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# The influence of animal fat type and purification conditions on biodiesel quality

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ABSTRACT

Production of biodiesel from waste animal fats has a great potential since this feedstock does not compete with the food industry and leads to the global reduction of wastes. The type of feedstock as well as the presence of impurities highly influences the quality of biodiesel. Too high concentrations of glycerol and glycerides in biodiesel negatively influence the fuel quality and can generally reduce the engine durability, so crude biodiesel needs to be purified. One alternative method of purifying biodiesel is extraction with deep eutectic solvents.

Biodiesels were synthesised from five types of waste animal fats: veal and beef tallow, lard, chicken and goose fat, by means of chemical transesterification catalysed by alkali catalyst. Due to the fact that the presence of impurities negatively influences the quality of biodiesel, crude biodiesels were purified. Liquid-liquid extraction with previously prepared deep eutectic solvent choline-chloride/ethylene-glycol (molar ratio 1:2.5) was selected as the purification method. Experiments were performed at different mass ratio solvent/biodiesel in a laboratory scale batch extractor equipped with mechanical stirrer and optimal mass ratio was defined. Biodiesels were characterised and their properties were compared with the standard specification. Free glycerol from animal fats biodiesels was efficiently removed by the selected solvent.



## 1. Introduction

During the past decade a great attention has been paid to the development of alternative fuels that could partially or fully replace the existing fossil fuels [1,2]. An alternative fuel has to be technologically acceptable, economically competitive, environmentally friendly and easily accessible. The greatest potential is observed in biodiesel because previous studies showed that the combustion of biodiesel greatly reduced emissions, so biodiesel is now the most commonly used renewable energy source [3]. In addition to reduced emissions, biodiesel production will greatly relieve the transport sector, i.e. its dependence on fossil fuels and it will encourage economic development because of the raw materials that are available, renewable and environmentally friendly [4].

Biodiesel is by definition a mixture of mono-alkyl esters of long chain fatty acids derived from different types of oils or animal fats. Commercially, it is produced by chemical transesterification of oil with alcohol in the presence of a catalyst. Despite the fact that biodiesel is mostly produced from fresh and vegetable oils, various feedstocks can be used, many of them investigated during the past decade. Based on the type of feedstock biodiesel can be categorised as first-, second-, third- and fourth-generation biodiesel [5]. First generation biodiesel refers to a fuel produced from edible oils and fats. Second generation biodiesel is produced from nonedible crops and wastes, while third generation biodiesel is produced from microalgae.

The quality of biodiesel produced by transesterification is influenced by the type and quality of feedstock used, reaction conditions (alcohol to oil molar ratio, temperature, catalyst) and present impurities like moisture or free fatty acids [6]. In the production of biodiesel from lower quality feedstock, it is necessary to pretreat the raw material or, if this does not guarantee satisfactorily low

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**Nomenclature**

| | |
|---|---|
| AMe | integration values of the methyl ester peak |
| ACH2 | integration values of the glyceridic peaks in triacylglycerides |
| CN | cetane number |
| db | number of double bonds |
| DES | deep eutectic solvents |
| FAME | fatty acid methyl esters |
| FFA | free fatty acid |
| FP | flash point |
| FTIR | Fourier transform infrared spectroscopy |
| HHV | higher heating value |
| $^1$HNMR | proton nuclear magnetic resonance |
| IL | ionic liquids |
| $w$, $w_i$ | weight fraction, % |
| $w_F$ | weight fraction of glycerol in biodiesel before extraction, % |
| $w_R$ | weight fraction of glycerol in biodiesel after extraction, % |
| X | carbon number |
| $\varepsilon$ | extraction efficiency, % |
| $\upsilon$ | kinematic viscosity, $m^2\ s^{-1}$ |
| $\eta$ | dynamic viscosity, Pa s |
| $\rho$ | density, kg $m^{-3}$ |

