Parameters affecting oleochemical production from waste bleaching earth via alcoholysis

ÖMER FARUK GÜL*, MELEK TUTER and FILIZ KARAOSMANOĞLU

Department of Chemical Engineering, Istanbul Technical University, Maslak, Istanbul, Turkey
e-mail: gulomerfaruk@yahoo.com; tuter@itu.edu.tr; filiz@itu.edu.tr

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Abstract. The edible oil industry is one of the largest industries in the world. In the edible oil refining process, large amounts of waste are discarded every day. Evaluation of these wastes is vital for environmental issues. Most of this waste is due to the bleaching process in which bleaching earths are largely used. Due to its high adsorption capacity, bleaching earth adsorbs oil nearly 40% of its weight. In order to evaluate this waste for oleochemical production, alcoholysis reactions were investigated. Parameters affecting the reaction, such as catalyst type and amount, alcohol type, alcohol:oil molar ratio and temperature, were investigated. The reactions were conducted in the presence of different catalysts such as NaOH, NaOCH₃ and homogeneous alkali polymeric gel catalyst (HAPJEK) and performed at a temperature range of 60–78°C and in the presence of a catalyst (1–2% based on oil weight) at alcohol:oil molar ratios of 5:1–7:1. Based on optimisation by response surface methodology (RSM), the critical synthesis conditions for 210 min reaction time with a maximum of 85.8% methyl ester content were determined as temperature: 68.4°C, catalyst amount 1.5% based on oil weight and methanol/oil molar ratio: 6.4.

Keywords. Waste bleaching earth; oleochemicals; fatty acid ester; response surface methodology; biodiesel.

1. Introduction

Energy consumption and waste production always occur all around the world, so it must be properly organised and managed. In recent years, due to increasing numbers of legislations on environment, waste treatment and disposal have become significant. For this reason, biomass and biodegradable part of municipal and industrial wastes should be evaluated as beneficial product via thermochemical and biochemical conversion processes [1].

Solid wastes from vegetable oil refining industry have turned out to be an important source for producing organic compounds. Bleaching earth is one of the most commonly used adsorbents due to its high adsorption capacity [2, 3]. However, only a small amount of waste bleaching earth (WBE) is utilised and most of it is disposed at landfills [4].

Oleochemicals are derivatives of fats and oils that are used in the chemical industry to produce several products and these products are then used in numerous applications. Oleochemicals are produced from glycerin, fatty acids, esters, amines, amides, alcohols and other compounds. The competitiveness of the oleochemicals and their opportunities usually lie not only with economics, but also with awareness of environment protection [2].

Fatty acid esters are widely used as intermediates in oleochemistry. From fatty acid esters, various types of products such as super amides and fatty alcohols, biosurfactants, hydraulic and drilling fluids, and biodegradable polyesters can be synthesised [5]. There are also other industrial applications as lubricants, anti-rust agents and plasticisers. In recent years, fatty acids alkyl esters have come out as potential substitutes of conventional diesel fuel [6–10].

Fatty acid esters are conventionally produced by transesterification of vegetable oils and fats. In these reactions, oil reacts with short-chain alcohols such as methanol or ethanol in the presence of a suitable catalyst [11–15].

Although alkyl esters are produced in volume, their high price limits their applications. Some of these markets purchase raw materials based on price alone, so the lowest-quality oils are usually preferred. A successful operation can take the cheapest waste oils and convert them into high-value end products. A good example of this is the conversion of spent restaurant grease and municipal sewage sludge into biodiesel fuel [16, 17]. Waste vegetable oil from edible oil refining industries is also a suitable substrate for ester production [16, 18].

WBE from crude oil refining industries that contains up to 40% waste oil is also a suitable raw material for alcoholysis reaction [18]. There are several studies on utilisation of WBE. Solvent extraction is the most extensively

*For correspondence

used method for recovery of residual oil from WBE in research studies [4, 19–23]. The other recovery studies are on supercritical CO₂ extraction [4, 24, 25] or lye extraction [26].

Park *et al* [16, 27] studied the utilisation of WBE generated from soybean, rapeseed and palm oils refinery facilities in biodiesel by production by lipase catalysis. They have found the highest conversion yield to be 55% (w/w) with palm oil after 96 h of reaction.

In our previous work on utilisation of WBE, response surface methodology was used to optimise the parameters affecting biodiesel production in the presence of NaOH catalyst. Critical values were determined to be a temperature of 57.3°C, a catalyst amount of 2.1% (based on oil weight), and an oil/methanol molar ratio of 1/6.3 [18].

