

DEEP EUTECTIC SOLVENTS FOR PURIFICATION OF WASTE COOKING OIL AND CRUDE BIODIESEL

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ABSTRACT:

The goal of this work was to explore the applicability of deep eutectic solvents in biodiesel production process. Biodiesel was produced from waste cooking oil via base-catalysed transesterification. The efficacy of two base catalysts KOH and NaOH on the conversion of triglycerides into biodiesel was tested. Eutectic mixtures DES 1 ($K_2CO_3 : C_2H_6O_2 = 1 : 10$) and DES 2 ($C_5H_{14}ClNO : C_2H_6O_2 = 1 : 2$) were prepared. DES 1 was used for feedstock deacidification and DES 2 for biodiesel purification via extraction. Effects of DES 2 to biodiesel ratio and the extraction duration on free glycerol removal were tested. Samples were analysed using FTIR and 1H NMR spectroscopy. Synthesis of biodiesel was carried out for 3 h at $60^\circ C$ with mass ratio KOH : methanol : oil = 1 : 40 : 100. DES 2 was effective for purification of biodiesel. Mass ratios 0.5:1 and 1:1 proved best and 45 minutes of extraction was enough to reduce free glycerol and increase the content of fatty acid methyl esters.

KEYWORDS: biodiesel, glycerol, extraction, deep eutectic solvent, waste edible oil

INTRODUCTION

The last decade has seen great interest in development of alternative fuels that could potentially replace existing fossil fuels [1]. Studies have shown that biodiesel has a great potential as an alternative fuel because its combustion reduces emissions compared to fossil fuels and it relieves dependence of the transport sector on fossil fuel prices and availability. It can also encourage economic development due to its available, renewable and environmentally friendly raw materials [2], [3].

Biodiesel is a mixture of fatty acid alkyl esters. It is produced from triglycerides via transesterification. Potential feedstocks for biodiesel production include not only high quality vegetable oils but also used animal fat, waste cooking oil, algae and even waste coffee ground oil [1], [4]. The reaction can be catalysed homogeneously and heterogeneously. Homogenous catalysis can be acidic or basic and heterogeneous catalysts can be solid catalysts or enzymes [5]. Most commonly, biodiesel is produced from vegetable oils and methanol in the presence of a basic catalyst such as sodium or potassium hydroxide. The reaction is fast and results in high content of fatty acid methyl esters (FAME) but it is very sensitive to impurities in the feedstock, most notably free fatty acids and water [6]. Potassium carbonate based deep eutectic solvent was previously used for deacidification of different

feedstocks and the same method was applied to waste cooking oil in this work [7].

A by-product of transesterification reaction is glycerol. After the reaction, FAME and glycerol are separated under the force of gravity since the density of glycerol is higher than of FAME, but a small amount of glycerol is soluble in biodiesel and therefore has to be extracted from it [8]. Additionally, crude biodiesel may also contain unreacted methanol and mono-, di- and triglycerides, leftover catalyst and potentially formed soap [9]. All those impurities can negatively impact biodiesel storage properties and engine performance, making crude biodiesel purification a necessary step in the biodiesel production process.

Deep eutectic solvents are liquid mixtures consisting of two or three components, usually environmentally acceptable, cheap and non-toxic. Components bind together with hydrogen bonds and the resulting mixture has a lower melting point than the starting components [10].

A potential method for biodiesel purification is liquid-liquid extraction with deep eutectic solvents. Studies have shown that extraction with deep eutectic solvents reduces the content of all present impurities in biodiesel [11]-[13]. In this work, choline chloride based deep eutectic solvent was used to purify crude biodiesel.

MATERIALS AND METHODS

The goal of this work was to examine the applicability of deep eutectic solvents for purification of waste cooking oil and crude biodiesel produced via base catalysed transesterification. Experimental part includes characterisation and purification of the feedstock, preparation of deep eutectic solvents and lastly synthesis, characterisation and purification of crude biodiesel with deep eutectic solvents.

