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SYNTHESIS OF TRIMETHYLOLPROPANE ESTER BASED ON CHICKEN FAT AS BIOLUBRICANTS

SÍNTESIS DE ÉSTERES DE TRIMETILOLPROPANO A PARTIR DE GRASA DE POLLO COMO BIOLUBRICANTES

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Abstract

In this project, chicken fat was transesterificated to methyl esters of chicken fat (MECF) with an efficiency of 80%, subsequently added trimethylolpropane (TMP) to get as majority product esters of trimethylolpropane (biolubricants). Temperature, molar ratio MECF:TMP and catalyst were evaluated using a mixed-level factorial design. The higher yield was 47%, temperature and the molar ratio were the factors that influenced statistically. Conditions to obtain the higher yield were 150 °C, molar ratio of 3:1 MECF:TMP and 0.5 % of catalyst.

Keywords: chicken fat, transesterification, trimethylolpropane, biolubricant, waste.

Resumen

En este proyecto la grasa de pollo se transesterificó para obtener primeramente ésteres metílicos de grasa de pollo (EMGP) con eficiencia de 80%, posteriormente se adicionó trimetilolpropano (TMP) para obtener como producto mayoritario ésteres de trimetilolpropano (Biolubricantes). Mediante un diseño factorial multinivel se evaluaron los factores temperatura, relación molar EMGP:TMP y cantidad de catalizador. La mayor conversión obtenida fue de 47%, siendo la temperatura y la relación molar los factores que influyeron estadísticamente. Las condiciones para obtener la mayor conversión fueron 150 °C, relación molar EMGP:TMP de 3:1 y 0.5% de catalizador.

Palabras clave: grasa de pollo, transesterificación, trimetilolpropano, biolubricante, residuo.

1 Introduction

The main function of lubricants is to reduce friction, transmit energy, protect against corrosion and wear of mechanical working machinery. They usually come from hydrocarbons of mineral origin that contain linear, branched or aromatic alkanes that are poorly degradable and have a toxic effect on the environment. Currently, the global consumption of these reaches more than 47 million tons per year, of which 50% ends up in the environment due to evaporation, leak and spills (Mobarak *et al.*, 2014). For countries where the economy depends on petroleum, have agroindustrial resources and present a great natural diversity (such as Mexico), biolubricants represent an opportunity for development and technological innovation (Sacramento-Rivero *et al.*, 2010). Therefore, to meet the future demand for lubricants and reduce pollution, the development of biolubricants is important since it eliminates dependence on petroleum, using renewable raw materials and generating products with lower environmental impact (Zainal *et al.*, 2018). The cost of biolubricants is higher than lubricants based on conventional mineral oil, but they have the advantages that, in short, medium and long term, they can balance the difference with environmental and health benefits (Ing, 2009).

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The generation of biolubricants leads to the search for environmentally sustainable alternatives that meet the characteristics of functionality, as well as being technologically efficient and competitive (Gawrilow, 2004). The ideal raw material is the use of natural oils. However, consumer acceptance requires overcoming certain disadvantages, in particular, thermal-oxidative instabilities, high pour points, and limited viscosity ranges, which prevent their use in extreme conditions (Sripada *et al.*, 2013). The investigations are directed to the chemical modification of the fatty acids present in natural oils, being the transesterification reaction, the most used transformation (Arbain and Salimon, 2011).

