

Biodiesel Preparation from Non-Food, Conventional, and Waste Oils by Two-Stage Heterogeneous Transesterification

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Abstract

Preparation of biodiesel by commonly used homogeneous transesterification produces a large amount of wastewater as well as other disadvantages like soap formation, difficult separation, dirty glycerin, and limitation of homogeneous catalyst used by the content of free fatty acids. The paper focuses on testing mixed oxide catalyst (La-Ni/MgAl) in a two-stage transesterification on various types of oils as sources for biodiesel preparation. The tested oils include commercial sunflower and corn oil, hemp oil (commonly used in cosmetics), oil extracted from spent coffee grounds, and non-food oil derived from the *Camelina sativa* (L.) Crantz plant. Heterogeneous transesterification offers cleaner products, easier separation, and the possibility of reusing catalysts. La-Ni/MgAl mixed oxide was obtained from hydrotalcite, prepared by co-precipitation. The novelty of this study lies in comparing the transesterification process using different types of oils and evaluating the impact of their composition on catalyst activity. In addition, a unique feature of this study is the incorporation of a two-stage transesterification process, which allows for the reaction of any unreacted oil and achieves a content of FAME in biodiesel that meets European standards. The results showed that using two-stage transesterification with mixed oxides can achieve a FAME content higher than 98 % for all tested oils.

Keywords: Transesterification; Biodiesel; Mixed oxide; FAME; *Camelina sativa*.

1. Introduction

Decreasing crude oil reserves, climatic changes, and increasing energy demands lead to the need to search for new energy and fuel sources [1]. Biofuels, as a liquid fuel made from biomass for transport, are suitable as an alternative fuel to replace fuels from crude oil. Four main types of biofuel generations are divided based on the source for biofuel preparation. First-generation is made mainly from food plants such as sugar, starch, corn, and others. The drawback of this nowadays most commonly used generation of biofuels is that as a source of biofuels are used food crops, which can be used as a source for humans or animals. That is the reason why other generations of biofuels are studied. Second-generation fuels are made mostly from residues from crops or planted non-food crops that are not used as a food source. The third biofuel generation belongs to biofuel from microalgae. The fourth generation of biofuels is made mainly from genetically modified microalgae [2].

Vegetable oils or animal fats are mainly used for biodiesel production. From a perspective of physicochemical properties, using vegetable oils is advantageous [3]. Although commercial vegetable oils such as rapeseed, sunflower, or corn oil are commonly used, they are food sources. To address this issue, non-food oils such as *Camelina sativa* oil could be utilized for biodiesel preparation [4]. *Camelina sativa* (L.) Crantz is a non-food crop from the Brassicaceae family, also known as "false flax" or "Gold of pleasure". *Camelina* is adaptable to different climatic conditions and can grow on different soils; the only limitation is heavy organic soils. *Camelina* can grow with low pesticide and fertilizer input and is relatively drought-resistant. Seeds from *Camelina sativa* consist of 37-45 % of oil, and from CS, seeds can be obtained with 100-150g/kg of oil [5]. Another option is the use of waste biomass – waste oils. One of

the studied options is using coffee oil from coffee waste. Around 10 million tons of coffee grounds are produced annually [6].

Biodiesel from vegetable oils is prepared by transesterification reaction of the oil with methanol in the presence of a catalyst. The catalyst used in the transesterification process could be of heterogeneous or homogeneous type. Homogeneous catalysts are most commonly used due to their high activity, high yields, and mild conditions needed to obtain high biodiesel yields. The main drawback of homogeneous transesterification is the large amount of wastewater used to wash out the catalyst from biodiesel caused by the problematic separation of biodiesel and catalyst. On the other hand, after heterogeneous transesterification, biodiesel is clear; its separation from the solid catalyst is simple, and it is possible to reuse the catalyst. The disadvantage, however, remains a longer reaction time and a higher ratio of methanol to oil required to achieve a high FAME content in the biodiesel [7].