Table 1. Chemicals used in this work

Chemical	Manufacturer
Diethyl ether, (C ₂ H ₅) ₂ O	Honeywell
Ethanol, C ₂ H ₅ OH	KEFO
Ethylene glycol, C ₂ H ₆ O ₂	T.T.T.
Choline chloride, C ₅ H ₁₄ ClNO	Acros Organics
Potassium carbonate, K ₂ CO ₃	Lach-Ner
Potassium hydroxide, KOH	Kemika
Methanol, CH ₃ OH	J.T. Baker
Sodium hydroxide, NaOH	T.T.T.

PREPARATION OF DEEP EUTECTIC SOLVENTS

Choline chloride, potassium carbonate and ethylene glycol were dried in a vacuum drier for 8 hours at 60 °C and pressure less than 10 mbar. After drying, components were weighed in a round bottom flask and mixed on a rotary evaporator until a clear homogenous liquid was formed. DES 1 was prepared for purification of the feedstock and it consists of potassium carbonate and ethylene glycol in molar ratio 1:10. DES 2 was prepared for purification of crude biodiesel and it consists of choline chloride and ethylene glycol in molar ratio 1:2.5.

PURIFICATION OF WASTE COOKING OIL

Waste cooking oil, obtained from a local company Agroproteinka, is a thick, viscous liquid containing different impurities such as metals and free fatty acids. In order to make it suitable for base catalysed transesterification, the feedstock was purified via extraction with DES 1. Waste cooking oil was first heated to 60 °C for 30 minutes and filtered to remove solid particles and a sample was taken to determine its acid number. After filtration it was mixed with DES 1 (mass ratio of DES 1 to fat was 1:10) for 30 minutes and then the mixture was separated and a sample of feedstock was taken to determine its acid number. Total acid number was determined titrimetrically according to the method ISO 660:2009.

BIODIESEL SYNTHESIS

Biodiesel was synthesized via base catalysed transesterification with potassium and sodium hydroxide dissolved in methanol. Hydroxide was dissolved in methanol and then added to preheated waste cooking oil and mixed for 3 hours at 60 °C. After synthesis, biodiesel was separated from glycerol using a centrifuge. Samples of biodiesel were taken for further analysis. Mass ratio of catalyst:MetOH:feedstock was 1:40:100. Efficacy of both catalysts was determined and potassium hydroxide was chosen for further experiments.

In order to determine the optimal amount of catalyst and methanol needed, experiments were carried out with different KOH:MetOH:feedstock mass ratios. First the optimal amount of catalyst was determined and then, with the chosen ratio of KOH to feedstock, amount of methanol was varied.

Table 2. Biodiesel synthesis was carried out for 3 hours at 60 °C and following mass ratios:

mass ratio – catalyst:methanol:feedstock		
0.1:40:100	0.5:40:100	1:40:100
1:30:100	1:40:100	1:50:100

PURIFICATION OF CRUDE BIODIESEL

Synthesized biodiesel contains a small amount of free glycerol and unreacted mono-, di- and triglycerides. Purification was conducted via extraction with DES 2. It was conducted in a glass reactor on a magnetic stirrer and afterwards the mixture was separated using a centrifuge. Four different DES 2 to biodiesel mass ratios were tested and after determining the optimal ratio, influence of extraction duration was investigated.

Table 3. Purification of crude biodiesel was conducted at room temperature under the following conditions:

Duration: 60 min	DES 2:biodiesel mass ratio			
	0.1:1	0.25:1	0.5:1	1:1
	Extraction duration [min]			
DES 2:biodiesel= 1:1	45	60	75	90

All biodiesel samples were analysed using FTIR and ¹HNMR spectroscopy.

RESULTS AND DISCUSSION

FEEDSTOCK PURIFICATION

Total acid value of the feedstock was 2.362 mg KOH/g feedstock. It was purified in order to avoid saponification during biodiesel synthesis. After 30

minutes of extraction with DES 1, total acid value of the feedstock was reduced to 0.574 mg KOH/g feedstock.

