

# Biodiesel preparation from *Camelina sativa* oil by homogeneous and heterogeneous transesterification

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**Abstract.** Biodiesel is one of the possible alternatives to diesel fuel to address the issue of fossil fuels and their impact on the environment. Substituting homogeneous transesterification with heterogeneous offers advantages such as improved catalyst and product separation, catalyst regeneration, and avoidance of saponification during the reaction. To compare homogeneous and heterogeneous transesterification, the commonly used homogenous catalyst NaOH was tested. As a heterogeneous catalyst, a mixed oxide prepared from hydrotalcite with added nickel in its structure was used. By employing suitable conditions, it is possible to achieve biodiesel through heterogeneous transesterification with a comparable FAME (Fatty acid methyl ester) content to homogeneous transesterification, meeting the standardized value of over 96.7 wt.%. Implementing a two-step heterogeneous transesterification process decreases the reaction time needed to reach the desired FAME quantity. Furthermore, following heterogeneous transesterification, glycerol as a valuable secondary product showed visibly higher purity.

## 1 Introduction

With the increasing number of cars and the demand for suitable alternatives to fossil fuels, one of the possible options is biofuels. Biofuels can be categorized based on the source of their production into first to fourth-generation biofuels. In the case of the first generation, these are fuels primarily prepared from food sources such as rapeseed or corn. The second generation of biofuels consists of fuels prepared from waste sources, such as waste biomass or non-food plants. The third tested category includes biofuels prepared from algae. The fourth and final category is synthetic fuels [1].

Biodiesel, a blend of methyl esters of fatty acids, is a renewable, biodegradable, non-toxic, sustainable, and environmentally friendly alternative fuel to commonly used diesel fuel prepared from crude oil [2]. The primary method utilized for biodiesel production is the transesterification reaction of triacylglycerides with alcohol to get fatty acid alkyl esters [3].

Biodiesel can be produced from vegetable oils or animal fats. Due to the physicochemical properties of animal fats, preference is given to vegetable oils. Currently, the most commonly

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used vegetable oils for biodiesel production are of a food nature such as rapeseed oil and corn oil [4]. One of the main drawbacks of these types of oils is their food nature. In light of this, there is growing interest in exploring alternatives of non-food oils for biodiesel production, such as *Camelina sativa* oil [5]. *Camelina sativa*, known for its potential as a biodiesel feedstock, exhibits notable advantages such as adaptability to less fertile soils, relative resistance to drought, and reduced dependence on fertilizers and pesticides [6].

Biodiesel is commonly prepared through homogeneous transesterification, due to its short reaction time, catalyst availability, and mild conditions. The most commonly used catalysts for homogeneous transesterification are sodium or potassium hydroxide, but currently, sodium methoxide is most commonly used. The advantage of homogeneous transesterification is the short reaction time as well as low reaction temperature and pressure. Disadvantages of homogeneous transesterification are problems with saponification, no recycling of catalysts, and difficult separation problems of biodiesel and catalyst, which produces a large amount of wastewater from catalyst residue removals [7]. By using a heterogeneous catalyst, it is possible to solve the separation problem. It is also possible, when choosing an appropriate catalyst, to regenerate and reuse it.

The selection of a suitable heterogeneous catalyst is one of the main research topics. Among the tested catalysts that show promising activity are metal oxides such as CaO [8], mixed metal oxides, as well as hydrotalcite as a source of mixed oxide structure.

Hydrotalcites, which belong to the group of layered double hydroxides (LDH), offer a layered structure as a starting material for the preparation of mixed oxides [9-11]. Their layered structure consists of alternating positively charged octahedral layers with incorporated metal cations and interlayer space containing water and anions [12]. The choice of different metal cations can significantly influence the properties of mixed oxides as well as their activity in biodiesel production. Additionally, the straightforward preparation of hydrotalcite offers another advantage over conventional catalysts.

The research focused on in the presented article involves comparing homogeneous and heterogeneous transesterification of non-food oil. The novelty lies in testing two-step transesterification on mixed oxides prepared from hydrotalcite to achieve the minimum standardized amount of methyl esters in biodiesel. The comparison is also made not only in terms of catalyst activity but also in terms of the influence of oil refinement on catalyst activity and deactivation.