Hydrotalcite-like materials belong to the layered double hydroxides and anionic clays. Their particular layered crystal structure comprises octahedral cationic layers similar to the brucite structure, which are compensated by interlayer space containing anions and water molecules [8]. Basic hydrotalcite contains magnesium and aluminium cations, but it is possible to incorporate other divalent and trivalent cations such as nickel, manganese, and iron. The incorporation of different cations has a significant impact on the physicochemical properties of hydrotalcite and catalytic properties. Interlayer space is composed of anions and water molecules that stabilize crystallite structure. Mainly, the impact of nickel and iron incorporation was observed as effective in improving properties [9]. Different methods could prepare hydrotalcite; the most used is co-precipitation. During the calcination of hydrotalcite at a temperature from 400 - 500°C, decomposition (removing water and anions from interlayer space) occurs, and the layered structure passes to the structure of mixed metal oxides. Mixed oxides reached better catalytic properties than hydrotalcite, mostly with higher specific surface area, basicity, pore volume, and pore diameter. The main advantage of using mixed oxides as a catalyst for heterogeneous transesterification is their simple and quick preparation, high activity in biodiesel preparation, stability, and the possibility of catalyst regeneration and reuse [10].

The primary objective of this study is to investigate the impact of mixed oxide on the transesterification of different vegetable oils. The novelty of this research lies in the exploration of diverse oil types. The oils included commonly used ones like sunflower, corn, and *Camelina sativa* oil, a non-food source. Additionally, coffee oil derived from spent coffee grounds and cosmetic-grade hemp oil were also subjected to testing.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite was prepared in one batch for all transesterifications to ensure the same catalyst properties. The co-precipitation method with a constant pH was used for hydrotalcite preparation. Three different solutions for precipitation were prepared: (1) the salt solution (1 mol/dm³) containing nitrates (Mg(NO₃)₂, Al(NO₃)₃, Ni(NO₃)₂, La(NO₃)₃) as a source of cations; (2) the solution of NaHCO₃ (1 mol/dm³); (3) the solution of NaOH (3 mol/dm³) for holding pH on a constant value. Solution 1 was slowly added to solution 2 for one hour under intensive stirring. A pH electrode controlled the addition of solution 3. After precipitation, hydrotalcite was aged for 24 hours and washed out to obtain a neutral pH of washing water. Overnight at the temperature of 80°C, hydrotalcite was dried. Before transesterification, mixed oxides were obtained by calcination at 450°C.

2.2. Oil preparation

Camelina sativa (L.) Crantz var. Śmíłowska plant was cultivated at The National Agricultural and Food Centre in the Slovak Republic. Oil was obtained by cold pressing at the Energy 21 organization. Before transesterification, *Camelina sativa* oil was raffinate (degummed). Specific degummed processes and oil properties are described in a previous publication [11]. The used hemp oils were cosmetic-grade (suitable for producing soaps, body products, and lip

balms) and not intended for consumption. The oil was commercially refined. Because it is hemp oil, its THC content was tested, and it measured 9.8 ppm, which is below the maximum allowable limit of 10 ppm. The corn and sunflower oil used for transesterification were purchased as food-grade oils and were refined using a process for edible oils. The coffee oil was obtained by hexane extraction from dried spent coffee grounds. After the extraction, the oil was processed using a refining method described in detail in the article, which was used for refining *Camelina sativa* oil [11].

2.3. Oil characterization

The iodine value in oil was determined according to the conditions and procedures specified by EN 14111. The determination of the acidity value of fatty acid methyl esters was carried out based on the EN 14104 standard, which specifies the standardized method for determining the acidity value of biodiesel as one of the standardized properties monitored for biodiesels. The composition of the oils was measured using the TLC method, which stands for thin-layer chromatography.

2.4. Transesterification reaction

The transesterification reaction was carried out in a batch reactor (Parr Instruments, model 4520) made of nickel-chromium steel. Stirring was provided by a magnetic stirrer for all reactions at a rate of 500 rpm. The heating ring heated the reactor to the required temperature. The transesterification proceeded in two stages (described in Figure 1). Both stages were carried out under the same conditions, i.e. at 140°C for three hours. The first stage introduced dried methanol, refined oil, and calcined catalysts. After three hours of reaction, the reaction was stopped. Unreacted methanol was separated, and the resulting glycerol was removed. The mixture of unreacted oil and FAME went into the second stage of the reaction. In the second stage, dried methanol from the first stage of transesterification and fresh catalyst were added. The second stage also proceeded at 140°C for three hours of reaction. Unreacted methanol was removed by vacuum evaporation.

