Technological Aspects of Vegetable Oils Transesterification with Ethanol in the Presence of Metal Oxides

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Y. Melnyk,* *R. Starchevskyi*, and *S. Melnyk*

Department of Organic Products Technology, Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

Abstract

Transesterification of vegetable oil with ethanol in the presence of fine metal oxide particles as catalysts has been investigated. Zinc and nickel(II) oxides were shown to have the highest catalytic activity. In their presence, the conversion of sunflower oil triglycerides, after 150 min, reached 95.3 and 94.2 %, respectively. The optimal mass fraction of zinc oxide catalyst was found to be 0.25–0.31 %. In the presence of zinc oxide, with mass fraction of water in ethanol of 5 and 10 %, the conversion of triglycerides was 98.5 and 94.8 %, respectively.

Keywords

Transesterification, triglycerides, metal oxides, ethanol

1 Introduction

The main catalysts for the transesterification of vegetable oils triglycerides with lower alcohols are the basic compounds – hydroxides and sodium or potassium alcoholates.[1]

Heterogeneous catalysts, unlike homogeneous catalysts, can be easily separated from the reaction mixture and used many times. Moreover, when using heterogeneous catalysts, it is easier to realize a continuous process.[2,3] That is why a great number of investigations today focus on heterogeneous transesterification catalysts.

One of the applications of heterogeneous catalysts is the heterogenization of conventional homogeneous catalysts on a carrier. *Ilgen and Akin* showed the possibility of using aluminium oxide coated with NaOH, LiOH, KOH, Na_2CO_3, K_2CO_3 for transesterification of canola oil with methanol.[4] KOH/γ-Al_2O_3 was found to be the best catalyst allowing a fatty acid methyl esters yield of 82.29 % after 9 h.

Silicon oxide has been proposed as a carrier for the K_2CO_3 catalyst.[5] This catalyst was investigated in the transesterification reaction of palm oil with methanol. In such a case, the yield of fatty acid methyl esters was 98.10 %.

KOH/$Ca_{12}Al_{14}O_{33}$ was proposed as a catalyst for the transesterification of canola oil with methanol.[6] The determined conditions were: alcohol : oil molar ratio of 12 : 1, a reaction time of 60 min, and a catalyst mass fraction of 4 %. The reaction mixture was heated by microwave radiation. Under these conditions, the authors achieved a triglyceride conversion of 83.5 %. It is proposed to regenerate the catalyst by annealing at 700 °C.

As catalysts, the use of lithium, sodium or potassium nitrates supported on calcium and magnesium oxides[7] is also proposed. The highest conversion of rapeseed oil triglycerides transesterified with methanol was provided by the catalysts consisting of lithium nitrate supported on calcined calcium and magnesium oxides. *MacLeod et al.* have shown that the basicity of the most active catalysts is in the range of pH 11–15.[7] The decrease in pH value below 11 sharply decreased the catalyst activity, and the triglycerides conversion was 3–8 %.

Alkaline earth oxides are also proposed as transesterification catalysts. Calcium oxide was proposed as a catalyst for transesterification of crude *Salvadora alii* oil and *Thespesia populneoides* oil with methanol.[8] The mentioned catalyst allowed a 90 % yield of fatty acids methyl esters at 65 °C, methanol : oil molar ratio of (6–10) : 1 and catalyst mass fraction of 3–3.5 %. To intensify the process, ultrasonic radiation was used.

Martinez-Guerra and Gude investigated the transesterification of used vegetable oil with methanol in the presence of barium oxide.[9] The yield of fatty acid methyl esters was found to be 93.5 % at alcohol : oil ratio of 6 : 1, catalyst mass fraction of 0.75 %, and combined treatment with ultrasonic waves and microwave radiation with a total power of 200 watts.

Xiang et al. studied the catalytic transesterification of waste cooking oil with methanol in the presence of ultrasonic radiation.[10] It was found that at alcohol : oil molar ratio of 10.71 : 1 and modified coal ash mass fraction of 4.97 %, the yield of methyl esters reached 95.57 %. The catalyst was modified *via* hydrothermal treatment in the presence of potassium hydroxide.

