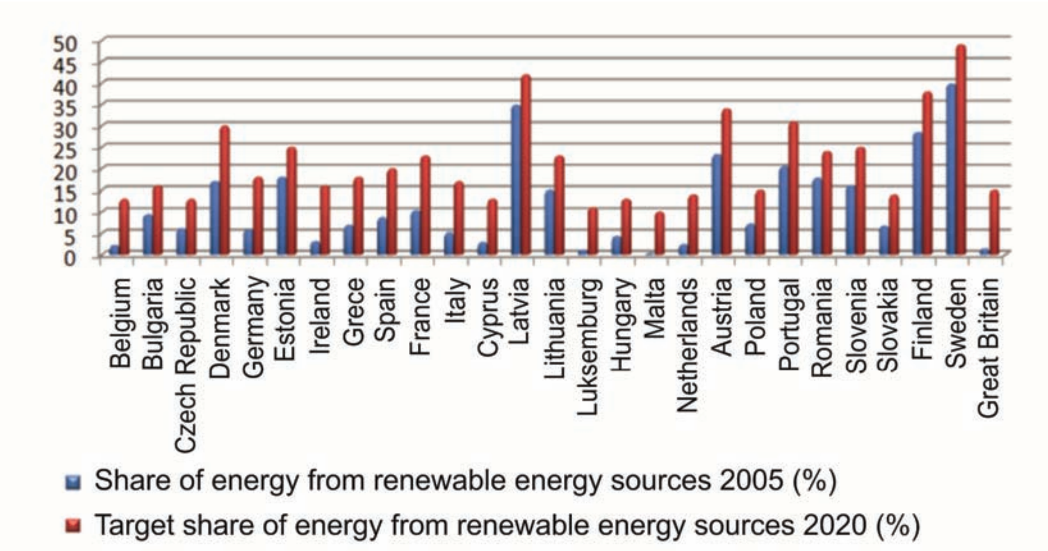

Fig. 1. National overall targets for the share of renewable energy in final energy consumption in 2020

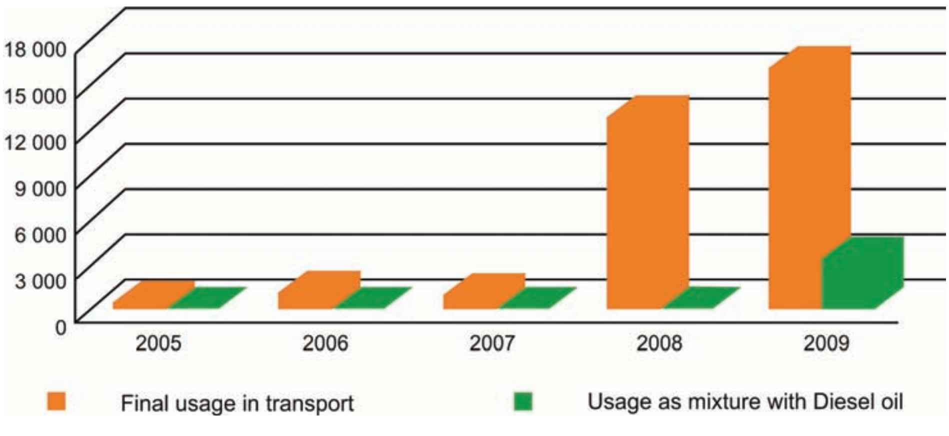

Fig. 2. Biodiesel usage in 2005-2009(TJ)

The above documents show that in order to use materials which can become explosive in mixtures (such as alcohol used in ester production), premises and the surrounding area have to be appropriately protected and marked in case of explosion. Thus an esterification plant has to be located (or already existing buildings have to be adapted) in an appropriate distance from other buildings, so that no extra damage is done in case of explosion. Such areas are not easy to find. Moreover, it is required to present a number of documents and permits, which generates additional costs and lengthens the time of getting the system ready to produce biofuels and commence the production process.

Yet, there is a way to omit part of obstacles posed by the Polish law with respect to building esterification plants. It is to place the esterification system on a movable transportation platform which can be placed in an area distant from buildings, where neither toxic fumes of catalytic mixture nor explosive alcohol fumes will pose a threat to people or possessions. Such a solution can be illustrated by a field esterification plant of the Mechatronics Chair of Warmia and Mazury University in Olsztyn (Fig. 3).

Fig. 3. Star 266, on which the plant is built

A mobile system to produce biodiesel was built on the basis of Star 266 medium load capacity off road truck. This way it can be moved without any construction limitations and fuel can be produced directly at the premises of the consumer.

