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Production of biodiesel from rapeseed oil

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Abstract: Many chemical suppliers are looking to alternative, eco-friendly raw materials. One of the main sources of renewable feedstocks are plant oils. The use of vegetable oils in organic synthesis is consistent with principle of sustainable development and reduces demand for petrochemical oil. It is important to use the fuels containing biocomponents from renewable sources. Rape is one of the most cultivated oil plant which is a renewable raw material for production of liquid biofuels. The work presents both process of obtaining rapeseed oil and describes stages of transesterification process efforts to receive biodiesel.

Keywords: renewable feedstock, biodiesel

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1. Introduction

The principle of sustainable development takes into account the three pillars: social, economic and environmental protection. It can be defined as the compatibility between progress and protection of natural environment, being rational use of natural resources to meet social needs without reducing the opportunities to use them for future generations.

In recent years, there is a significant technological progress and consequently increase in demand for vegetable fats, which results from the improvement of production of biofuels, especially biodiesel for automotive and transport, as well as finding the unique characteristics and applications for oleochemicals. The most popular oil produced in huge quantities by American companies is soybean oil, while in Europe, the most popular and cheap oil is rapeseed oil [1-4].

The term biofuel defines liquid or gaseous fuel produced primarily from biomass and intended for the transport sector. Currently, two types of biofuels are produced on a world scale i.e. bioethanol and biodiesel [4-6]. Bioethanol is an anhydrous ethyl alcohol obtained on a large scale by alcoholic fermentation of sugar from sugar beets, sugarcane, corn, wheat, straw or wood. At present, bioethanol is used in car engines as a maximum of 15% additive to gasoline [4].

However, biodiesel is a natural fuel defined mainly as methyl esters (FAME) of long-chain fatty acids derived from renewable biological sources, such as vegetable oils and animal fats. Compatibility of biodiesel with mineral oils allows to combine them in order to obtain a stable fuel mixture. It can be used in the form of pure methyl esters of fatty acids as well as mixed with diesel fuel containing up to 30% of bio-component [2,6-8].

The idea of using vegetable oils as fuel comes from time when Rudolph Diesel tested them as fuel for engine (about 100 years ago). In the early 70's vegetable oils became an alternative to fossil diesel due to the petrol crisis. Next, in the 80's there was the development of biodiesel production [8]. There are several methods of producing biodiesel from vegetable oils i.e. direct use and blending of raw oils, thermal cracking (pyrolysis), microemulsions and transesterification method, which is mainly used on an industrial scale. Transesterification process involves preparation of esters of lower alcohols and fatty acids of vegetable oils in the reaction of oil mixture with ethyl or methyl alcohol in the presence of catalyst. During the transesterification reaction, glycerol is also created. Apart from oilseeds, also animal fats as well as waste and used oils can found application in this method. The basic oil for biodiesel production is rapeseed oil which is the third oil produced in the world mainly by US, Malaysia and China [1,3,4,6,7,9].

2. The technological process of obtaining biodiesel

2.1. Preparation of rapeseed oil

The biodiesel is produced mainly from rapeseed with doubly improved varieties of seeds. The composition of rapeseed oil must meet specific quality requirements that are included in the standard for methyl esters as fuels for diesel engines [2,6].

Vegetable oils can be obtained by mechanical or/and chemical extraction. Crushing of seeds is a traditional way of producing oils using different types of presses. However, chemical extraction is a modern way of obtaining vegetable oils using solvent extracts (e.g. hexane). These methods can be combined e.g. residue after pressing is subjected to solvent extraction. Some smaller plants are rather only press-plants without applying the step of solvent extraction [6].