BIODIESEL SYNTHESIS

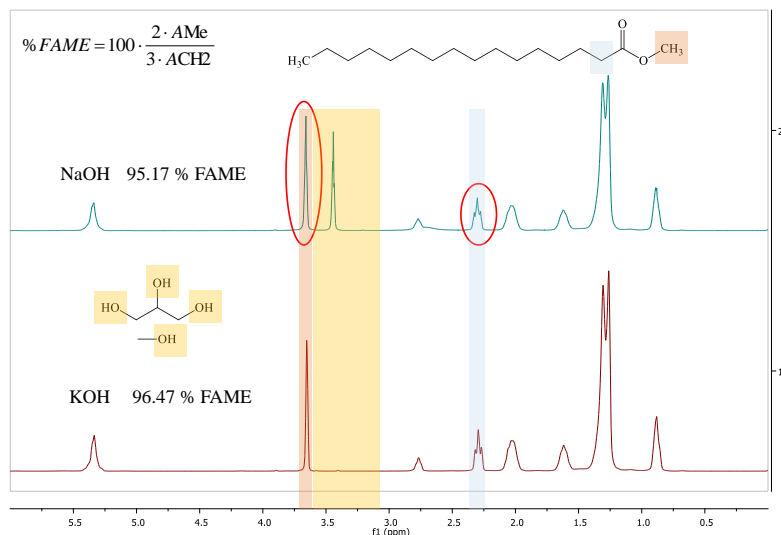


Figure 1. ^1H NMR spectra of biodiesel samples synthesized with NaOH and KOH catalysts

In order to choose a catalyst for further investigation, two experiments were conducted – biodiesel synthesis was done using potassium and sodium hydroxide as catalysts. Mass ratio of catalyst:methanol:feedstock was 1:40:100. ^1H NMR spectra of resulting biodiesel samples are shown in Figure 1. Several peaks can be observed here: the peak of ester groups at 3.64 ppm, which is characteristic for biodiesel and the peak of $-\text{OH}$ groups at 3.45 ppm – corresponding to glycerol and unreacted methanol. The peak at 2.35 ppm corresponds to CH_2 group and

the area under that peak was used, together with the area of the ester peak, to calculate the share of FAME in the sample. Biodiesel standards require a share of FAME higher than 96.5 %. Biodiesel produced with NaOH had 95.17 % of FAME and the one produced using KOH had 96.47%. Potassium hydroxide was chosen as a catalyst for further experiments, not only because it yielded a higher content of FAME but also because it dissolved in methanol much faster during preparation, saving valuable time.

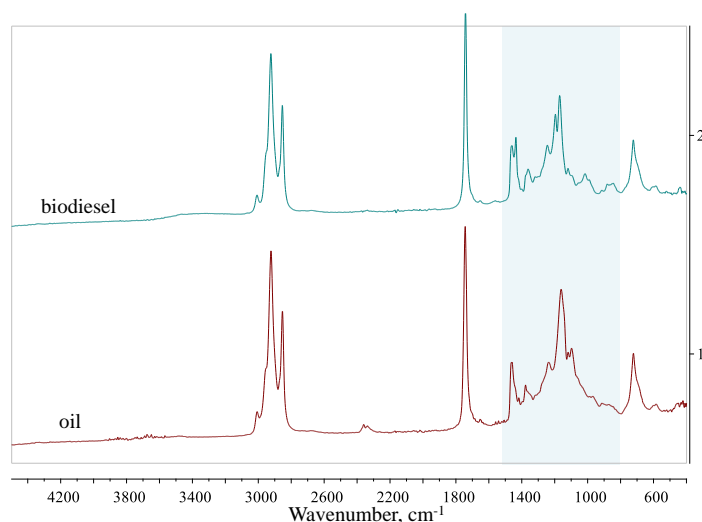


Figure 2. FTIR spectra of the feedstock and biodiesel (KOH:MetOH:feedstock mass ratio = 1:40:100)