In all the studies on WBE, free fatty acid contents of the extracted oils are high. Those oils are not suitable for food applications. However, it is worthy that it could be converted to valuable products such as alkyl esters [4, 18, 27, 28].

In addition to all these research efforts, there is still no significant research on comparison of catalyst application in waste bleaching earth oil utilisation. The aim of this work is to investigate parameters such as catalyst amount and type, oil:alcohol molar ratio and temperature affecting alcoholysis reaction using WBE. Furthermore, the results were integrated with experimental design and the response surface methodology for discussing the effects of parameters on reaction.

2. Experimental section

2.1 Materials and methods

WBE was provided from Besler Gıda San. Tic. A.Ş (Istanbul, Turkey). All the other chemicals were of analytical grade and were purchased from Merck Chemical Co. (Darmstadt, Germany).

2.2 Waste bleaching earth oleochemicals production unit (WBE-OCPU) process and equipment

Oleochemicals production unit (figure 1) was designed and constructed to produce alkyl esters from waste bleaching earth in the presence of different types of alkali catalysts. The main equipment in the unit is a continuous operating reactor equipped with a cooling jacket for temperature control. The capacity of the reactor is 500 mL. Agitation was controlled by an agitator (Yellowline, IKA Werke GmbH & Co. KG Germany). Temperature was controlled by a circulated water bath (Julabo, Germany). At the end of the reaction, ester was recovered using neutralisation and washing steps. The system consists of a solvent tank, an

extractor, a reactor for the transesterification reaction and a condenser for solvent recovery.

2.3 Characterisation of oil

Waste oil was extracted from WBE via solvent extraction. WBE was mixed with n-hexane at room temperature (25°C) for 10 min then the mixture was decanted and oil phase was separated from mixture in n-hexane. The hexane was removed with a rotary evaporator at 70°C under vacuum. The oil content of WBE was determined as 27% (w/w). The characterisation studies of WBE oil were conducted to determine its acid value, saponification value, iodine value, polar material content and density. Then fatty acid methyl esters were prepared by BF₃–methanol reagent esterification according to the AOCS Official Method Ce 2–66. Then the produced esters were analysed by GC-FID using an Agilent 6890 series chromatograph coupled with flame ionised detector and a column (DB-Wax 30 m, 0.32 mm (ID), 0.25 µm (film thickness) with a maximum temperature of 250°C). Standard methyl esters of fatty acids were used to determine peak identification of each fatty acid esters by comparing relative retention times. The peak areas were obtained from the computer and the percentages of the fatty acids were calculated as the ratio of the partial area to the total area. Methyl heptadecanoate was used as an internal standard. GC conditions for analysis is that FID temperature 250°C, injection temperature 250°C, oven temperature 200°C (12 min), 200–230°C (5°C/min) and 230°C (10 min).

2.4 Alcoholysis reactions

The reactions were carried out in the WBE-OCPU system. The stirring rate was adjusted to 600 rpm, and the reaction temperature was kept constant with an accuracy of 2°C by the temperature controller of circulated water bath. In the present study, methanol or ethanol was used as a reactant.

In the first part, methanol was used as the reactant. First, methanol and catalyst were added to the reactor, waste bleaching earth was added to the extractor simultaneously, then a solvent (in this case, n-hexane) was added to extract the oil, and then the extracted oil is fed to the reactor to initiate the reaction. The reaction temperature was kept constant at 69°C, which is the boiling point of n-hexane; the stirring rate was fixed at 600 rpm. After the reaction, ester phase was recovered using neutralisation and washing steps. To monitor the reactions, samples (1 mL) were taken at selected time intervals and cooled in an ice-water bath for 15 min to terminate the reaction.

In the present study, methanol or ethanol was used as a reactant.

Figure 1. Waste bleaching earth oleochemicals production unit (WBE-OCPU).

In the second part, ethanol was used as the reactant. Since ethanol can be used as solvent for oil, in this case n-hexane was not used. For ethanolysis, first, half part of ethanol and catalyst were added to the reactor, waste bleaching earth was added to the extractor simultaneously, then the other part of ethanol was added to the extractor to extract the oil, and then the extracted oil was fed to the reactor to initiate the reaction. The reaction temperature was kept constant at 78°C, which is the boiling point of ethanol; the stirring rate was fixed at 600 rpm. After the reaction, the ester phase was recovered using neutralisation and washing steps. To monitor the reactions, samples (1 mL) were taken at selected time intervals and cooled in an ice-water bath for 15 min to terminate the reaction.