Transesterification is an ester reaction where it is transformed into another ester through the interchange of the alkyl group (Panchal *et al.*, 2017). Biolubricants are obtained by a multi-step process. First, the triglycerides are reacted with a short chain alcohol (methanol) in the presence of a catalyst (acid/alkaline) to produce methyl esters of fatty acids. The resulting methyl esters are then reacted with polyols such as TMP, NPG or PE, in the presence of an acid (sulfuric acid, *p*-toluenesulfonic acid) or basic catalyst (potassium hydroxide, sodium methoxide, calcium methoxide) to produce triesters (Yunus *et al.*, 2005; Ghazi *et al.*, 2009; Arbain and Salimon, 2011; Gunam Resul *et al.*, 2012; Masood *et al.*, 2012; da Silva *et al.*, 2013; Surapoj *et al.*, 2013; Koh *et al.*, 2014; Wang *et al.*, 2014). This process is one of the most reported in the literature, due to the wide variety of reagents that can be used, resulting in biolubricants with variable properties for various applications. Generally, the transesterification of methyl esters with polyols leads to the decrease of pour points and increases the thermo-oxidative stability, maintaining the viscosity and lubricity characteristics of the base oils (Gryglewicz *et al.*, 2003; Gryglewicz *et al.*, 2013; McNutt and He, 2016).

Numerous research groups have reported the use of vegetable oils as raw material for the synthesis of biolubricants. Ghazi *et al.*, (2009) synthesized esters of TMP from jatropha oil using a 4:1 molar ratio (oil:TMP), at 150 °C. The product, obtained in 80% yield, had higher viscosity and a pour point below zero degrees centigrade. Gunam, *et al.*, (2012) synthesized esters of TMP from jatropha (JME) using sodium methoxide as a catalyst. The effects of temperature on the synthesis were evaluated in a range of between 120 °C and 200 °C. According to the results, they concluded that the optimum temperature was 150 °C. The molar ratio oil: TMP was maintained at 3.9:1, and catalyst at 1% (wt/wt) of the total reactant weight. Wang *et al.*, (2014) used residual cooking oil as a raw material and performed the synthesis with TMP in 85.7% yield, studying the reaction parameters, temperature, molar ratio oil:TMP, amount of catalyst and pressure. On the other hand, Ocholi *et al.*, (2017) studied the optimization of the transesterification reaction of sesame methyl esters (SME) with TMP, evaluating the effects of temperature, molar ratio and reaction time on yield. The optimum conditions were obtained at a temperature of 150 °C, a molar ratio of 6:1 and a time of 197 min for a yield of 80.02% of biolubricant. However, a little or null studies have reported the synthesis of biolubricants using animal oil. In the Mexican Republic, more than 2 million tons of chicken/year are produced, of which 15% corresponds to fatty residues (chicken skin), making this residue an abundant raw material (Zelaya-García, 2007). Lee and Foglia (2000) mention that chicken fat can be considered a source of monounsaturated fatty acids (45-50%), which makes it an attractive raw material for use as a source of biolubricant by transesterification.

The objective of the present work was to analyze the feasibility of using chicken fat for the synthesis of base oil for biolubricants from transesterification with TMP, under a mixed-level factorial design. Three main controllable factors were investigated to obtain maximum conversion: temperature, molar ratio MECF:TMP and amount of catalyst. The temperature levels were 120 °C and 150 °C, the molar ratio level of MECF: TMP was 3:1, 4:1 and 5:1, the amounts of catalyst were 0.5, 1.0 and 1.5% (wt/wt). The controllable factors and their levels for the parameters of the process were selected based on what was reported in the literature.

2 Materials and methods

2.1 Raw material

The fatty waste used (chicken skin) in this investigation was collected in the different chicken markets and outlets of the municipality of Tuxtla Gutiérrez, Chiapas. The obtaining and purification of chicken fat was carried out according to the methodology reported by Hernández-Cruz *et al.*, (2017).

2.2 *Transesterification*

The synthesis process of the biolubricant involved the transesterification of the chicken fat in two stages. The first stage was to produce the methyl esters, while the second stage consisted of the conversion of the methyl esters to TMP esters.

2.2.1 *Synthesis of methyl esters of chicken fat (MECF)*

100 g of purified chicken fat were transesterified at 60 °C for 1 h with methanol using KOH as a catalyst. The molar ratio oil:methanol 1:6, and 1% (wt/wt) of catalyst was used (Alptekin and Canakci, 2010).