The process of rapeseed oil preparation consists of seed cleaning, preconditioning, flaking, cooking, screw pressing, solvent extraction, desolventizing, distillation and degumming. Rapeseed cleaning involves aspiration, screen separation to remove oversized particles, and screen separation to remove undersized particles. Next, the whole seeds are preheating prior to processing (to about 30-40°C) by indirect heating or direct hot air contact. Cell walls must be ruptured in order to extract the oil. Moreover, it allows a solvent to get into cellular structure dissolving and diluting the lipid portions which then are separated from the solid flake. Next, the preheated rapeseed oil is flaked between two smooth surface cast-iron rolls. Extraction of oil from flaked rapeseed proceed mostly by pre-press solvent extraction. Then there is further extraction of oil seeds and press cake with hexane. In the next step, the hexane solvent is removed from the extracted cake and then distilled from the rapeseed oil. The phospholipids or gums need to be removed in a degumming step. Next, free from moisture and cooled oil is transferred to the refining process or into a storage. Crude oil obtained by extraction contain many undesirable substances such as mucoid substances, coloring matters and free fatty acids. Therefore, it has to be refined to obtain a high quality oil. The refining process involves degumming, neutralization, drying, bleaching, and deodorization. Gums compose about 2% of solvent-extracted rapeseed oil. Degumming treatment uses hot water or steam and phosphoric acid, citric acid, or other acidic materials. Precipitated gums are removed by centrifugation. Free fatty acids can be neutralized with alkali solution. After that, the oil is washed with hot water to remove traces of soaps that can reduce stability of oil. Next, the oil is dried to remove traces of water. Bleaching process proceeds by adsorption of the color producing substances on an adsorbent material such as bentonite or Fuller's earth. The next step i.e. deodorization is a vacuum steam distillation process in order to remove trace constituents giving rise to undesirable odors in oils [2,6].

The high contents of free fatty acids and water in the collected oil are responsible for secondary reactions during transesterification. Therefore, a pretreatment of oil is necessary before load the reactor to produce biodiesel. Oil refining aims to remove the excess of phospholipids, salts of iron or copper and obtain low peroxide number as well as low acid number (less than 1mg KOH/g) i.e. low content of free fatty acids which react with basic catalyst during transesterification to form soap making difficult purification of glycerin phase and increasing the demand for catalyst. The presence of phospholipids in the oil increases its resistance to oxidation, but also emulsifying reaction system makes it difficult separation of glycerol and ester phase. The phosphorus content in the oil directed to transesterification shouldn't exceed 10 ppm. Rapeseed oil led to methanolysis should be deprived of moisture (water content<0.5%), because its presence causes the hydrolysis of triacylglycerol, resulting in the formation of free fatty acids. Some factors decide about quality of rape seeds i.e. the degree of seeds maturity, the presence of damaged seeds, seed moisture content and storage times and conditions. Higher free fatty acids content can be stated in the seeds of inferior quality [2,7,8].

2.2. Transesterification of rapeseed oil

Transesterification is the best way to obtain biodiesel because it is well-known and cheap process which gives less problems for the engines than another methods. In a standard process of production biodiesel from rapeseed oil there are following process steps i.e. esterification of rapeseed oil, separation of esterification products, methanol distillation and purification of the ester. The main stage of the process is based on the transesterification reaction of rapeseed oil with an alcohol (methanol, ethanol) which results in formation of esters of alcohols and glycerol. The reaction is reversible due to formation of water, which is responsible for shifting the equilibrium towards the reagents. In order to move the chemical equilibrium towards the ester, an excess of alcohol is used. The transesterification involves three consecutive and reversible reactions. Each molecule of alcohol makes with the residue of fatty acid a distinct monoester molecule. If the triglyceride contains three different fatty acids in its molecule, a mixture of rapeseed oil esters is obtained [1-4,6,7,9].

There are used various chemical catalysts in the transesterification reaction i.e. acids, alkalis and enzymes. Some of them are the most effective i.e. alkaline catalysts and their methoxides. Only anhydrous reactants should be used, because the water decomposes catalyst and leads the reaction to the side of the reactants. The amount of the catalyst depends on its type, quality of substrates, reaction time and temperature. Its value varies from 0.2% to 2% by mass relative to the weight of oil. Unrefined oil requires more catalyst. Free fatty acids content in oil shouldn't exceed 0.5-1%. The higher the water content in methanol, the greater the consumption of catalyst and higher contents of free fatty acids as well as soaps. Forming of soaps reduces the activity of the catalyst and increases the viscosity, so the separation of the glycerol is more difficult [6,7].