The system contains all the elements necessary for it to function properly:

- a transesterification reactor equipped with a water jacket, a heating system and a stirrer,
- separators where ester and glycerine phases are separated,
- containers for substrates and ready products,
- an electrical system and control panel with electrical protection elements, PLC-HMI controller with a steering panel and energy producing unit,
- hydraulic infrastructure which enables substrates and products of the process to flow, with pumps facilitating the flow process,
- energy producing unit,
- compressed air system with infrastructure, equipped with a pressure regular,
- appropriate sensors and actuators.

Figure 4 presents the interior of the car with the post reaction products containers and the reactor, and Fig. 5 presents operator control panel.

Fig. 4. A panoramic photograph of a mobile diesel production plant, built on a chassis of a Star 266 vehicle. The transesterification reactor(R) with the post-reaction mixture separators (A, B, C)

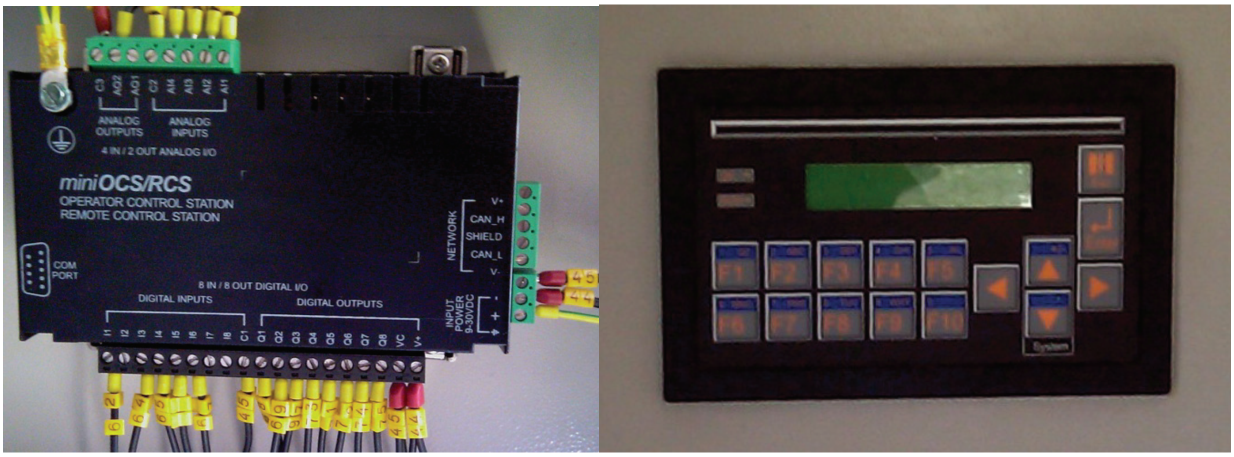

Fig. 5. PLC-HMI controller with a control panel

The system works in a periodical mode. It means that esters are produced in portions. Components are delivered to the reactor and then undergo the process of transesterification. An appropriately programmed controller with a measuring device programs and supervises the process.

In order to minimize a risk of explosion while the system is working, both the compressor and the energy producing unit are located outside the vehicle. The process requires only running water (necessary to cool the heat exchangers which cool down alcohol fumes which are by-products of the whole process).

The following components needed to produce one portion of the product in one cycle of the esterification plant's work are:

- 45 dm3 of oil with low content of free fatty acids (free fatty acids react with alkaline catalyst, creating unwanted soaps),
- 22.5 dm3 of dehydrated ethyl or methyl alcohol,
- catalyst mixture containing potassium hydrate, in a quantity equal in weight to 1% of the mass of oil used in the process, dissolved in 5 dm3 of alcohol.

The whole process of esterification, together with heating the system and delivering components lasts for about 3 hours, and the very transesterification reaction – about 1 hour. The system is able to produce up to 300 kg of esters, while working non-stop for 24h, using in this time up to 300 kg of oil, 45 kg of alcohol and 3 kg of catalyst.

3. Characteristics of the process proposed for a field esterification plant

In 1846, Rochleder for the first time described reaction of alcoholises of plant oils [3]. Since then, a lot has been published on the topic of transesterification of fats (mainly plant oils) with low molecular weight alcohols. The publications concerned research into thermodynamics and kinetics of the very reaction as well as ways of conducting it. The esters of fatty acids derived in the process of transesterification drew attention, since it was discovered that they can be used to fuel CI engines.

Ethyl esters of fatty acids are derived from raw rapeseed oil in a chemical process known as transesterification, which is presented by a scheme in Fig. 6.

Transesterification is a reaction as a result of which glycerol present in a molecule of oil (triacyloglycerol) is replaced by low-molecule aliphatic alcohols (most common methanol and ethanol).