2.2.1.1 *Average molecular weight of fatty acids*

The molecular weight of a fat depends on its fatty acid profile. Fatty acid profile is the relative proportion of different fatty acids in a fat. In order to determine the fatty acid profile, the oil is usually converted into alcohol esters of fatty acid and then their proportionate weight is measured using gas chromatography using method described by Hernandez-Cruz *et al.*, (2017). The relative proportions of the esters are then converted back to corresponding amounts of fatty acids.

$$mwfa = \sum MW_i * \left(\frac{f_i}{100}\right) \quad (1)$$

$$MW = 3 * mwfa + 38.049 \quad (2)$$

where:
f_i are the weight fraction of a reported fatty acid
MW_i, molecular weight of fatty acid
38.049 is the weight of glycerol backbone

2.2.2 *Synthesis of trimethylolpropane esters (biolubricant)*

The obtained methyl esters were reacted with trimethylolpropane (TMP) in batches of 50 mL using sodium methoxide (NaOH in 30% methanol) as a catalyst. The production of trimethylolpropane esters (ETMP) was carried out using different molar ratios MECF: TMP (3:1, 4:1, and 5:1); Catalyst percentages wt/wt (30% NaOMe) (0.5, 1, 1.5) and reaction temperatures (120,150 °C). A mixed-level factorial design was used, the response variable was the percentage of conversion of the MECF.

Table 1. Independent variables and their levels for mixed-level factorial design of the transesterification reaction.

Independent variables		Variable levels		
		-1	0	+1
Ratio of MECF:TMP (mol)	X_1	3:1	4:1	5:1
Catalyst (%,wt/wt)	X_2	0.5	1	1.5
Reaction temperature (ºC)	X_3	120		150

The results were analyzed by means of an ANOVA with a value of $p \leq 0.05$. All treatments were performed in duplicate.

2.3 *Experimental Design and Statistical Analysis*

To explore the effect of the operation variables on the response in the region of investigation, a mixed-level factorial design was performed. Ratio of MECF/TMP (mol, X_1), catalyst (%wt/wt, X_2) and reaction temperature (ºC, X_3) were selected as independent variables. The range of values and coded levels of the variables are given in Table 1. A polynomial equation was used to predict the response as a function of independent variables and their interactions.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} x_i x_j \quad (3)$$

where β_0, β_i, β_{ii} and β_{ij} are constant, linear, square and interaction regression coefficient terms, respectively, and x_i and x_j are independent variables. The STATGRAPHICS Centurion XV was used for multiple regression analysis, analysis of variance (ANOVA). The goodness of fit of the model was evaluated by the coefficient of determination R^2.

2.4 *Analysis of the transesterification product*

For the identification and quantification of the reaction products, a Perkin Elmer reflex HPLC system with UV detection at 210 nm was employed. A ZORBAX ODS column (4.6 × 250 mm, 5 μm, Agilent), as reported by (Allen and Ott, 2012). Standards used for retention time determination of methyl esters and triester (TE) were purchased from Sigma-Aldrich of 99% purity.