The reactions were conducted in the presence of different catalysts such as NaOH, sodium methoxide (NaOCH_3) and homogeneous alkali polymeric gel catalyst (HAPJEK).

2.5 Experimental design

Experimental design and a response surface methodology were conducted to study the effects of the process variables on esterification reaction. The temperature, catalyst amount and oil:alcohol molar ratio was selected as the influence (independent) variables, and the ester content of product (%) were selected as the dependent variable.

3. Results and discussion

3.1 Characterisation of oil

The main characteristics and fatty acid compositions of WBE oil are shown in table 1. According to the fatty acid composition of WBE oil, the calculated mean molecular weight is 889.9 kg/kg-mol.

Table 1. The properties of waste bleaching earth oil.

Property			WBE oil
Acid value (mg KOH g)			20.62
Saponification value (mg KOH g)			190.74
Iodine value (g I 100 g oil)			62
Polar material (%)			4.00
Density (g ml)			0.9382
Calculated mean molecular weight (kg kmole)			889.9
Fatty acids contents (%wt)			
Miristic acid; C14:0	0.15	Arasitic acid; C20:0	0.77
Palmitic acid; C16:0	18.40	Eicosenoic acid; C20:1	3.01
Stearic acid; C18:0	8.69	Behenic acid; C22:0	1.86
Oleic acid; C18:1	50.13	Erucic acid; C22:1	0.79
Linoleic acid; C18:2	14.46	Lignoceric acid; C24:0	0.27
Linolenic acid; C18:3	0.99	Nervonic acid; C24:1	0.47

3.2 Alcoholysis reactions

In the studies, the methanolysis and ethanolysis reactions, in which temperature and stirring rate were kept constant in the presence of different catalysts and catalyst amounts (1–2% based on oil weight), were conducted.

The influence of agitation rate was not very significant. In fact, in transesterification reaction, the reactants initially form a two-phase liquid system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. While methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant [29, 30].

In these experiments, NaOH, sodium methoxide (NaOCH_3) and HAPJEK were used as catalysts. Experimental results of the ester content (%wt) for ethanolysis and methanolysis are shown in figures 2 and 3, respectively. As shown in the figures, the highest ester contents were

obtained in the presence of 2% NaOCH_3 catalyst as 89.4% in methanolysis and 71.7% in ethanolysis reaction. Although necessity of solvent usage is a drawback for methanolysis reactions, ester contents obtained in the methanolysis reaction are higher than that in the ethanolysis reaction. This can be explained by the higher solubility of free fatty acids in methanol due to its high polarity.

As can be seen in figures 2a and 3a, the alkyl ester contents were lower with NaOH catalyst than with the other catalysts. This can be explained by the difficulty in separation of oil phase and glycerin phase because of saponification in the presence of NaOH catalyst.

As can be seen in figures 2b and 3b, since saponification is lower in the reaction conducted with NaOCH_3 , higher ester content was obtained than NaOH-catalysed reactions.

HAPJEK was the other catalyst used in the studies. Since water was kept by HAPJEK, reactions were very fast and separation of phases was the easiest among all the catalysts. As a result, ester contents obtained were also higher.

Figure 2. Ethanolysis reactions in the presence of different cat: oil amount; at 78°C, 600 rpm in the presence of catalyst. (a) NaOH catalyst. (b) NaOCH_3 catalyst. (c) HAPJEK.

Figure 3. Methanolysis reactions in the presence of different cat: oil amount; at 69°C, 600 rpm in the presence of catalyst. (a) NaOH catalyst. (b) NaOCH₃ catalyst. (c) HAPJEK.

Table 2. Three-level, three-factor face-centered cubic design and responses for methanolysis.

	X1		X2		X3		Ester content (%wt) Value
	Code	Value	Code	Value	Code	Value	
1	-1	0.01	-1	5	-1	60	65.2
2	-1	0.01	+1	7	-1	60	69.3
3	+1	0.02	-1	5	-1	60	69.2
4	+1	0.02	+1	7	-1	60	71.6
5	-1	0.01	-1	5	+1	70	84.4
6	-1	0.01	+1	7	+1	70	89.4
7	+1	0.02	-1	5	+1	70	87.3
8	+1	0.02	+1	7	+1	70	85.9
9	0	0.015	0	6	-1	60	71.7
10	0	0.015	0	6	+1	70	88.6
11	-1	0.01	0	6	0	65	84.6
12	+1	0.02	0	6	0	65	87.0
13	0	0.015	-1	5	0	65	83.0
14	0	0.015	+1	7	0	65	87.0
15	0	0.015	0	6	0	65	86.7
16	0	0.015	0	6	0	65	86.9
17	0	0.015	0	6	0	65	86.2

3.3 Experimental design

Higher ester content was obtained in methanolysis than in ethanolysis; therefore, experimental design reactions were

continued with methanol. Although ester content was higher for reactions in the presence of HAPJEK, NaOCH₃ was selected as the catalyst, because gel formation was encountered in HAPJEK-catalysed reactions.

