Heterogeneous catalytic transesterification of waste vegetable oil using modified natural zeolite

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Objectives: In the search of an economical process for biodiesel synthesis, waste cooking oil was analyzed as a potential feedstock. The influence of different concentrations and granulations of the zeolite catalyst on the yield and quality of the final product was also investigated.

Methods: The pretreatment of waste oil was carried out using the simple processes of filtration and drying with $CaCl_2$, after which its physicochemical properties were determined. Transesterification of waste oil with methanol was carried out using zeolite clinoptilolite as the catalyst. Its preparation included modification with sodium hydroxide, drying at 105°C and calcination at 300°C. As for the waste oil, the density, acid and peroxide number, moisture content, kinematic viscosity and flash point of the obtained biodiesels were determined by standardized methods. After the synthesis, the Fourier transformation infrared (FT-IR) spectra of the obtained biodiesel and waste cooking oil were recorded and compared.

Results: The process of transesterification with methanol was found to be suitable due to the high conversion of waste oil esters under relatively mild reaction conditions. Moreover, modified natural clinoptilolite proved to be a suitable catalyst for the process of biodiesel production. At each catalyst concentration and granulation, the biodiesel yield was satisfactory and its quality parameters met the prescribed standards.

Conclusion: The basic characteristics of the biodiesel obtained from waste cooking oil enable its potential application. Moreover, the properties of clinoptilolite, such as concentration and particle size, can be adjusted for each transesterification process to attain high quality product. The performed experiment presents an example of the efficient linking of biofuel production and waste oil disposal processes.

Introduction

Global oil demand is expected to increase to over 16 billion liters per day by 2025, while until 2040 this number will rise to 19.1 billion liters per day, posing insurmountable environmental challenges [1, 2]. In the search of a solution, biofuels have become one of the fastest growing markets in the current bioeconomy, but the main drawback is the fact that their production is not profitable on a commercial scale [3]. Liquid or gaseous fuels from biomass are divided into 4 generations depending on the used feedstock and production method. The first generation, bioethanol and biodiesel, has provided the best results as substitutes for petroleum and its derivatives [4]. Biodiesel is a mixture of monoalkyl esters of long-chain fatty acids derived from triacylglycerides, the main components of vegetable oils and animal fats [5]. There are several methods of industrial biodiesel production, of which transesterification with methanol (alcoholysis) is the most commonly used, because the viscosity of the oil is reduced [6].

In addition to the mixing rate, reaction time and temperature, the molar ratio of alcohol to oil, the type of catalyst, and the composition of the feedstock are the most important parameters of the transesterification process [3]. The use of edible oils grown on agricultural fields intended for food production has led to the infamous "food or fuel" dilemma [7]. Inedible oils, fats as well as edible waste oils can also be used as feedstocks. The cost of the production process from edible waste oils is higher due to the required additional pretreatment and the higher free fatty acid (FFA) content resulting from heating processes [8]. FFA are the hydrolysis products of oil and fat oxidation during heating or frying, and in addition to high temperature, the level of FFA also depends on moisture content [9]. The presence of water and a high level of FFA in a starting material leads to parallel, undesirable saponification reaction that produces soaps, resulting in an emulsion that significantly complicates the separation process of glycerol from biodiesel, leads to the consumption of alkaline catalysts and the formation of water in the final product [10]. Alkaline catalysts are sensitive to the FFA content, while acid catalysts have a lower reaction rate and require harsher reaction conditions [11]. Furthermore, homogeneous catalysts do not offer the possibility of reuse and aggravate product separation, while heterogeneous catalysts are more expensive and require a longer reaction time [12, 13]. In addition to low cost, characteristic acidic sites and shape selectivity, the use of natural zeolites also offers the possibility of regeneration and structural modification [14]. For example, in the basic treatment of zeolites, Si is extracted from the structure by hydrolysis in the presence of OH⁻. As a result, the specific surface area and pore size are changed, mesoporosity is formed, and the adsorption capacity and accessibility of active catalyst sites are improved [15].

In this study, waste cooking oil was analyzed as a potential feedstock for biodiesel production. The influence of concentrations and granulations of the catalyst on yield and quality of the final product was also investigated.

Materials and methods

The processes of transesterification and zeolite modification were carried out according to the procedure described in the literature [16]. The used alcohol was methanol, and the

drying agent was $CaCl_2$. The raw material for biodiesel synthesis was a purified mixture of soybean oil and sunflower oil, used in household for frying. Clinoptilolite, a natural zeolite manufactured by *Rota Mandencilik AS* (Istanbul, Turkey) was used as a catalyst. Modification of clinoptilolite with NaOH was applied in order to increase its catalytic activity. The effects of its concentration and particle size on biodiesel yield and quality parameters were also investigated. All chemicals used for modification of clinoptilolite, transesterification and determination of physicochemical properties of oils and biodiesel were from the same supplier (*Kemika*, Zagreb, Croatia).