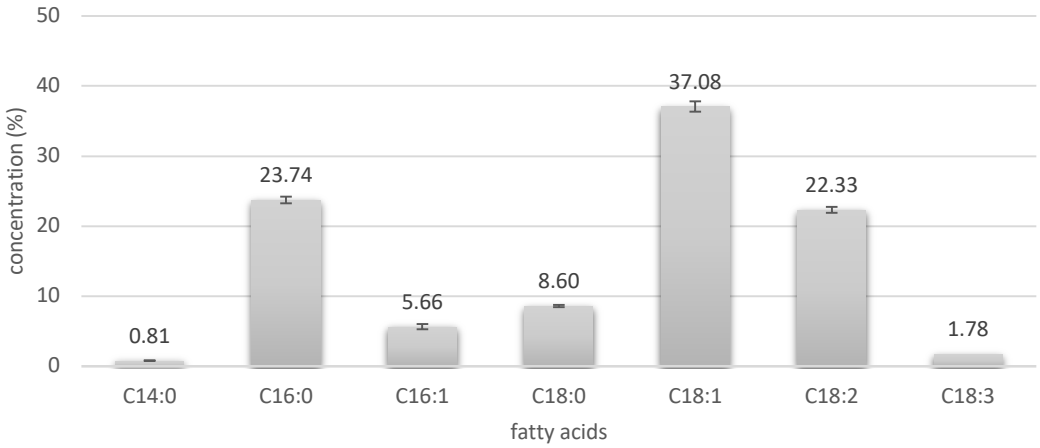

Fig. 1. Content of fatty acids in purified chicken fat.

The evaluation of the reaction was also carried out by thin layer chromatography (TLC) using Kieselgel 60 F254 plates (Merck) and as a mobile phase a mixture of n-heptane/AcOEt (83:17), which were revealed with UV light to 254 nm.

3 Results and discussion

3.1 Obtaining and characterization of raw material

The average extraction yield of chicken fat was 49%, compared with the literature (48.53-69.24%) (Arteaga *et al.*, 2010). Subsequently, was purified in a 67% yield of liquid fat at room temperature, according to the methodology described by Hernández-Cruz *et al.*, (2017). The purification process allowed elimination of color and odor because in the process activated carbon was used, which has a large surface area (500-1500 m^2/g), high adsorptive capacity of apolar molecules and high molecular volume, such as hydrocarbons, phenols, and dyes that are present in the fat (Sevilla, 2010).

In the analysis of the fatty acid composition obtained at the end of the purification process (Fig. 1), it was observed that the unsaturated fatty acids present in chicken fat are mainly monounsaturated (42.74%) with a predominance of oleic acid (18:1). The polyunsaturated fatty acids are in 24.11%, with mainly linoleic acid (18:2) and saturated ones in 33.15%, palmitic acid (16:0) being a mayority. These values are similar to that reported by Galeano Leon and Guapacha Marulanda (2011), they found that chicken fat contained 71.7% unsaturated fatty acids and 28.13% saturated fatty acids. This proportion of fatty acids favors the liquid state of the fat and the homogenization during the processes of transesterification with methanol and TMP.

Considering the proportions and molecular weights of fatty acids, was the average molecular mass of the purified fat calculated by Eq. (1). With the above, it was possible to perform the calculations to know exactly the amount of methanol and trimethylolpropane that should be used in the reactions, depending on the molar ratio to be studied.

3.2 Synthesis of biolubricant

The determination of the reaction products was carried out by HPLC and the conversion (%) was calculated applying Eq. (3).

$$\%CONVERSION = \frac{\sum A_{MECFinitial} - A_{MECFfinal}}{A_{MECFinitial}} \times 100 \quad (4)$$

where $\sum A_{MECF}$ is the sum of the area of the methyl ester peaks present in the sample. The results obtained from the observed experiments are summarized in Table 2. The results developed a second-order polynomial equation (in coded units) that could relate the performance of TMPE.

Table 2. Mixed-level factorial design arrangement and % conversion response for TMPE.

Run no. no.	Temperature (°C, X_3)	Molar ratio (X_1)	Catalyst (% w/w, X_2)	Conversion (%)
1	150.0	5.0	0.5	35.76
2	120.0	4.0	1.5	20.99
3	120.0	5.0	0.5	18.75
4	150.0	3.0	1.0	37.03
5	120.0	4.0	0.5	16.53
6	150.0	5.0	1.5	25.27
7	120.0	3.0	1.0	28.11
8	120.0	5.0	1.5	20.05
9	120.0	4.0	1.0	23.78
10	150.0	4.0	1.5	25.04
11	120.0	3.0	1.5	27.08
12	150.0	4.0	1.0	30.45
13	150.0	5.0	1.0	34.19
14	150.0	4.0	0.5	23.9
15	150.0	3.0	0.5	47.04
16	120.0	3.0	0.5	25.14
17	120.0	5.0	1.0	26.01
18	150.0	3.0	1.5	39.15