According to a stoichiometric pattern of the reaction, in alcoholises of 1 mole of triacyloglycerol, 3 moles of ethyl alcohol are used, as a result giving 3 moles of fatty acids esters

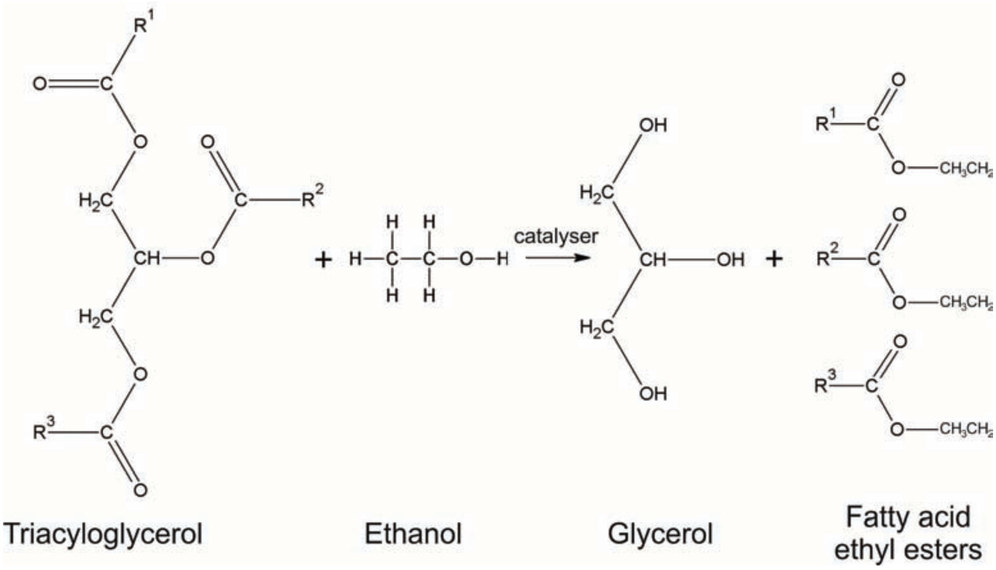

Fig. 6. Reaction scheme of transesterification esters of rapeseed oil with ethanol

and 1 mole of glycerol. Since the reaction of alcoholises is a balance reaction, in order to achieve better results, it is necessary to use an excess of one of the substrates (usually alcohol) or conduct the reaction in stages, retrieving by-products (glycerol) after every stage. Alcoholises takes place until the reaction reaches a balance, which is dependent on the proportion of compounds which are involved in the reaction. In reality, the reaction gives intermediate products, in order of appearance: diacyloglycerols and monoacyloglycerols, as Fig. 7 shows.

The degree of the reaction of triacyloglycerol in the process of transesterification depends on:

- mol proportions of oil to alcohol,
- chemical composition of plant oil and the level of its purity (water content, free fatty acids content),
- a kind of alcohol used,
- temperature in which the process is performed,
- how long the process lasts,
- a kind of catalyst used.

Depending on the conditions in which the reaction is performed, its general degree can reach 99%, yet in the final product one can trace products of intermediate stages of the reaction, which is unfavourable since the produced ester reveals worse properties.

4. By-products of rapeseed oil esterification

Rapeseed oil is a tri-ester of glycerine and fatty acids. In the cold-pressed oil there are up to 2% of remaining non-fatty substances. Conversion of 1000 litters of rapeseed oil into ethyl esters requires about 114 litters of ethanol. In fact, a 40-60% excess of ethanol is applied, which amounts to 180 litters of ethanol per 1000 litters of oil. As a result of transesterification reaction, 70 litters of glycerine remainder are produced. In reality, its amount is definitely larger and can reach up to 250 litters per 1000 litters of oil. The derived glycerine fraction contains 50% of glycerine, 20% of fatty acids, 5% of catalyst and about 10% of alcohol. Because of high acid number of rapeseed oil (up to 3 mg KOHL/g), during the process of esterification about 1.5% of the oil is transformed into soaps. In the case of refined oils the quality of glycerine fraction is higher. The remaining contaminations of the production process are the mono- and di-acyloglycerides, phospholipids, collared substances, water and others [4]. The composition of glycerine fraction does not depend only on the characteristics of rapeseed, but also on the parameters of the esterification process and even on the way rapeseed is stored.