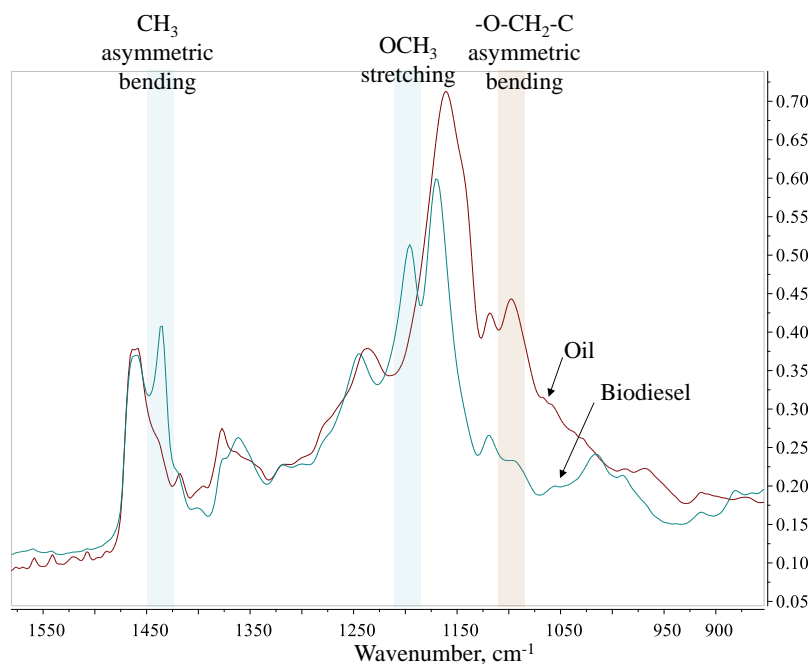


Figure 3. Enlarged part of the overlapped spectra of oil and biodiesel

FTIR spectra of the feedstock and biodiesel (KOH:MeOH:feedstock mass ratio = 1:40:100) are shown in Figure 2. An enlarged part of the overlapped spectra of oil and biodiesel is shown in Figure 3. Most notable differences can be observed at 1436 cm^{-1} , 1196 cm^{-1} and 1099 cm^{-1} . Peaks characteristic

for oil disappear (asymmetric bending of $-\text{O}-\text{CH}_2-\text{C}$ group at 1099 cm^{-1}) and peaks characteristic for biodiesel appear (asymmetric bending of CH_3 group at 1436 cm^{-1} and stretching of $-\text{OCH}_3$ group at 1196 cm^{-1}).