## 2 Materials and methods

### 2.1 Catalyst preparation

For homogeneous transesterification, a commonly used solution of NaOH in methanol was used. Heterogeneous transesterification was tested using mixed oxide obtained from the hydrotalcite structure.

#### 2.1.1 Hydrotalcite – mixed oxide synthesis

Hydrotalcite was prepared using the commonly used method of co-precipitation. Three basic solutions were used for synthesis. The first was a sodium bicarbonate ( $\text{NaHCO}_3$ ) solution with a concentration of  $1 \text{ mol/dm}^3$ . The second solution consisted of metal nitrates ( $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Ni}(\text{NO}_3)_2$ ) with a concentration of  $1 \text{ mol/dm}^3$ . The last solution was a sodium hydroxide ( $\text{NaOH}$ ) solution ( $c=3 \text{ mol/dm}^3$ ) used to maintain a constant pH value. The precipitation process took place for one hour at a temperature of  $25^\circ\text{C}$  and pH of 10. After the reaction was complete, the sample aged for 24 hours. Subsequently, it was filtered and

rinsed with deionized water. Before transesterification, the obtained hydrotalcite was calcined at a temperature of 450°C for 3 hours to obtain a mixed oxide structure.

## 2.2 Heterogeneous catalyst characterization

The properties of hydrotalcite and the obtained mixed oxide were tested using multiple methods. The content of incorporated metals was measured using ICP-EOS method (Inductively Coupled Plasma – Optical Emission Spectroscopy) on the Optima 7000 DV PerkinElmer Instrument. The samples were measured by dissolving it in hydrochloric acid.

The textural properties (SBET, pore volume) were measured using nitrogen physical adsorption at a temperature of liquid nitrogen (-196°C) on the ASAP2400 instrument (micrometrics). The obtained data were evaluated using the BET isotherm.

## 2.3 Vegetable oil

The test reactions were performed using *Camelina sativa* oil. The oil was obtained by cold-pressing seeds of the *Smilnowska* variety, which were cultivated at the National Agricultural and Food Center in Vígľaš-Pstruša, Slovakia. The raw oil, without any specific treatment after obtaining oil, was tested. Refined oil was also tested in transesterification. The detailed procedure of the refining process and the properties obtained after refining are described in the article [7].

## 2.4 Transesterification reaction

Transesterification of both refined and raw oil was tested using heterogeneous and homogeneous transesterification methods.

### 2.4.1 Homogeneous transesterification

The homogeneous transesterification took place in a round-bottom flask equipped with a reflux condenser. The amount of catalyst used was 1 wt.% of NaOH to amount of oil. The molar ratio of methanol to oil was 6/1. The reaction temperature was maintained at 65 °C (Fig. 1 B).

### 2.4.2 Heterogeneous transesterification

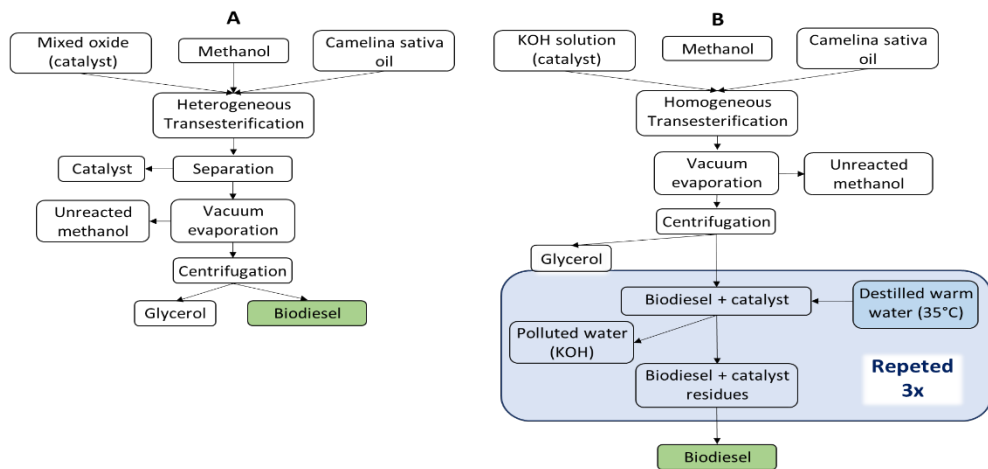
Transesterification using a heterogeneous catalyst (mixed oxide) was measured in a nickel-chromium batch reactor (Parr model 4520). Transesterification was performed in two modes: one-step transesterification and two-step transesterification (Fig.1). Before the transesterification, the batch reactor was purged with nitrogen and pressurized to a pressure of 5 bars. The reaction temperature was 140°C.