Pretreatment of the waste oil

Pretreatment of the oil included removal of solid particles by filtration and removal of water, first by heating and then by addition of a drying agent [17]. The oil was heated to 60°C, in order to reduce the viscosity, then filtered and reheated at 110–120°C for 15 minutes. After cooling, the oil was dried overnight by adding $CaCl_2$, then filtered and stored at 4°C.

Clinoptilolite modification

The zeolite mineral contained 85–95% clinoptilolite. Table S1-1 (**Appendix 1**) lists basic information and physical and chemical properties from the material safety data sheet and information supplied with the product. A catalyst was prepared with two different concentrations with respect to the weight of the starting material, namely 5% and 10%, and particle sizes of 10 and 50 microns. After annealing at 300°C for 2 hrs, the clinoptilolite suspension in water was made, the solution of NaOH was added in the suspension and stirred at 60 rpm for 24 hrs. The precipitate was then dried in an oven at 120°C for 24 hrs. After drying process, calcination was carried out at 300°C for 2 hrs.

Transesterification process

To carry out the transesterification process, 100 g of the pretreated oil was added to the batch reactor and heated to 60°C. Double the stoichiometric amount of methanol (27.4 mL) with suspended catalyst was added. Since oleic acid esters are most abundant in edible oils, the calculation of methanol and biodiesel yield is based on oleic acid triglyceride [18] as shown in the following equation:

1 mol of oleic triglyceride + 3 mol of methanol → 3 mol of methyl ester + 1 mol of glycerol (1)
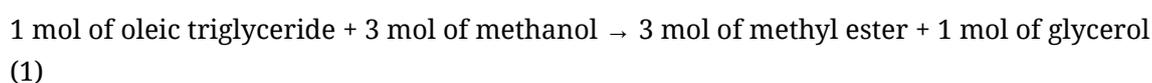
M_m of triglyceride (oleic) = 885 gmol^{-1}, and since the mass of the oil is 100 g, it follows that the amount of oleic triglyceride is 100/885 = 0.113 mol.

The molar ratio of methanol and oil in reaction (1) is 6:1 (double the stoichiometric amount), and the molecular weight of methanol is 32 gmol^{-1}, so the amount of methanol required is as follows: 0.113 × 6 = 0.678 mol × 32 = 21.7 g / 0.75 gcm^{-3} = 28.9 cm^3.

The theoretical biodiesel amount, i.e. methyl ester with a molecular weight of 296 gmol^{-1} (oleic acid methyl ester) is the following: 0.113 × 3 = 0.339 mol, while the theoretical mass of biodiesel is 0.339 × 296 = 100.34 g.

Actual biodiesel yield in percentages:

$$\eta = (\text{mass of the biodiesel obtained} / 100.34) \times 100.$$

The reaction mixture was vigorously stirred at 60°C for 3 hours. The ester and glycerol phases were separated by settling overnight. The resulting soaps and excess methanol were removed by rinsing the biodiesel with distilled water.

Determination of physical characteristics of waste oil and biodiesel

Specific gravity was determined using an areometer at 23.5°C based on Archimedes' principle. Kinematic viscosity was determined using an Ostwald viscometer at 40°C and expressed in mm^2s^{-1}. The peroxide number was determined by addition of KI and titration with $Na_2S_2O_3$, while the acid number was determined by titration with KOH. A Pensky-Martens apparatus was used to determine the flash point of the samples. Infrared spectroscopic analysis was carried out using a Spectrum One infrared spectrometer with Fourier transformation (Perkin-Elmer, USA) in the wavenumber range of 500 to 4000 cm^{-1} and with a resolution of 4 cm^{-1}. FT-IR Spectra of oil and biodiesel were recorded using the capillary film technique.
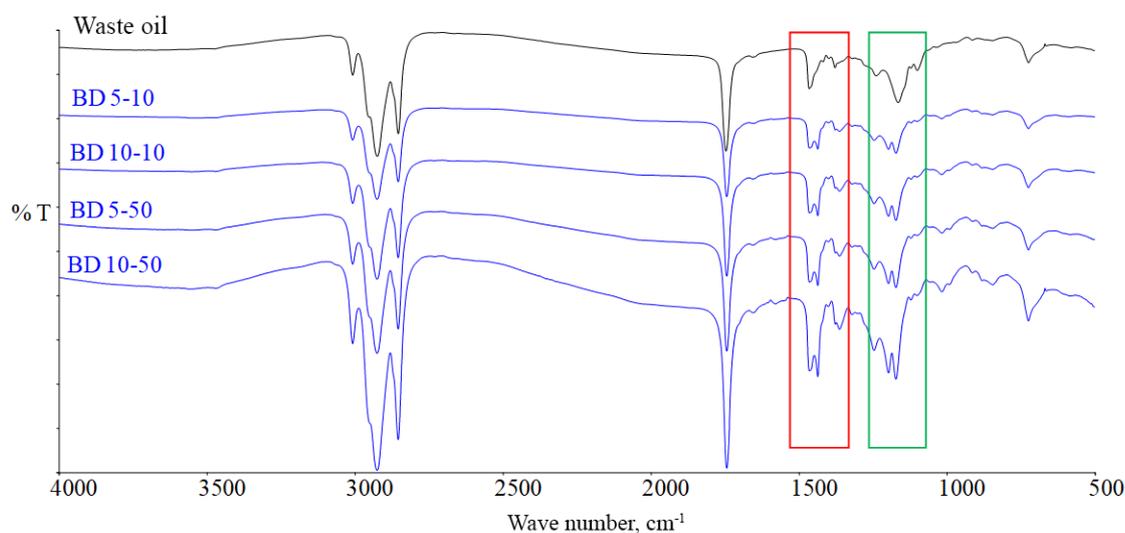
Results