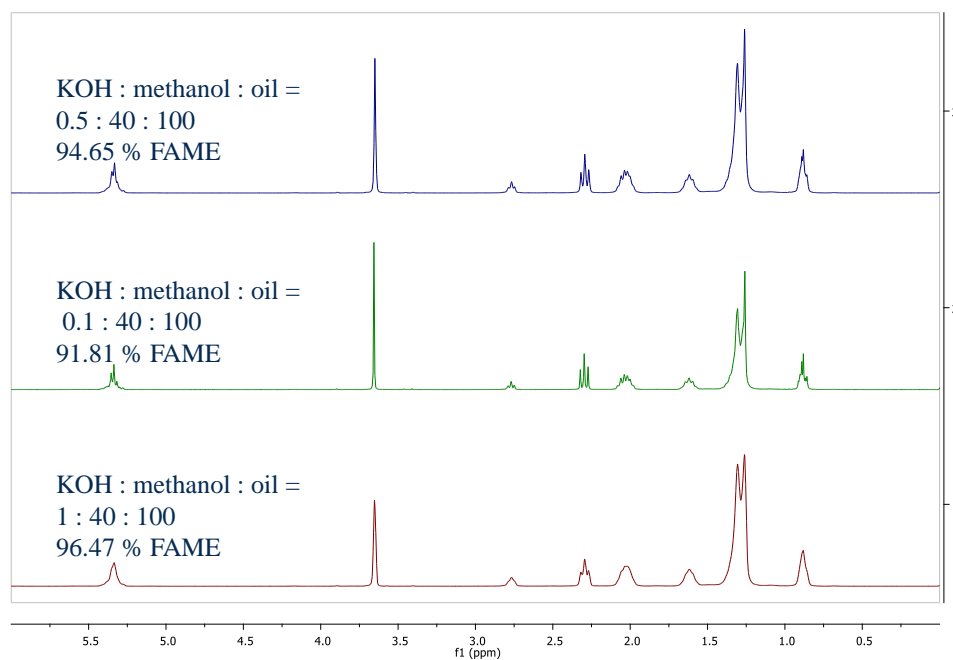


Figure 4. ^1H NMR spectra of biodiesel samples synthesized at 60 °C for 3 hours – influence of catalyst ratio on the amount of FAME in biodiesel

Next part of the investigation included finding the optimal amount of catalyst and methanol needed for transesterification. First set of experiments was conducted with three different amounts of KOH and fixed ratio of methanol to feedstock (as explained in Table 2).

¹HNMR spectra of the resulting biodiesel samples are shown in Figure 4. It can be observed that the share of FAME in biodiesel depends on the amount of catalyst used and the highest FAME content was obtained with the highest catalyst ratio. The best result was 96.47 % of FAME, which is very close to the 96.5 % limit required for biodiesel. Since crude biodiesel contains impurities such as free glycerol, mono-, di- and triglycerides and possibly unreacted methanol, it was expected that the share of FAME in biodiesel will increase after purification.

After determining the optimal amount of catalyst, mass ratio of catalyst to feedstock was fixed to 1:100 and the amount of methanol was varied (mass ratios for the experiments KOH:MetOH:feedstock were 1:x:100, x=30, 40, 50). The resulting biodiesel samples had a content of 96.12, 96.47 and 97.25 % FAME, respectively.

PURIFICATION OF CRUDE BIODIESEL

The last part of this work was focused on biodiesel purification in order to remove impurities and increase its FAME content. A larger amount of biodiesel was synthesized for next experiments (mass ratio KOH:MetOH:feedstock was 1:40:100). Influence of the amount of solvent used and extraction duration was investigated. First set of experiments was conducted for 60 minutes with varying mass ratios of DES 2 to biodiesel (0.1, 0.5, 0.75 and 1:1). Resulting FAME contents calculated from ¹HNMR spectra of the samples are given in TABLE. All obtained biodiesel samples had well above 96.5 % of FAME. Second set of experiments was conducted with mass ratio of DES to biodiesel 1:1 for 45, 60, 75 and 90 minutes. Results are given in Table 4. It was observed that 45 minutes was the optimal time of the extraction. Longer extraction duration resulted in the decrease of FAME content.

Table 4. Purification of biodiesel via extraction. Initial FAME content was 98.51 %

DES 2:biodiesel mass ratio	0.1:1	0.25:1	0.5:1	1:1
% FAME	97.98	98.04	99.02	98.55
Extraction duration [min]	45	60	75	90
% FAME	98.99	98.55	97.57	96.71

CONCLUSION

Applicability of two different deep eutectic solvents for purification of waste cooking oil and crude biodiesel was investigated. Potassium carbonate based DES proved successful for deacidification of the feedstock and choline chloride based DES was effective for purification of biodiesel.

For base-catalysed transesterification, KOH proved to be a better choice than NaOH, yielding a higher FAME content while also dissolving much faster in methanol during preparation.

The results show that FAME content increased with increasing catalyst and methanol to feedstock ratio. Varying catalyst ratio had a greater effect on the total FAME content than that of methanol.

Purification of biodiesel with DES 2 was conducted with different DES to biodiesel mass ratios. The ratios 0.5:1 and 1:1 were chosen as the best and further experiments were carried out with the ratio 1:1. Extraction duration of 45 minutes was found to be enough to extract free glycerol from crude biodiesel. Longer extraction times resulted in a small decrease of FAME content indicating possible occurrence of a partial extraction of FAME.

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