- One-step transesterification (Fig.1)

In the case of one-step transesterification, the reaction occurred with a molar ratio of methanol to oil of 18/1, using a catalyst amount of 3 wt.% to the amount of oil.

- Two-step transesterification (Fig.1)

In the case of two-step transesterification, the first step proceeded in the same manner as described in the previous section. After removing the methanol and glycerol, the mixture of unreacted oil and FAME was transferred back to the reactor. In the second step, the conditions from the first step were maintained. The ratio of methanol and the amount of catalyst was calculated based on the overall mixture not just unreacted oil.



**Fig. 1.** Steps of homogeneous (A) and heterogeneous (B) transesterification.

## 2.5 Product analysis

The amount of FAME in the obtained product was measured using a standardized GC method with a flame ionization detector on instrument Agilent 7890 A series) with a split/splitless injector. The internal standard method was used with nonadecanoic acid methyl ester as the internal standard.

## 3 Result and discussion

### 3.1 Content of incorporated metal to hydrotalcite structure

The layered structure of hydrotalcite consists of alternating positively charged octahedral layers and interlayer anions. The basic cations incorporated in the structure are aluminum and magnesium. Different metal cations can be incorporated into the structure, which not only affects the material structure but also its physicochemical properties and catalytic activity [6]. Table 1 shows the content of incorporated metals in the cationic layer of hydrotalcite.

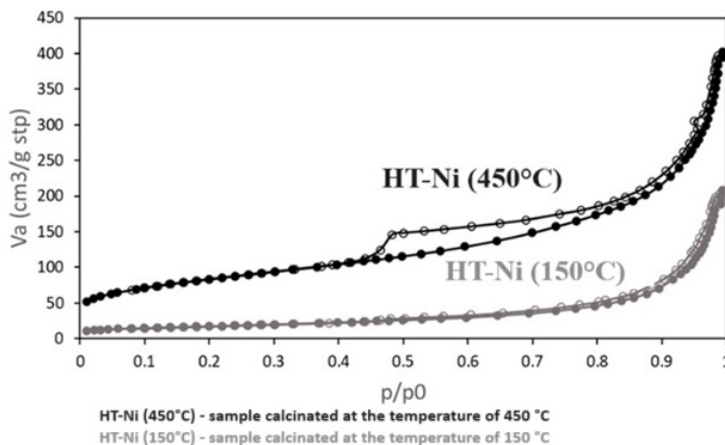
**Table 1.** Content of incorporated metals.

	WMg (wt.%)	WAl (wt.%)	WNi (wt.%)
Ni/MO	15.7	11.1	10.4

### 3.2 Textural properties of heterogeneous catalyst

The textural properties of heterogeneous materials are important properties of catalysts linked with their activity in reactions. During calcination, when a mixed oxide structure is obtained from hydrotalcite, interlayer anions, and water are removed, resulting in the formation of the mixed oxide structure. Mixed oxides have better textural properties compared with

hydrotalcite. In Figure 2. can be seen the adsorption-desorption isotherm of the hydrotalcite structure along with the isotherm of the mixed metal oxide structure.



**Fig. 2.** Adsorption-desorption isotherm of HT-Ni catalyst.

In the case of mixed oxides, the presence of a hysteresis loop can be observed. Based on the shape and hysteresis, it can be inferred that the material exhibits a mesoporous character. Unlike the hydrotalcite structure. In Table 2, the specific surface areas and pore volume of hydrotalcite as well as those of mixed oxide are displayed. As can be seen, the specific surface area as well as the pore volume increased by changing the structure to mixed oxides.