Transesterification of waste oil, the properties of which are listed in Table S1-2, resulted in yields greater than 80% for all four catalysts (**Appendix 1**). Although the peroxide number is higher than for pure vegetable oils, it is within the acceptable limits for waste cooking oils [19]. The acid number shows that the feedstock has a low content of fatty acids. The addition of $CaCl_2$ reduced the already low moisture content to below 0.05%.

Doubling the catalyst concentration resulted in doubling the acid number of the biodiesel (**Table 1**). The viscosity and flash point of the biodiesel obtained with a 5–10 (mass in g - granulation in μm) catalyst are at the upper limit of the prescribed values for biodiesel (**Table 1**). The highest biodiesel yield was obtained with a process in which 10% catalyst, based on the weight of the oil, was added with a particle size of 10 μm.

Table 1. Biodiesel yield and comparison of its properties obtained with different catalyst concentration and particle sizes with ASTM D6571-02 standard

Property	Catalyst mass (g) – granulation (μm)				ASTM-D6571-02
	5-10	10-10	5-50	10-50	
Yield / %	82.2	83.7	82.6	83.6	-
Flash point / °C	169.5	170.0	172.0	168.50	130 (min)
Kb / mg KOHg-1	0.19	0.37	0.19	0.37	0.80 (max)
v at 40°C / mm2s-1	6.10	5.40	5.10	5.40	1.9-6
ρ at 25°C / kgm-3	887	880	881	878	868-880

Comparison of FT-IR spectra (**Figure 1**) and values (Table S1-3, **Appendix 1**) in which characteristic bands appear confirmed the transesterification of oils, fatty acid esters into methyl ester (biodiesel).

Figure 1. FT-IR spectra of waste oil and biodiesel (red and green frame: the area where new peaks occurred as a result of conversion of triglycerides into monoglycerides).

Like other carbonyl compounds, esters are primarily recognized by a strong carbonyl band (1740 cm^{-1}) and are characterized by a single-band C-O vibrational control band at 1200 cm^{-1} [20]. The most important change as a result of transesterification is the appearance of a new peak at 1435 cm^{-1}, due to the deformation vibrations of the methyl ester group. The intense and broad peak at 1163.88 cm^{-1} in the waste oil was split into a doublet with two distinct peaks at 1171 cm^{-1} and 1197 cm^{-1}, indicating conversion to methyl ester. Peaks in the range of 1465 cm^{-1} to 1435 cm^{-1} indicate asymmetric bending of CH$_3$ group.

Discussion

Upon completion of the transesterification of waste oil, two easily separable phases were obtained: biodiesel and glycerol as the valuable by-product. Chemical modification of the catalyst with NaOH provided a sufficient yield of the starting material. A simple pretreatment eliminated main disadvantages of waste frying oil as a feedstock for biodiesel synthesis. The influence of particle size and concentration of modified clinoptilolite on the quality of the obtained biodiesel was also investigated. In general, a smaller particle size also means a larger active surface area and thus improved mass transfer. Conversely, a higher catalyst concentration does not always mean a better yield. It can also lead to absorption of the product and make its separation more difficult [21]. In the literature [16] biodiesel yield was over 90%. However, process was carried out on a smaller scale (20 g of waste oil), so the results cannot be adequately compared. Moreover, the biodiesel yield in microreactors reaches up to 97% under optimized conditions [22]. Based on the results presented in this paper, it was found that lower catalyst concentration leads to slightly lower biodiesel yield and acid number regardless of particle size, while higher granula-

tion leads to a product with lower kinematic viscosity regardless of catalyst concentration. Since it is easier to separate larger granulation catalysts, the use of clinoptilolite with a particle size of 50 microns proved to be more economical. The kinematic viscosity of the obtained biodiesels indicates that the products could be used as fuel, and a higher flash point is of practical importance as it allows safer operation and storage.

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