Anion exchange resin Amberlyst A26 OH was investigated as heterogeneous catalyst of tallow fat methanolisys. The

* Corresponding author: Yurii Melnyk, PhD
Email: yurii.r.melnyk@lpnu.ua

result of this investigation was a biodiesel yield of 90–95 % after 360 min.[11]

Melnyk et al. demonstrated the possibility of using CU-2-8 cation exchange resin with immobilized metal ions as catalysts for transesterification of vegetable oils.[12] Under the optimal conditions, in the presence of the best catalysts, when using ethanol, the triglycerides conversion was more than 99 %, and when propan-1-ol was used, the conversion exceeded 97 %.

The use of metal oxides as heterogeneous catalysts for transesterification of sunflower oil with butan-1-ol has been investigated by *Melnyk et al*.[13] In order to intensify the process, the authors investigated the transesterification of sunflower oil triglycerides in the presence of ultrasonic waves. Zinc and nickel(II) oxides as catalysts achieved a conversion of triglycerides above 97 % at a molar ratio of butan-1-ol:triglyceride equal to 15 : 1, and almost complete conversion of triglycerides at the molar ratio of 20 : 1 after 150 min.

The above data indicate the effectiveness of heterogeneous transesterification catalysts. However, the amount of metal oxides studied in this process is quite limited. Therefore, the aim of this research was to investigate the technological aspects of using a fairly wide range of metal oxides in the transesterification reaction of vegetable oils with ethanol.

2 Experimental

2.1 Materials

Sunflower (refined, DSTU 4492:2005), rapeseed (cold-pressed, DSTU 8175:2015) and linseed (refined, DSTU ISO 150-2002) oils were used as fatty raw material and triglyceride sources. Analytical grade ethanol was used. Fine powders of the metal oxides ZnO, NiO, MgO, SnO_2, MnO, PbO, Al_2O_3, Cr_2O_3 (all of analytical grade) were used as catalysts.

2.2 Experimental procedure

Transesterification of sunflower oil triglycerides (TG) was carried out with anhydrous ethanol at 75 °C and ethanol : TG molar ratio of (3.6–5.7) : 1. The amounts of triglycerides were recalculated relative to glycerol trioleate. The mass fraction of catalyst was 0.25 %. The effect of the catalyst mass fraction was studied using zinc oxide. Its mass fraction in the reaction mixture varied in the range from 0.13 to 0.50 %. The transesterification reaction was carried out during 150 min.

The transesterification reaction was carried out in a glass three-necked reactor equipped with a reflux condenser under stirring. The samples were taken every 30 min. The ethanol content was determined by chromatography, the acid number – by titrimetry after 150 min of the reaction.

Ultrasound was used for transesterification of sunflower oil with ethanol in the presence of zinc oxide. The mass fraction of water in ethanol was 5 and 10 %. To study the effect of ultrasonic waves on the transesterification reaction, the reaction mixture was treated in the reactor using a UZDN-2T ultrasonic disperser throughout the reaction time. Nominal ultrasonic power was 400 W, and oscillation frequency was 22 kHz.

2.3 Physicochemical analysis

Chromatographic analysis of the reaction mixture was performed using a gas-liquid chromatograph LHM-80 with a thermal conductivity detector under the following conditions: column with diameter of 3 mm, and length of 2000 mm filled with 5 % Silicone SE30 on a Chromaton N-AW; carrier gas was helium with a volume flow rate of 3.0 $l\,h^{-1}$; the temperatures of column thermostat, detector, and evaporator were 120 °C, 220 °C, and 230 °C, respectively; current strength on the detector was 140 mA; sample volume was 2 µl.[14] The acid number was determined by alkalimetric titration.[15]

2.4 Data analysis

Chromatographic analysis was used to determine the ethanol content in the reaction mixture. In accordance with the values of ethanol concentration at the initial and current times, the ethanol conversion, and then the conversion of triglyceride regarding the glycerol trioleate were calculated.

The initial and final values of the acid number of the reaction mixture were used to calculate the conversion of acid groups present in the free fatty acids (FFA) of oils. The initial rate of transesterification reaction was calculated as the ratio of the modulus of the difference in triglyceride concentration at the current and initial time to the time interval. The initial rate was calculated after 30 min of reaction.