**Table 2.** Textural properties of Ni-HT hydrotalcite and mixed oxide.

	Hydrotalcite		Mixed oxide	
	$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)
Ni-HT	150	0,302	285	0,575

### 3.3 Transesterification of camelina sativa oil

Given the drawbacks of homogeneous transesterification as well as the use of food sources, heterogeneous transesterification of alternative sources is one option for replacing the homogeneous one. However, the disadvantage of heterogeneous transesterification remains the longer reaction time, higher reaction temperatures, and higher consumption of catalyst and methanol.

In comparing homogeneous and heterogeneous transesterification, camelina oil was tested. One of the tested oils was raw oil obtained by cold pressing of camelina sativa seeds. The second sample was oil refined through a process that removed phospholipids and other substances from the oil. The presence of phospholipids in oil can cause problems with fuel injection into the engine when using biodiesel as fuel. It can also clog the heterogeneous catalyst and reduce its activity.

In Table 3, it is possible to see the content of FAME achieved by the process of homogeneous and heterogeneous transesterification along with the conditions used during the reaction.

**Table 3.** Comparison of reaction conditions and results of homogeneous and heterogeneous transesterification.

	<b>Homogeneous transesterification</b>		<b>Heterogeneous transesterification</b>		
	Refined	Raw	Refined	Refined	Raw
<b>Oil treatment</b>	Refined	Raw	Refined	Refined	Raw
<b>Reaction type</b>	One-step	One-step	One-step	Two-step	Two-step
<b>Reaction time (h)</b>	1	1	7	3 + 3	7
<b>Mola ratio</b>	6/1	6/1	18/1	18/1	18/1
<b>Methanol/Oil</b>					
<b>Amount of catalyst (wt.%)</b>	1	1	3	3	3
<b>Catalyst – first step</b>	NaOH	NaOH	Ni/MO	Ni/MO	Ni/MO
<b>Catalyst – second step</b>	-	-	-	Fresh Ni/MO	Fresh Ni/MO
<b>Temperature (°C)</b>	65	65	140	140	140
<b>FAME content (wt.%)</b>	<b>98.2</b>	<b>97.0</b>	<b>96.7</b>	<b>99.0</b>	<b>40.2</b>

From the result, it can be seen that when using refined vegetable oil, a common homogeneous transesterification process achieved a FAME content of more than 98 wt.% after one hour of reaction. The required minimum FAME according to European standards is 96.5 wt.%. In the case of heterogeneous transesterification, a one-step transesterification was tested, where the reaction ran for 7 hours with higher amounts of methanol and catalyst. After seven hours, a FAME content of 96.7 wt.% was achieved. When using a two-step transesterification, a FAME content of 99 wt.% was achieved after the second step.

In the case of using raw oil that has not undergone refinement, a significant impact on the transesterification process can be observed. In the case of homogeneous catalysis transesterification, the difference in FAME content between raw and refined oil was minimal. For heterogeneous transesterification, it is evident that the presence of phospholipids in raw oil significantly reduced the catalyst activity. After seven hours of reaction, the FAME content in the product was just slightly above 40 wt.%.

## 4 Conclusion

Homogeneous transesterification, as well as heterogeneous transesterification, have both advantages and disadvantages. From an environmental perspective, homogeneous transesterification is a less acceptable option. By finding a suitable heterogeneous system, reaction conditions, and catalyst with the possibility of regeneration, it would be possible to completely replace homogeneous transesterification. A comparison of homogeneous and heterogeneous transesterification has shown that using refined oil can achieve comparable results in both processes. The disadvantage remains the longer reaction time and higher temperature. The higher amount of methanol used is not problematic since it can be recycled after the reaction. In the case of catalyst reuse, a higher amount of catalyst used is also not

problematic. Results also showed that using raw oil for heterogeneous transesterification is problematic due to the presence of phospholipids, which reduce the catalyst's activity.

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