



Optimization of raw material mixtures in the production of biodiesel from vegetable and used frying oils regarding quality requirements in terms of cold flow properties

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ABSTRACT

In the production of biodiesel the need for using more inexpensive and alternative raw materials arises. This is due to the limited amount of traditional raw materials in the market and their high prices. Very convenient alternative raw material which is also cost effective is used frying oil (UFO). The quality of the final product greatly depends on the quality of raw materials. By using only used frying oil (UFO) as raw material it is not always possible to obtain a good quality product. Therefore, it is necessary to make a mixture of raw materials to obtain a high quality product and at the same time to minimize the costs. The purpose of this paper is to investigate the impact of various raw material mixtures of rapeseed and used frying oil on the most important physico-chemical characteristics of biodiesel, viscosity and cold flow properties. It is shown that portion of UFO in raw material mixtures does not have significant impact on viscosity of final product, but only cold flow properties. We discovered linear correlations between cold flow properties of product formed from mixtures of raw materials, and cold flow properties of the product formed from pure raw materials. Cold flow properties of raw materials and cold flow properties of products are also in linear correlation. CFPP of the final product from the raw material mixture is equal to the sum of the product of portion of particular raw materials in the mixture and CFPP products from the same raw material. These findings can be implemented in determining optimal raw material mixture. We made a short overview of one such model, which is also included in this work.

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1. Introduction

High production costs of biodiesel are caused mostly by the cost of raw materials, whose share in the cost exceeds 80% [1], which implies that the production cost can be significantly lowered if the raw material or part of it is replaced by a suitable alternative raw material.

Cheaper raw materials usually have lower quality. Disadvantages of raw materials of lower quality may not always be removed by cost-effective treatment processes preceding methyl ester production process, and hence the quality of biodiesel is heavily conditioned by the quality of raw materials, which is primarily related to the oil composition and its technological properties. Even if the material is suitable for processing with the relevant process technology, raw material composition will affect the characteristics of the final product. The most widely used oil for biodiesel production in Europe is rapeseed oil. A very suitable raw material for biodiesel production, which is also cheaper, is used frying oil (UFO). Methanolysis of UFO is possibility for producing cheap alternative fuels, which could reduce pollution and protect the environment [2]. Before using this, oil had nutritional

quality, i.e. it does not contain gums and phosphorus or other impurities that could interfere with the production process. Using used frying oil as a feedstock for biodiesel production is a significant environmental aspect, because it reduces the problems associated with pollution of the environment of this waste product. The ratio of net energy in the production of biodiesel from UFO is 5–6, as opposed to 1.9 to 2.9 for rapeseed oil [3].

By use of common technological processes in plants for manufacturing biodiesel from vegetable oils using only cheaper raw materials no product of appropriate quality can be produced. In these plants it is best to mix raw materials and so make optimum raw material mixtures that will meet the quality requirements, and maximally reduce costs. In order to make an optimal raw material mixture, it is necessary to have data on the characteristics and prices of raw materials and models that will predict the properties of final products and raw materials to make the optimal mixture. The most important physico-chemical properties of biodiesel, which are reflected in its use-value, and directly depend on raw material composition, are viscosity and cold properties. The purpose of this paper is to examine the extent to which cold properties and viscosity depend on raw material composition and create models to determine the optimal raw material mixture that will provide a product that meets quality requirements, whereby different mixtures of rapeseed and used frying oils will be tested.

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2. Background

Biodiesel is an alternative fuel for diesel engines which is produced by chemical reaction of vegetable oils or animal fats with alcohol, usually methanol [4]. The reaction is carried out with a catalyst, usually a strong base such as sodium or potassium hydroxide. Raw, half-refined or refined vegetable oil is used for the production. In the case of using raw or half-refined vegetable oil, it must first undergo a pre-treatment process that consists of degumming and neutralization. Degumming has purpose to remove gummy substances mainly on the basis of phospholipid and proteins. Gums would make the separation phase after transesterification difficult. In order to make oil suitable for the transesterification process, it must contain less than 50 ppm of phosphorus, which requires the water and acid degumming process. The aim of neutralization is to remove free fatty acids which would neutralize alkaline catalyst in the process of transesterification and thus lower the conversion, and the resulting products would make the separation of the ester and glycerin phase difficult. Degummed and neutralized vegetable oil, if necessary, may undergo the dewaxing process, after which the oil is ready for the transesterification process and post reaction processing. Since used food oils are formed by frying of refined vegetable oils and fats that have undergone the process of refining, no gummy substances are formed, and thus oil degumming is not required.

A special pretreatment process, the so-called alcohol neutralization eliminates free fatty acids and water from oil by mixing and extraction with glycerine from the first transesterification. If required, in the first transesterification glycerine, before being used for rafination, can be additionally alkalized with KOH solution. Oil transesterification is carried out by mixing oil with methanol in which there is already a dosed and dissolved alkali catalyst. Due to the complete reaction and saving the reactants transesterification is usually carried out in 2 or 3 stages, and after each stage it is followed by separation of the glycerin phase [5].