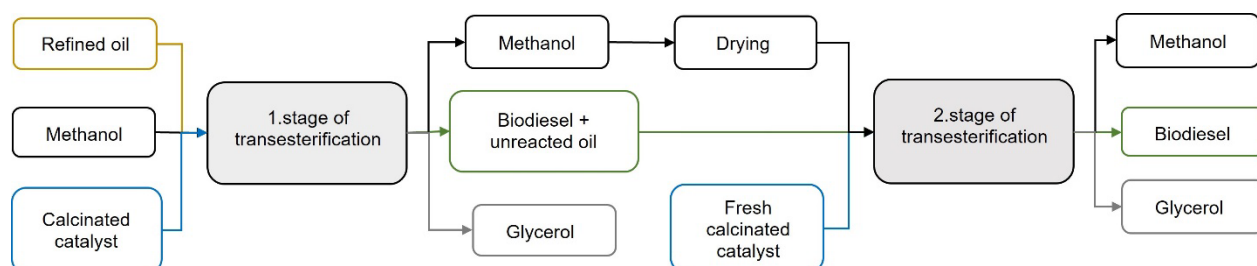


Figure 1. Scheme of two-stage transesterification.

2.5. FAME content analysis

GC determined fatty acid methyl ester content in biodiesel with a flame ionization detector (Agilent 7890 A series with split/splitless injector) based on standard EN 14103. Agilent technologies column BD-EN 14103 with dimensions 30 m x 0.32 mm and 0.25 µm film thickness was used. As the internal standard, the nonadecanoic acid methyl ester was used. The final content was calculated based on the peak area and weights of the standard and sample. This method also measured the representation of fatty acids in used oils.

3. Results and discussion

The composition and properties of the oil used in transesterification impact the resulting properties of biodiesel. Various types of oil were used to test the two-stage transesterification process and the catalyst activity. Tested oils were commercial, waste, and non-food grade oil. Before actual transesterification, the properties of each oil were measured. Table 1 shows the acidity and iodine number of oils.

Table 1. Iodine and acid number of used oils.

Property	Camelina oil	Hemp oil	Coffee oil	Corn oil	Sunflower oil
Iodine number, (g I ₂ / 100 g)	153.0	149.6	92.0	122.2	130.2
Acid number, (mg KOH/g)	0.96	0.18	2.21	0.17	0.08

Table 1 shows that the oils used for transesterification have an iodine number higher than the allowed value in biodiesel (up to 120 g I₂/100 g). Given that the iodine number does not change during transesterification, the resulting iodine number will also be high. From this perspective, waste coffee oil is the only oil suitable for preparing biodiesel. Regarding acidity number, the highest value is achieved with coffee oil. However, the acidity number can change during transesterification due to esterification, which occurs on the acidic sites of the catalyst into the desired products, fatty acid methyl esters.

The composition of measured oils using the TLC method is shown in Table 2. Differences can be observed in mono, di, and triacylglycerol distribution among the individual oils. Compared to commercial oils, camelina oil and coffee oil contain significantly lower amounts of triacylglycerols, but the amount of monoacylglycerols compensates for this.

Table 2. Composition of refined oils measured by TLC, wt%.

	Camelina oil	Hemp oil	Coffee oil	Corn oil	Sunflower oil
Monoacylglycerols	7.7	2.1	6.0	2.4	2.2
1.2-diacylglycerols	3.0	2.7	1.3	3.0	3.1
1.3-diacylglycerols	4.3	4.1	2.8	4.3	4.0
Triacylglycerols	44.2	78.9	59.4	70.4	72.7
Sterols	20.9	5.6	16.1	3.4	3.7
Others	7.5	6.6	14.4	16.4	14.4

The transesterification in the first stage of all tested edible oils showed the activity of the La-Ni/MgAl mixed oxide, with a FAME content in the range of 90-92 wt.% in the case of *Camelina sativa*, corn, and sunflower oils. After further reaction with a fresh catalyst, the FAME content after the second stage was above 98 wt.% or both oils, which meets the minimum required FAME content in biodiesel (Table 3). In the case of cosmetic hemp oil, the FAME content after the first stage was lower, but after further reaction with fresh La-Ni/MO catalyst, the FAME content reached a comparable amount of FAME in biodiesel (Table 3). After the first stage of transesterification of the coffee oil on the La-Ni/MO mixed oxide, the FAME content was lower than that of other oils. After the second transesterification stage with a fresh catalyst, the FAME content reached 99.6 wt.%, significantly exceeding the minimum FAME content according to the standard.