3 Results and discussion

3.1 Effect of metal oxide

Melnyk et al. found that among zinc, nickel(II), iron(II), copper(II), and cobalt (II, III), as well as cobalt(III) oxides, such as ZnO and NiO, exhibit the highest activity in the transesterification reaction of sunflower oil triglycerides with ethanol.[14] However, they investigated a rather limited range of metal oxides under restricted conditions of the transesterification process.

The results of transesterification of sunflower oil triglycerides with ethanol in the presence of zinc, nickel(II), magnesium, tin(IV), manganese(II), lead(II), aluminium, and chromium(III) oxides show a correlation between the initial reaction rate and triglyceride conversion achieved after 150 min (Table 1). None of the studied oxides was found to provide triglyceride conversion comparable with the most active zinc and nickel(II) oxides. Manganese(II), magnesium, and tin(IV) oxides also exhibit high activity in the transesterification reaction. However, in their presence, the conversion of triglycerides failed to exceed 87–88 % after 150 min.

The oxides of aluminium, chromium(III), and lead(II) showed the lowest activity. The initial transesterification rate of sunflower oil triglycerides in their presence was in the range of $(2.09–2.44)\cdot10^{-4}$ mol/(L×s), *i.e.*, 1.5–1.8 times lower than that in the presence of zinc oxide, and 1.3–1.5 times lower than with nickel(II) oxide. The conversion of sunflower oil triglycerides *per* 150 min of reaction in the presence of Al_2O_3, Cr_2O_3 and PbO was only 67.4–73.1 %.

Table 1 – Indicators of sunflower oil triglycerides transesterification with ethanol in the presence of metal oxides. (Temperature 75 °C, catalyst content 0.25 wt%, molar ratio ethanol : TG 3.8 : 1)

Catalyst	TG conversion / %		Initial reaction rate / $r\times10^4$, mol/(L×s)
	30 min	150 min	
ZnO	76.7	95.3	3.75
NiO	64.7	94.2	3.16
MnO	70.7	86.9	3.45
Al_2O_3	47.4	70.0	2.31
Cr_2O_3	42.8	67.4	2.09
SnO_2	73.3	88.2	3.58
MgO	80.4	94.0	3.93
PbO	50.0	73.1	2.44

We can represent the following activity ranges of the investigated metal oxides:

according to the initial reaction rate

$$MgO > ZnO > SnO_2 \approx MnO > NiO \gg FeO > PbO \approx \approx Al_2O_3 > CuO > Co_3O_4 \approx Cr_2O_3 > Co_2O_3$$

according to the triglycerides conversion achieved after 150 min

$$ZnO \approx NiO \approx MgO > SnO_2 \approx MnO > FeO > CuO \approx \approx PbO > Al_2O_3 \approx Cr_2O_3 > Co_2O_3$$

3.2 Effect of process technological parameters

The effect of the ethanol : TG molar ratio on the transesterification of sunflower oil triglycerides was investigated using zinc oxide as the catalyst. With the increase in alcohol content, both the initial conversion of triglycerides and their conversion after 150 min increased monotonically. Moreover, at the molar ratio of 3.6 : 1, the triglycerides conversion after 150 min was almost 98 % and increased by only 1 % with a further increase in the molar ratio to 5.7 : 1 (Fig. 1).

The increase in ethanol : TG molar ratio had a more significant effect on the initial conversion of triglycerides: from 81.2 % (at 4.1 : 1) to 85.0 % (at 5.7 : 1) after 30 min. Such results were expected, since the increase in the molar ratio, and therefore the ethanol concentration in the reaction mixture, caused the increase in the transesterification rate in the initial period (Table 2). The increase in the molar