Transesterification is followed by vacuum evaporation in thin-film evaporators to extract methanol, followed by cleaning esters either with extraction with water or adsorption agents, and finally vacuum evaporation to remove water, followed by filtration, and if necessary aditivation.

2.1. Rapeseed oil

Oils with fatty acids of a higher degree of saturation have lower fluidity at low temperatures, and easily lead to solidification. Oils with a high degree of unsaturation and a low degree of polyunsaturation, i.e. with a high portion of monounsaturated fatty acids, reach the best cold properties. Rapeseed oil has such composition, and this is the reason why it is mostly used in biodiesel production in Europe. Crude rapeseed oil contains 98% triglycerides. Oleic (>60%) and linoleic (>20%) acids [6] are less present in triglycerides.

2.2. Used frying oil

European and international statistics show that 40–50% of cooking oil used to prepare food is consumed in restaurants and industry, and the rest in households, of which about 50% is absorbed by food, while the rest remains as waste. If it is assumed that oil for biodiesel production is collected exclusively from restaurants, it is estimated that the potential quantity of such a raw material ranges from 20 to 25% of the amount of oil that is consumed for food preparation [7]. According to data from the European Union the total amount of used frying oil is about 5 kg per capita per year [8].

2.2.1. Changes during frying and composition of used frying oil

Frying foods is carried out at temperatures from 160 to 200 °C, whereby a portion of oil is absorbed by the product, and part of the

product being fried is disintegrated and separated and remains in the oil. Reactions in the oil and oil and food reactions, and thus absorbed oil in the food, cause physical and chemical changes on the surface and the product itself, and this is reflected in changing nutritional, sensory and rheological properties of the fried product.

The most important changes that occur in oil during frying are hydrolysis, auto oxidation and oxidative and thermal polymerization. These processes have an effect on the increase in acid number, iodine value reduction, and increased water content. Physical changes in oil resulting from chemical changes are an increase in viscosity, smoke point, tendency to foaming, refractive index and color that becomes dark brown to red [9] (Table 1).

By degradation of oil about 500 compounds are formed, and among them toxic acrolein and heterocyclic amines.

Compounds formed by chemical changes in oil can be divided into volatile and non-volatile compounds. Volatile compounds are those which during frying evaporate together with part of oil and water vapor, while non-volatile compounds remain in oil. The most important non-volatile compounds formed by decomposition of oil are monoacylglycerols, diacylglycerols, oxidized triacylglycerols, triacylglycerol dimers, triacylglycerol trimers, triacylglycerol polymers, and free fatty acids, while the most frequent volatile compounds produced by decomposition of oil are hydrocarbons, aldehydes, ketones, alcohols, esters and lactones.

In frying oil changes in physical and chemical properties occur which are the consequence of chemical reactions in oil itself and reactions of oil with water and oxygen at an elevated temperature. Hydrolytic cleavage of oil occurs in the presence of water which enters oil from food. One part of water quickly evaporates, while the other part is absorbed in the oil, cleaving it into free fatty acids and glycerol. The oxygen absorbed from the air reacts with the unsaturated acylglycerols producing various oxidation products. The first step is the oxidation of unsaturated acylglycerols whereby hydroperoxides are formed. Saturated and unsaturated aldehydes, ketones, hydrocarbons, alcohols, acids and esters are formed as products of the hydroperoxide decomposition. Most of these products being formed in reactions of radicals, i.e., dimeric and polymeric acids, and dimeric acylglycerols and polyglycerols remain in the oil increasing its viscosity. The rest breaks up further to volatile compounds, i.e., hydroxy acids and epoxy acids that evaporate from the oil.

The increased portion of polar and polymer compounds is an important parameter for determining the degree of oil degradation, and due to the increased portion of polar compounds used frying oil is absorbed and a greater amount of water in comparison to fresh oil.

Degradation of oil adversely affects the sensory and healthy safety of products, and hence oil for frying needs a regular change. European legislation requires that oil should be replaced when the portion of polar compounds in oil exceeds 25%, or when the portion of polymer compounds exceeds 10% [8].

Used frying oil and other organic waste consume oxygen through their decomposition and thus remove it from water and soil, which

Table 1
Main changes and resulting compounds in oil during frying [9].

Change	Change factor	Resulting compounds
Hydrolysis	Water	– Free fatty acids – Diacylglycerols – Monoacylglycerols
Oxidation and oxidative polymerization	Oxygen	– Oxidized monomer triacylglycerols – Oxidized dimer and oligomeric triacylglycerols – Volatile compounds (aldehydes, ketones, alcohols, hydrocarbons etc.)
Thermal polymerization and degradation	Temperature	– Cyclic monomer triacylglycerols – Cyclic dimer triacylglycerols – Non-polar dimer and oligomeric triacylglycerols

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