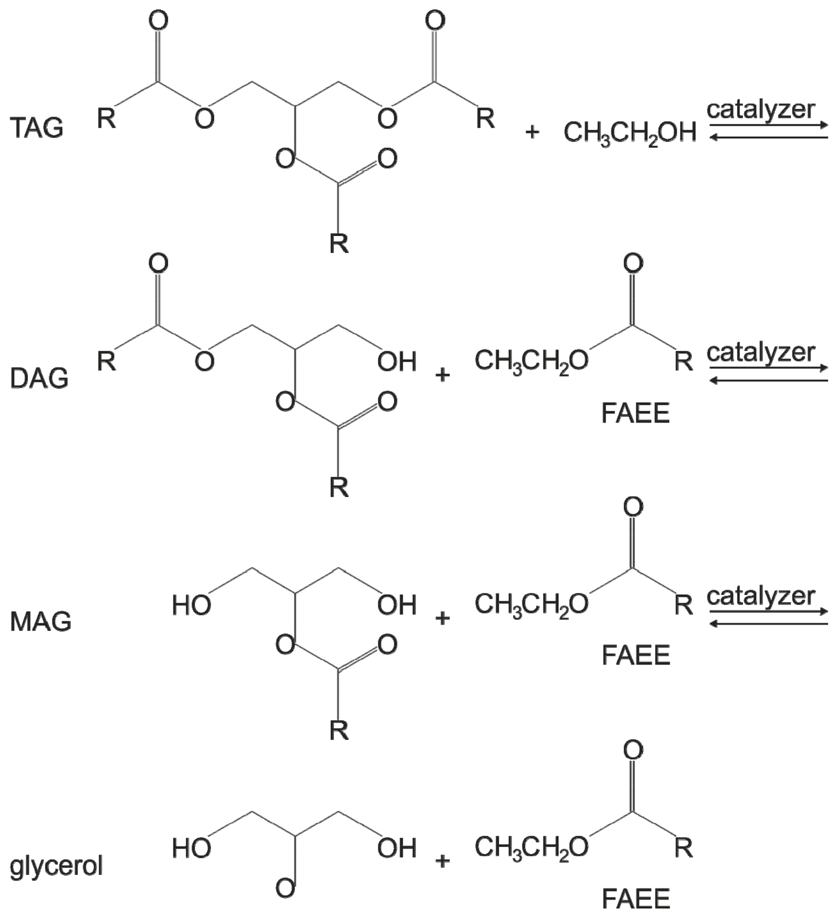

Fig. 7. Diagram of the transesterification reaction

The glycerine fraction, consisting of a mixture of glycerine, alcohol, soaps and fatty acids, is a source of valuable substances, which can be retrieved in specialist plants. The technology of processing the glycerine remainder consists in alcohol evaporation, and then deacidifying soaps and separating fatty acids. As soaps decompose, fatty phase is separated, and it contains mono- and diglycerides, free fatty acids and esters. Raw glycerine contains 70% of glycerine, about 10% of salt, and water [4].

The content of glycerine remainder after esterification of rapeseed oil amounts to 10-20% of the oil used in the production process.

In Poland, the use of glycerine is estimated at 6 000 tons annually [4]. Glycerine is needed in the pharmaceutical and food industries, mainly in chewing gum production (about 50%), and in varnish and paint production – 25%. Glycerine is also used as a supplement in food for animals (5-10%), as well as in producing polymers and in pharmaceutical processes.

5. Properties of methyl and ethyl esters

Esters constitute an alternative to diesel. Parameters met by diesel are different than those which must be met by esters. Tab. 1 contains a comparison of chosen parameters for both fuels. Methyl and ethyl esters are produced in similar processes, so they have to meet similar parameters. Polish standard PN-EN 14214 features these parameters, defining requirements which esters must meet in order to consider them fuels appropriate for cars as well as describing methods to analyze the proposed requirements. The norm pertains mainly to methyl esters of fatty acids, which are available on the Polish market. There are also ethyl esters of fatty acids (EEFA), yet their production is limited mainly due to prices of ethanol, but also because ethanol has to be deeply dehydrated (≤ 0.2% H2O), which is necessary in the transesterification process. What is more, ethyl esters or of higher calorific value, as there is one more atom of carbon in one molecule of an ethyl ester. Additionally, combustion products do not contain formaldehydes, which appear when methyl esters combust. Ethyl esters have also a lower pour point, which influences the low-temperature properties of the fuel [5].

Tab. 1. Comparison of chosen parameters for esters and Diesel oil [6] [7]

Parameter	unit	esters	Diesel oil
Density in 15°C	kg/m^3	860-900	≥845
Viscosity in 40°C	mm^2*s^{-1}	3.5 – 5	2.5-4.0
Flash point	°C	≤ 101	≤ 55
Cetane number		≤ 51	≤ 51
Sulphur content	mg/kg	≥ 10	≥ 10
Iodine number	g of iodine/100g	< 120	< 1

6. Conclusions

A technical solution which allows using a movable esterification plant to produce biofuels seems to be really advantageous for biofuels producers. A mobile system does not have to meet a number of strict requirements which are posed before systems installed in buildings. Moreover, it is possible to produce esters at the premises of the consumer, which facilitates fuel distribution. The quality of esters produced in this way meets all the requirements proposed by the legislator. The system which has been described does not require any complicated procedures, with optimal control parameters identical for every process. The production process can be pursued cycle after cycle, with no need for pause. The accessories which are part of the system enable good functioning without a need to plug into a stationary energy source or compressed air. Moreover, the vehicle on which the lorry is mounted is fuelled by biofuel produced by the system itself.

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