concentrations of free fatty acids, to carefully select a catalyst that will provide conversion of free fatty acids into high-quality oil. The most commonly used methods of pretreatment of raw materials with a high content of free fatty acids are the neutralization of acids or their esterification with acid catalysts, although vacuum steam distillation is sometimes used as well. Some alternative methods of pre-treatment of raw materials have been investigated, such as transesterification by glycerol, biological pretreatment by microorganisms or enzymes, adsorption, liquid-liquid extraction or extraction by supercritical fluids [7]. Each method has its advantages and disadvantages, but in most cases the economic aspect dictates the final decision regarding the selection of pretreatment method. Commercially, biodiesel is produced by a well established technology of chemical transesterification of refined oil in the presence of methanol and sodium hydroxide as catalyst [8–10]. This method requires high quality feedstock since in the presence of water or free fatty acids hydrolysis or saponification will occur. Lower quality feedstocks need to be pretreated or different types of catalyst should be used [11]. Marchetti [8] compared different technologies for biodiesel production. As mentioned, base catalysed homogeneous transesterification is sensitive to the presence of FFA and water, but the reaction is fast and technology is the cheapest. Purification of glycerol and biodiesel is difficult. All other technologies (enzyme, supercritical, monolithic, resin or acid) can produce biodiesel of good to high quality from the low quality feedstocks. The reaction time is longer, up to 70 h for acid and enzyme catalysed reactions, except for supercritical reaction (4–10 min). When enzymes, supercritical alcohol or heterogeneous catalyst is used, both biodiesel and glycerol can easily be purified. The major drawback of using enzymes or supercritical alcohol is high technology cost.

When biodiesel is synthesised it needs to be purified. The presence of various impurities, such as excess alcohol, residual catalyst, unconverted fats, soap, metals or glycerol [12] will negatively influence the quality of biodiesel as well as the engine performance. There are several methods that can be used for the purification of biodiesel [13–15]. In general, methods for purification of crude biodiesel can be divided in three groups: wet washing, dry washing and novel methods. Simple and effective wet washing methods use water, water and organic solvent or mineral acid and water. Those methods very successfully remove glycerol, methanol, soap and various hydrophobic compounds and the resulting biodiesel is of high purity. However, there are several major drawbacks. First of all, large amount of deionized water is used, and consequently large amount of waste water that needs to be purified is produced. Several steps of washing is followed by separation of biodiesel and water and finally it needs to be dried, so it can be stated that wet washing methods are space, time and energy consuming methods. Moreover, in the presence of water hydrolysis can occur, while in the presence of soaps stable emulsion can be formed.

Dry washing methods are based on adsorption and ion-exchange. Dry washing methods purify biodiesel in a shorter time, less space is required and there is no risk of residual water in biodiesel. However, biodiesel might not comply with the standard specification due to the difficult separation of adsorbents from biodiesel, and low efficiency of ion exchange resins in removal of glycerol and methanol. Besides, when ion exchange resins are used, solid waste that cannot be regenerated is produced.

In order to overcome disadvantages of both washing methods, scientists have started to investigate new environmentally friendly methods for biodiesel purification, liquid – liquid extraction with ionic liquids and deep eutectic solvents as well as membrane based separation. Ceramic membranes can remove catalyst, soap and glycerol from crude biodiesel. However, this method is expensive and membranes need to be cleaned up after usage.

Liquid – liquid extraction is a separation method that can be used at atmospheric pressure and room temperature [16]. If an environmentally friendly solvent that can be easily regenerated is used, this method is both environmentally and economically accepted. Ionic liquids are defined as salts composed of organic cation and organic or inorganic anion with the melting point below the room temperature [17]. Deep eutectic solvent, the greener alternatives to the ionic liquids, are a mixture of hydrogen-bond donor and hydrogen-bond acceptor with the melting point below the melting point of the individual components [18]. Both types of solvents have numerous advantages over commercially used organic solvents, but DESs can be easily prepared, and the majority of them are non-toxic and biodegradable. The properties of ILs and DESs can be altered by different combinations of cations and anions, or hydrogen-bond donors and hydrogen-bond acceptors. Because of their properties, these solvents found their place in various processes [19]. Considering only production of biodiesel, ILs and DESs were used for purification of feedstocks and biodiesel, as well as catalyst, solvent or cosolvent in esterification and transesterification steps [19–23]. Some studies on vegetable oils have shown that the use of DESs reduces the content of all impurities present in crude biodiesel [19,21,22,24,25]. The major drawback of utilization of these solvents in the purification step is the absence of the regeneration method. However, due to their high solvation capacity ILs and DESs can be reused multiple times without regeneration.

The aim of this research is to synthesise biodiesel from different types of animal fats by alkali-catalysed transesterification and purification of biodiesel by liquid – liquid extraction with deep eutectic solvent, choline chloride:ethylene glycol (molar ratio 1:2.5). Purified biodiesels were characterised and compared with biodiesel standard.

## 2. Material and methods

### 2.1. Material

Waste animal fats (veal, beef, pork, goose, chicken) were