THE USE OF BY-PRODUCTS OF BIODIESEL PRODUCTION FOR SYNTHESIS OF MONOGLYCERIDES

BIODĪZEĻA RAŽOŠANAS BLAKUSPRODUKTU IZMANTOŠANA MONOGLICERĪDU SINTĒZEI

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Summary. Biodiesel is produced by transesterification of variable vegetable oils or animal fats with lower alcohols in the presence of alkali catalysts; the crude glycerol is the main by-product of this process. The amount of the crude glycerol formed during transesterification processes is about 100 kg per tonne of oil. We have developed the method for synthesis of monoglycerides from crude glycerol. The yield of monoglycerides reaches 46.8%. The monoglycerides are valuable products for many applications - emulsifiers for both food and pharmaceutical industry, stabilizers in cosmetic industry; there is a large field in technical applications (e.g., modifying agents in the manufacturing of alkyd resins, detergents and other surface-active agents). Glycerolysis of fatty acids as well as triglycerides with crude glycerol (especially, if both raw materials are obtained as by-products) leads to more commercially viable biodiesel production.

The biodiesel is renewable, environmentally friendly diesel fuel. The EU Biofuels Directive 2003/30/EC schedules that the biofuel should compile at least 5.75% (on the basis of energy content) of total amount of fuel marketed for transportation means by the end of 2010. The first industrial production plant for rapeseed oil methyl esters was launched in 1991 (Aschach/Donau, Austria). The biodiesel production capacity of EU-27 on July 1, 2007 was 10,289,000 tonnes [1]. There are several biodiesel production enterprises in Latvia: *Delta Riga* Ltd. (capacity 12500 t/y), *Mežrozite* Ltd. (capacity 18000 t/y), *Mamas-D* Ltd. (capacity 4500 t/y). Beside that the new plant of *Bio-Venta* Ltd. will start a business in spring 2008 with planned capacity 100,000 t/y.

The biodiesel is obtained by transesterification of vegetable oils or animal fats. Most often reaction is carried out with lower alcohol (methanol or ethanol) in the presence of alkali catalyst (KOH, NaOH). The main by-product of this process is crude glycerol and sometimes (depending from the technology used) the small amount of free fatty acids (FFA), too.

Mono- and diglycerides are natural components of animal fats and vegetable oils. There are several methods for synthesis of monoglycerides. The glycerol and vegetable oil, animal fat, fatty acids in the presence of different catalysts can be used as reagents for production of monoglycerides. Nowadays different homogeneous and heterogeneous catalysts are applied in synthesis of monoglycerides: NaOH, KOH, $NaOCH_3$, *p*-toluenesulfonic acid, H_2SO_4, Fe, Fe_2O_3, Fe_2O_4, FeOH, Co, CoO, $CoCl_2$, Mn [2, 3]. In order to increase the yield of monoglycerides the reaction mixture should be homogenised - it can be achieved by solvents containing hydrophilic and hydrophobic groups in the molecule, e.g. *tert*-butanol [2] or lactic acid [4]. The synthesis of monoglycerides has been realized in the presence of sodium or potassium soaps – in this case pure glycerol and individual fatty acids or a mixture of fatty acids have been used; the yield of monoglycerides reaches 47.6% [5]. Glycerolysis of pure glycerol has been extensively studied while the information on the glycerolysis of crude glycerol derived from the biodiesel is rare – several publications disclose use of such glycerol for glycerolysis of methyl esters [6, 7] and triglycerides [6, 8-10], which leads to mono- and diglycerides.

Our investigations were devoted to application of crude and technical glycerol in synthesis of monoglycerides from free fatty acids as well as rapeseed oil. The composition of crude glycerol strongly depends on the biodiesel feedstock – the particular vegetable oil or animal fat. In average, this composition is following: glycerol - 42%, sodium salts of fatty acids - 21%, mono-, di-, triglycerides - 18%, methanol - 15%, water and other components (styrenes, terpenes etc.) - 4%.

We used different raw materials - pure glycerol (99%), technical glycerol (≥86%) and crude glycerol (after evaporation of water and other volatile substances) - and conditions for synthesis of monoglycerides. Triglycerides (rapeseed oil) as well as mixtures of fatty acids (separated from the crude glycerol during biodiesel production process) were subjected to glycerolysis. The reaction was carried out in the presence of homogeneous catalysts (NaOH or sodium soaps) and heterogeneous catalyst (Fe_2O_3). We used *tert*-butanol to provide homogeneous media. In case of the heterogeneous catalyst, the mixture was heated at 190^{o}C under N_2. The best result was obtained when crude glycerol containing sodium salts of fatty acids (which act as catalysts and homogenise reaction mixture) was applied.

We studied an effect of the mass ratio of reagents (glycerol and fatty acids) on the yield of monoglycerides (according to GC analyses). The best result (46.8%) was achieved when ratio of glycerol and fatty acids was 1:1.

The monoglycerides can be used as emulsifiers in food and cosmetic industries and agriculture, as constituents of antiseptical means, as modifying agents in the manufacturing of alkyd resins, detergents and other surface-active agents; there is a large field in technical applications.

We have developed a convenient method for production of monoglycerides - widely applicable multifunctional product. This method leads to more commercially viable biodiesel production and remarkable reduction of waste.

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