The following quadratic model was optimized by the Marquardt method:

$$Y = 365.413 - 4.351X_3 - 48.256X_1 + 62.02X_2 - 0.069X_3X_1 - 0.277X_3X_2 - 0.81X_1X_2 + 0.0194X_3^2 + 6.85X_1^2 - 11.48X_2^2 \quad (5)$$

The predicted values match the observed values reasonably well, with R^2 of 0.86, and the model was significant. Table 3 summarizes the analysis of variance (ANOVA) of all the responses of this study so that the temperature and the molar ratio had a significant statistical effect ($p \leq 0.05$) on the percentage of conversion. Figure 2 shows the effect of the increase of each factor with respect to the conversion (%).

According to the results (Table 4) it is observed that the highest conversion was 33% at the temperature of 150 °C. In Fig. 2 it is observed that there is a directly proportional relationship between the temperature and the increase in the conversion percentage. This behavior was observed by Gunam Resul *et al.*, (2012) when studying the formation of TMP esters from jatropha oil, in the range 120-200 °C. This effect is due to the fact that increasing the temperature increases the kinetic energy of the reaction, favoring the formation of the product (Surapoj *et al.*, 2013). However, Wang *et al.*, (2014), reported that the maximum temperature for the transesterification reaction from the residual cooking oil depends on the methyl esters present in the raw material. They concluded that at temperatures above 140 °C the FAME can evaporate and can accelerate the oxidation reactions, causing a decrease in the conversion and products with a darker color. This same effect was reported by Chang *et al.*, (2012). In addition, the authors also mention that high temperatures favor saponification, which decreases the activity of the catalyst by the formation of free fatty acids which leads to a competitive reaction with esters for transesterification. The 3:1 molar ratio of MECF: TMP allowed the highest conversion percentage of 33.92%. It was observed that upon increasing the molar ratio to 4:1, the conversion decreased, and at 5:1 there was no significant statistical difference with respect to 4: 1 (Table 4).

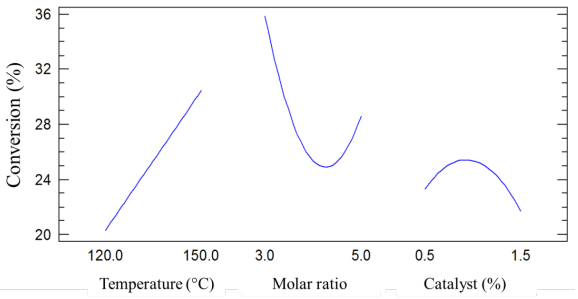

Fig. 2. Effect of temperature, molar ratio and catalyst on the % conversion of MECF to TMPE.

Table 3. Analysis of variance for the % conversion of MECF to TMPE.

Source	Sum of squares	Df square	Mean value	F	p-value
MAIN EFFECTS					
A: Catalyst	40.5319	2	20.266	3.45	0.1346
B: Molar ratio (MECF:TMP)	345.523	2	172.761	29.42	0.0041
C: Reaction temperature	464.007	1	464.007	79.01	0.0009
INTERACTIONS					
AB	78.3746	4	19.5936	3.34	0.1350
AC	63.0338	2	31.5169	5.37	0.0737
BC	51.254	2	25.627	4.36	0.0988
RESIDUAL	23.4901	4	5.87251		
TOTAL (CORRECTED)	1066.21	17			

The p-values prove the statistical significance of each of the factors. Values-$p \leq 0.05$ have a statistically significant effect on the conversion percentage with a 95.0% confidence level.