Table 3. FAME content in products after the first and second stage of transesterification.

Vegetable oil	1. stage X _{FAME} (%)	2. stage X _{FAME} (%)
Camelina	80.1	99.3
Corn	90.6	99.8
Sunflower	92.6	99.7
Hemp	79.9	98.2
Coffee waste	75.8	99.6

The activity of mixed oxides for transesterification has been demonstrated. De Souza *et al.* [12] also observed increased activity when adding lanthanum to the catalyst and achieved high FAME content in biodiesel. However, the FAME content was within the value required by European standards. One of the reasons for using a two-stage transesterification process is the problem of achieving a FAME content over 96 wt.%. By dividing the transesterification into two stages, the desired result can be achieved without increasing methanol consumption, as the unreacted amount from the first stage can be used in the second stage of transesterification.

At first glance, the disadvantage of coffee waste oil may be the higher acid number (Table 1). In the case of homogeneous transesterification, the use of an essential catalyst is limited by the content of free fatty acids. They neutralize the catalyst by forming soaps, thus requiring transesterification first with acid and then with a basic catalyst. In the case of refined coffee oil, the acidity number was 2.21 mg KOH/g sample. After the second transesterification stage, the methyl esters' acid number decreased to 0.18 mg KOH/g sample. In the case of *Camelina sativa* oil, the acid number of biodiesel after transesterification was 0.43 mg KOH/g. The acid number of other oils was already at a value meeting the standardized number before the transesterification. The maximum allowed acidity number is 0.5 mg KOH/g.

Mixed oxides, as a heterogeneous catalyst, contain basic and acidic sites. The reduction in FFA content and acidity number confirms the theory and possibility that there was not only transesterification of triglycerides on the basic sites but also esterification of free fatty acids on the acidic sites. This fact could be the answer to the transesterification of other waste oils, such as high FFA kitchen waste oils, without the need for acidic transesterification. Li. *et al.* [13] observed the activity of a catalyst, which also contained a lanthanum additive during simultaneous transesterification and esterification. The tested oil was acidic, with an FFA content higher than 60 %. A catalyst with both acidic and basic sites achieved an FAME content of over 90 wt.% in such oil [13].

One of the monitored properties of biodiesel is the content of linolenic acid. Linolenic acid contains three unsaturated bonds, which are directly related to oxidative stability and the associated iodine number. Table 4 shows the representation of methyl esters of fatty acids after transesterification of various oils. As can be seen, camelina oil contains an amount of linolenic acid higher than the maximum allowed amount (12 wt.%). One of the options for addressing the issue of high levels of unsaturated bonds is partial hydrogenation.

Table 4. Representation of fatty acids in biodiesel, wt%.

Distribution of fatty acid methyl esters	Camelina oil	Hemp oil	Coffee oil	Corn oil	Sunflower oil
C16:0	6.7	8.4	34.2	11.1	5.8
C18:0	2.8	3.2	6.8	1.8	3.2
C18:1	15.2	15.9	8.3	29.1	48.1
C18:2	19.3	51.6	43.4	52.6	40.1
C18:3	36.7	17.7	1.7	1.3	0.2
C20:0	1.2	-	2.1	0.4	0.2
C20:1	12.9	-	0.4	0.4	-
C20:2	1.6	-	0.1	-	-

4. Conclusion

Heterogeneous transesterification is one of the options for replacing the less environmentally friendly homogeneous transesterification. One catalytic option is the use of mixed oxides as heterogeneous catalysts. Mixed oxides prepared from hydrotalcites with the addition of nickel and lanthanum have shown their activity in transesterification. Since heterogeneous transesterification requires a longer reaction time, a higher methanol-to-oil ratio and a more significant amount of catalyst, one possibility is the confirmed two-step transesterification. Thanks to the two-step transesterification, a FAME content of more than 99 wt.% was achieved. Two-step transesterification was tested on various types of oils, including commercial (corn and sunflower), cosmetic (hemp oil), non-food (*Camelina sativa*), and oil derived from spent coffee grounds. The catalyst activity was confirmed for all mentioned oils, and a FAME content higher than the minimum standardized amount was achieved after two steps of transesterification.

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