In the majority of the biodiesel production processes, methanol is used, mainly due to the cost and its physical and chemical advantages (polar, shortest chain alcohol and the reactivity is easier).

For the basic-catalysed process, the optimal ratio is 6:1 (alcohol: oil). Applying alkaline catalysts in the reaction allow to carry out the transesterification process at room temperature. The reaction time is very diverse and can vary from several minutes to several hours (typically about 30-60 minutes). Mixing is important because of the lack of mutual solubility of the substrates. Appropriately intensive mixing of reactants increases the contact area. Using the refined oils with a higher purity as well as pure and anhydrous methanol, allows to obtain biodiesel with a high content of methyl ester (96.5-99%) [1,3,7,9].

In the transesterification reaction, the oil is converted to FAME (Fatty Acid Methyl Ester). The flow, which goes out from the reactor, should be purified. First, the methanol is recovered (94%) and then residue is carried to separation of glycerin. Next, the obtained biodiesel is purified to commit the standards of quality.

The primary by-products generated during the production of biodiesel include: oilseed meal, straw and glycerol. Oilseed meal is produced in the process of pressing oil from rapeseeds. It accounts for 70% by weight, and oil represents the remaining 30%. Oilseed meal can be used as a component of feed or as a component of the binder for the production of smokeless fuel, additive to fuel briquettes and as a basic component of mat to cover mine dumps [7].

Straw is formed at the beginning of the production cycle. Part of straw in the form of chaff can be plowed already on the field and is a valuable organic fertilizer. Properly prepared straw can also be used as a component of the roughage. Straw is also a valuable energy source, because its calorific value is about 30-40% of the calorific value of coal and the ash formed of its combustion can be used as a mineral fertilizer.

Glycerol is a byproduct formed in the esterification of rapeseed oil. In this process also are created soaps and free fatty acids. Glycerol phase constituting concentrated glycerol (about 80% solution) may be transferred to facilities specializing in treatment of glycerol (e.g. cosmetic, pharmaceutical). The cost of obtaining the crude glycerol during esterification of vegetable oils is lower than the cost of traditional methods that had been previously used in splitting of fats. Glycerol from vegetable oils is used both for cosmetic purposes and pharmacology. More often it is an ecological material for the manufacture of certain foods and it is used for making explosives. Using own purification of glycerol, receives an additional by-product in the form of valuable mineral fertilizer. In the case of small factories, where it is uneconomic to build installation of treatment and it is not organized buying glycerol, it can be disposed of by diluting with water in a ratio of 1:100 and added to the slurry [3,7].

Soaps and free fatty acids also may be forwarded to the appropriate processing plants, or used in their own farm. Mud can be a valuable addition to the feed for producing Californian earthworms Biohumus – mineral fertilizer.

Vegetable oil is low-density-energy biomass. It limits the scale of biodiesel production. However, there are advantages of biodiesel plant refinery such as low investment and rapid construction.

The main application of fatty acid methyl esters is biodiesel, generally as mixture with petro-diesel for engine use. After refinement, fatty acid methyl esters can be also used as biodegradable solvents. Additionally, there are a source of many commodity chemicals such as higher alcohols. Glycerol is an important chemical product mainly used in areas such as food, beverage, pharmaceutical, cosmetic, tobacco and paper making.

3. Conclusions

Legal regulations in force require the use of fuels containing biocomponents from renewable sources. Fuels derived from vegetable oils have widespread applications. However, its use is the most effective while adding to the fossil fuels. Rapeseed oil is the main source of quality biodiesel which is important platform chemicals produced by the oleochemical industry. Transesterification of vegetable oil is a process by which triglycerides react with methanol in the presence of a catalyst to obtain fatty acid methyl esters and glycerol.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

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