The probable cause is that there is a dilution of the catalyst as there is a greater presence of MECF. This effect agrees with that of Chang *et al.*, (2012) since they reported that, at a lower molar ratio, higher conversion. From the industrial point of view this result is favorable considering scaling of the production, since with the lowest MECF:TMP ratio (lower amount of reagents), a greater conversion was obtained; besides the elimination of excess MECF would require more energy. On the other hand, the concentration of the catalyst did not have a significant statistical effect on the conversion (Table 3).

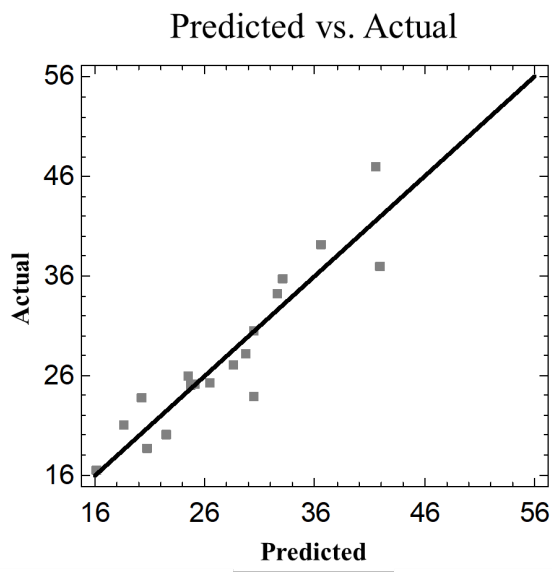

Fig. 3. Predicted vs. actual plot of % conversion (MECF to TMPE).

It was observed that when increasing the percentage of catalyst from 0.5 to 1.5%, there was no increase in the conversion percentage (Table 4). So that the greater amount of catalyst, the reversibility of the reaction can be favored Chang *et al.*, (2012). Therefore, the amount of 0.5% is considered adequate for the production of TMP esters. Optimum conditions of the experiment to obtain high conversion % of MECF were predicted at a molar ratio of MECF:TMP of 3:1, catalyst of 0.5% and reaction temperature 150 °C. At this condition, the MECF conversion % was 47 (Table 2). The observed value was reasonably close to the predicted value as shown in Fig. 3

Table 4. Temperature effect, catalyst and molar ratio MECF:TMP at different levels on the % conversion of MECF to TMPE.

Factor	levels	conversion (%)
Temperature (°C)	120	22.94b
	150	33.09a
MSD		3.17
Catalyst (%)	0.5	27.85a
	1	29.93a
	1.5	26.26a
MSD		4.98
Molar ratio MECF:TMP	3:1	33.92a
	4:1	23.45b
	5:1	26.67b
MSD		4.98

Equal letters in the column mean that there is no significant statistical difference ($p \leq 0.05$).

Conclusions

This study showed that a biolubricant can be successfully synthesized from a residue such as chicken fat by chemical modification. Quadratic polynomial model and ANOVA has well explained the interaction between the process variables. Further, the model was examined and validated for the best fit. However, the conversion performance was lower than that reported for vegetable oils (80-90%), so it is necessary to continue investigating the improvement of the process.

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Abbreviations

TLC	Thin layer chromatography
Rf	Distance traveled by the compound/ distance traveled by the eluent
MECF	Methyl esters of chicken fat
TMPE	TMP Esters
NaOMe	Sodium methoxide
ton	Ton
g	Grams
KOH	Potassium hydroxide
TMP	Trimethylolpropane
NPG	Neopentylglycol
PE	Pentaerythritol
AcOEt	Ethyl acetate
ME	Monoester
DE	Diester
TE	Triester
HPLC	High resolution liquid chromatography
UV	Ultraviolet radiation
FAME	Fatty Acids Methyl esters
wt/wt	weight/weight relation

Greek symbols

$\sum A$	Sum of total area of methyl ester peaks

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