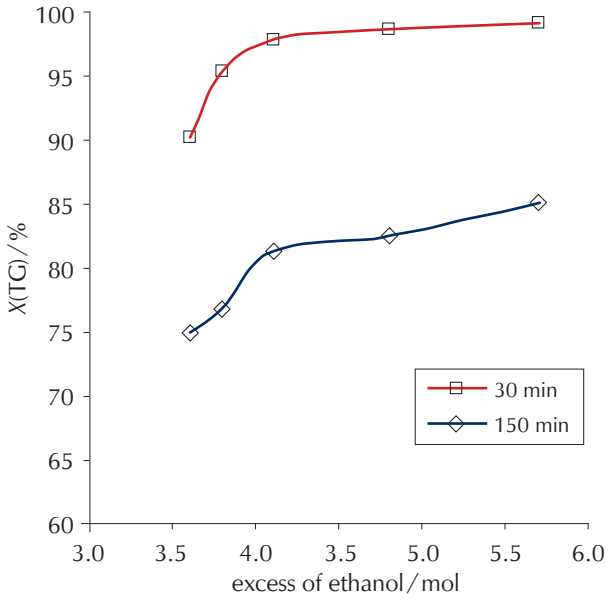

Fig. 1 – Dependence of TG conversion on the molar excess of ethanol in the transesterification reaction of sunflower oil. (Zinc oxide catalyst, catalyst mass fraction 0.25 %, temperature 75 °C).

excess of more than 4.1 : 1 led to no further increase in the conversion of triglycerides (Fig. 1).

Table 2 – Effect of ethanol : triglycerides molar ratio on initial transesterification rate of sunflower oil triglycerides. (Temperature 75 °C, zinc oxide catalyst, catalyst mass fraction 0.25 %)

Ethanol : TG molar ratio	Initial reaction rate / $r\times10^4$, mol/(L×s)
3.6 : 1	3.70
3.8 : 1	3.75
4.1 : 1	3.92
4.8 : 1	3.84
5.7 : 1	3.78

Melnyk et al. found that, during transesterification of sunflower oil triglycerides with butan-1-ol in the presence of metal oxides, an extreme dependence of TG conversion on the catalyst concentration was observed.[13]

Similar results were obtained for the transesterification of sunflower oil triglycerides with ethanol in the presence of zinc oxide (Fig. 2). It was established that within the catalyst mass fraction of 0.13–0.50 %, there was an extreme dependence of both the initial conversion of triglycerides and their conversion after 150 min.

An evident extremum of triglycerides conversion after 30 min was observed for catalyst mass fraction of 0.25 %. The maximum triglycerides conversion after 150 min was achieved with the mass fraction of zinc oxide 0.25–0.31 %.

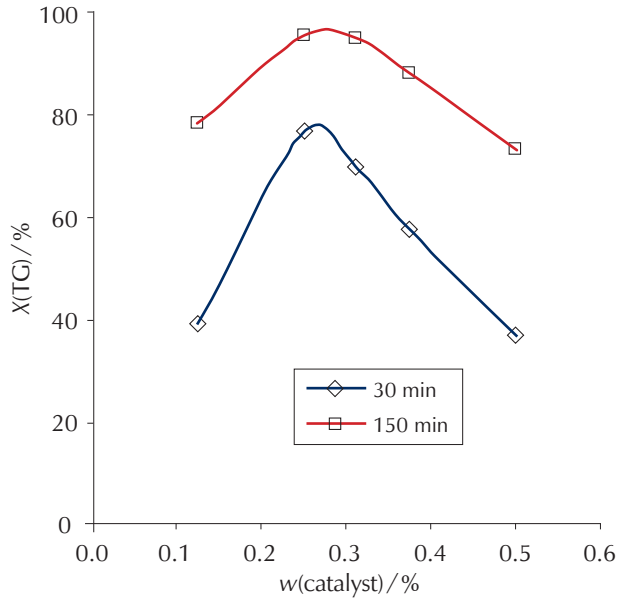

Fig. 2 – Dependence of TG conversion on the zinc oxide content for the transesterification of sunflower oil triglycerides. (Temperature 75 °C, molar ratio of ethanol : TG 5.7 : 1).

The most probable reason for the decrease in TG conversion with increasing catalyst content is the reduction of the catalyst active content due to its aggregation.[13]

Since one of the disadvantages of using homogeneous catalysts is the requirement for water absence in raw materials,[1] we studied the transesterification of sunflower oil triglycerides with ethanol in the presence of zinc oxide and mass fraction of water of 5 and 10 % (Table 3).

At mass fraction of water in ethanol of 5 %, the triglycerides conversion after 150 min was 98.5 %. This indicates the possibility of using zinc oxide as a catalyst for the transesterification of raw materials containing water. Further increase in mass fraction of water to 10 % led to some decrease in the triglycerides conversion after 150 min, but even in this case, it was 94.8 %. The use of ultrasonic waves in the transesterification process led to the decrease in the initial reaction rate and conversion of triglycerides (Table 3).