Table 3. The results of the analysis of variance (ANOVA).

Factor	Sum of square	Degree of freedom	Mean square	F value	p value
Cat amount (L)	6.561	1	6.5610	9.787	0.016645
Cat amount (Q)	1.652	1	1.6519	2.464	0.160455
Mol ratio (L)	19.881	1	19.8810	29.657	0.000960
Mol ratio (Q)	6.733	1	6.7327	10.043	0.015727
Temperature (L)	784.996	1	784.9960	1171.018	0.000000
Temperature (Q)	110.953	1	110.9528	165.514	0.000004
1L * 2L	8.201	1	8.2013	12.234	0.010023
1L * 3L	5.951	1	5.9512	8.878	0.020528
2L * 3L	1.051	1	1.0512	1.568	0.250685
Error	4.692	7	0.6704		
Total SS	1084.62	16		$R^2 = 0.97$	

The results of experimental design and response factors are given in table 2. The quadratic polynomial equation obtained from response surface methodology analysis of the experimental data is listed in the following equation:

$$\begin{aligned}
 Y = & 86.59 + 0.81 * X1 - 0.79 * X1^2 + 1.41 * X2 \\
 & - 1.59 * X2^2 + 8.86 * X3 - 5.89 * X3^2 + 6.44 * X3 \\
 & * X2 - 0.86 * X3 * X1 - 1.01 * X1 * X2
 \end{aligned}
 \quad (1)$$

(a)

(b)

(c)

Figure 4. 2-D contour plot showing the effect of variables on the methyl ester content. (a) Methanol:oil molar ratio vs. catalyst amount. (b) Temperature vs. catalyst amount. (c) Methanol:oil molar ratio vs. temperature.

where Y is the ester content (%), and X_1 , X_2 and X_3 are the coded values of independent variables representing catalyst amount, methanol:oil molar ratio and temperature, respectively.

The results of the analysis of variance (ANOVA) for the RSM model are given in table 3. Since the highest value of F model was obtained from temperature parameter, the most significant parameter can be determined as temperature. The high coefficient of determination ($R^2 = 0.97$) indicates that the quadratic regression model approximates 97% of the real data points. The significance of each regression coefficient is determined by p values. When p value of a corresponding coefficient is smaller, it is more significant.

The relationship between the responses and process parameters were examined by figure 4. As seen in figure 4a, when the methanol molar ratio was higher than 6.0, the higher ester content was obtained. Higher ester content was obtained with increasing catalyst plots regarding the effect of catalyst amount, temperature and their interactions on the methyl ester content. It can be seen in figure 4b that the temperature effect is very high on reaction. When the temperature was higher than 64°C, higher ester content was obtained. Contour plots in figure 4c show the effects of the methanol:oil molar ratio, temperature, and their interactions on the methyl ester content. The methyl ester content could reach values over 80% when the substrate molar ratio was between 5.6 and 6.4 at 64°C.

The critical values for 210 min reaction time with a maximum 85.8% methyl ester content were determined on the conditions of temperature: 68.4°C, catalyst amount (oil weight based): 1.5% and methanol/oil molar ratio: 6.4. This result was also confirmed by the reaction conducted under optimum conditions.

4. Conclusion

Waste bleaching earth (WBE) can be utilised in oleochemical production. The study results reveal that WBE oil can be recoverable and suitable for alcoholysis. Although necessity of solvent usage was a drawback of methanolysis reactions, higher ester contents were obtained in the methanolysis reaction than that in the ethanolysis reaction. This can be explained by better solubility of free fatty acids in methanol due to its high polarity. The highest ester content was obtained in the presence of HAPJEK and NaOCH_3 . Moreover, oil/glycerine phase separation was observed to be easier. The relationship between variables and ester content can be explained by an empirical model derived from RSM in oleochemical production via alcoholysis.

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