The effect of the oil type on the process was studied by using sunflower, rapeseed, and linseed oils. It is characteristic that rapeseed and linseed oils, as distinct from sunflower oil, contain FFA, as evidenced by the acid numbers defined for these oils (6.1 and 3.1 mg KOH/g, respectively). It was found that when using rapeseed oil, the zinc, and nickel(II) oxides provided a sufficiently high conversion of triglycerides after 150 min (Table 4). The initial acid number of sunflower oil was 0.2 mg KOH/g, therefore, its change during the reaction was not controlled.

When linseed oil was used, the triglycerides conversion after 150 min in the presence of nickel(II) oxide was only 88.3 %, whereas with the use of zinc oxide, a conversion of 93.0 % was achieved. It was established that along with the transesterification reaction, there was an esterification reaction of FFA present in the rapeseed and linseed oils. The conversion of acids, calculated by changes in the acid number of the reaction mixture at the beginning and end of the reaction, was 5.7–14.3 %.

Table 3 – Effect of water content in ethanol on the indicators of transesterification process of sunflower oil triglycerides with ethanol. (Temperature 75 °C, zinc oxide catalyst, catalyst content 0.25 wt%, molar ratio of ethanol : TG 5.7 : 1).

Ultrasound	Mass fraction of water in ethanol / %	TG conversion / %		Initial reaction rate / $r \times 10^4$, mol/(L×s)
		30 min	150 min	
+	5	79.5	91.4	3.54
–	5	84.6	98.5	3.77
+	10	75.2	87.2	3.35
–	10	83.7	94.8	3.72

Table 4 – Effect of oil type on the conversion of triglycerides and FFA of vegetable oils. (Temperature 75 °C, catalyst content 0.25 wt%, molar ratio of ethanol : TG 5.7 : 1).

Oil	TG conversion / %		Initial reaction rate / $r \times 10^4$, mol/(L×s)	Acids conversion / %
	30 min	150 min		
ZnO				
sunflower	85.0	99.1	3.78	–
rapeseed	83.7	96.7	3.72	14.0
linseed	76.2	93.0	3.39	14.3
NiO				
rapeseed	74.4	93.0	3.31	5.7
linseed	69.7	88.3	3.10	14.0

4 Conclusion

Studies have shown high catalytic activity of fine metal oxides as catalysts for transesterification of vegetable oils triglycerides with ethanol. Zinc and nickel(II) oxides were found to be the most active catalysts among the studied metal oxides. An optimum mass fraction of the mentioned catalysts (0.25–0.30 %) was determined. It was established that the increase in ethanol : triglycerides molar ratio resulted in almost complete conversion of sunflower oil triglycerides. When using zinc oxide as catalyst, raw materials containing up to 5–10 % of water may be applied for the transesterification reaction. It was also found that in the presence of zinc and nickel(II) oxides, along with the transesterification reaction of triglycerides, an esterification reaction of FFA present in the vegetable raw material takes place.

List of abbreviations

FFA – free fatty acid

TG – triglyceride

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SAŽETAK

Tehnološki aspekti transseterifikacije biljnih ulja etanolom u prisutnosti metalnih oksida

Yuriy Melnyk,* *Roman Starchevskyi* i *Stepan Melnyk*

Ispitana je transseterifikacija biljnog ulja etanolom u prisustvu sitnih čestica metalnih oksida kao katalizatora. Pokazalo se da najveću katalitičku aktivnost imaju cinkovi i nikl(II) oksidi. U njihovoj prisutnosti, konverzija triglicerida suncokretova ulja nakon 150 min dostigla je 95,3 odnosno 94,2 %. Otkriveno je da je optimalni maseni udio katalizatora cinkova oksida 0,25 – 0,31 %. U prisutnosti cinkova oksida, s udjelom vode u etanolu od 5 i 10 mas.%, konverzija triglicerida iznosila je 98,5 odnosno 94,8 %.

Ključne riječi
Transeterifikacija, trigliceridi, metalni oksidi, etanol

Department of Organic Products Technology,
Lviv Polytechnic National University
S. Bandery str., 12
Lviv, 79013 Ukrajina

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