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EVALUATION OF BIODIESEL PRODUCTION USING EXPERIMENTAL DESIGN

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ABSTRACT

The high cost and lack of availability of feedstocks is limiting the expansion of biodiesel production in Türkiye. The aim of this study was to examine the potential of waste frying oils as an alternative feedstock. Three waste frying oils were considered: olive oil, corn oil and sunflower oil. The process of biodiesel production by transesterification was performed based on an experimental design in the presence of KOH and methanol at 65°C. Parameters were the kind of vegetable oils, amount of catalyst and the volumetric ratio of alcohol to oil at 120 min. of agitation time, and coded as x_1, x_2 and x_3 investigated at three levels (-1, 0 and 1), respectively. The dependent variable, $y_{conversion}$, was taken as the conversion percentage of transesterification (%), which was calculated as the amount of free glycerol product. Furthermore, the work has also concluded requiring solutions to overcome technical problems based on usage of waste cooking oil.
Keywords: Biodiesel, Experimental design, Glycerol, Waste frying vegetable oil.

BİODİZEL ÜRETİMİNİN DENEYSEL TASARIMA DAYALI OLARAK DEĞERLENDİRİLMESİ

ÖZET

Türkiye'de hammadde azlığı ve yüksek maliyet, biodizel üretiminin yaygınlaşmasını etkileyen bir faktördür. Bu nedenle bu çalışmada, alternatif hammadde kaynağı olarak atık kızartma yağlarının kullanımı araştırılmıştır. Üç farklı atık yağ kullanılmıştır: zeytinyağı, mısır ve ayçiçek yağı. Transesterifikasyonla biodizel üretim prosesi, deneysel tasarıma dayalı olarak KOH ve metanol ortamında 65°C'de gerçekleştirilmiştir. 120 dakika süren deneylerde yağın cinsi, katalizör miktarı ve alkolün yağa hacimsel oranı parametre olarak seçilmiş ve x_1, x_2 ve x_3 şeklinde kodlanarak 3 seviyede (-1, 0 ve 1) incelenmiştir. Bağımlı değişken, transesterifikasyon dönüşüm oranı olup ($y_{dönüşüm}$) gliserin miktarından bağımsız ürün olarak hesaplanmıştır. Ayrıca, atık yağ kullanımından kaynaklanan teknik problemlere ait çözümler de tartışılmıştır.
Anahtar Sözcükler: Biodizel, Deneysel tasarım, Gliserin, Atık bitkisel yağ.

1. INTRODUCTION

Today, the use of biodiesel as alternative energy source all over the world attracts attention due to domestic utilization without requiring extensive engine modifications and having environmental benefits with lower emissions such as soot, particulates, carbon monoxide, hydrocarbons and

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other air toxics. Moreover, it is safe and biodegradable since it is made by chemically reacting alcohol with vegetable oils, fats, or restaurant greases [1-3]. Its performance, storage requirements and maintenance are similar those of petroleum diesel. It has a high cetane number, and is a superior lubricant.

Biodiesel is used primarily for on-road transportation, mining, and for marine watercraft. Although biodiesel is most often used in blends of 2% (B2) or 20% (B20) it may also be used as pure biodiesel (B100). In that case, B100 improves combustion due to presence of about 11 percent of oxygen content. However, B100 is sensitive to cold weather and acts like a solvent about components with rubber in vehicles manufactured before 1994 [4].

Table 1. Production Capacity in Europea [5]

European Countries	Production Capacity (2006)*
Germany	2681
Italy	857
France	775
UK	445
Spain	224
Czech Republic	203
Poland	150
Portugal	146
Austria	134
Slovakia	89
Belgium	85
Denmark	81
Greece	75
Sweden	52
Estonia	20
Slovenia	17
Hungary	12
Lithuania	10
TOTAL	**6069**

* Calculation based on 330 working days per year, per plant

Germany, France, Italy and Austria are leading nations in European biodiesel production, collectively accounting for 94% of European supply (Table 1). The main form of biodiesel in the United States is also soy diesel, which is made from soybean oil, and widely used as B20, and lower blends in transit systems and fleets such as postal vehicles, snowplows, road graders, and other highway maintenance vehicles. In some cities, biodiesel is produced using waste oil, and consumed by diesel-powered vehicles such as the city's transit buses, heavy-duty trucks, marine police boats, and in stationary generators in hospitals. The facts that it cannot completely replaced or displace a significant fraction of current petroleum-based fuel consumption in many countries for the near future. Because it is obvious that if all of the vegetable oil and animal fat are used to produce biodiesel, this amount will provide about 15% of the current demand for on-highway diesel fuel. Moreover, another obstacle for the market development is also the high price of biodiesel. Actually, the cost covers biodiesel's oil feedstock, processing, packaging, transportation, distribution and profit. The biggest contribution to price is about biodiesel's oil feedstock. Therefore, to lower costs and make biodiesel competitive, less-expensive feedstock such as waste frying vegetable oils, rendered animal fats or non-edible type oils could be used. Especially waste frying oils are cheaper than from other feedstock sources.

Nevertheless its capacity is limited, and requires recycling infrastructure [4-7]. Moreover, feedstock quality will usually be limited to free fatty acid (FFA) and water content; it needs to removal of inorganic salts and particles. Moreover, the use of homogeneous alkaline catalysts poses also great difficulties due to the higher FFA and water contents.

In Türkiye, many small facilities are involved in converting vegetable oils to biodiesel fuel activities as soon as possible. They are especially used waste frying vegetable oils. While state-of-the-art biodiesel in modern technology can accommodate up to 3% FFA they are not considered the amounts of FFA, therefore transesterification method is not successfully applied. As a result of that many facilities are produced multiple and huge amount of by-products to be considered. Many consumers are also having emissions with unpleasant smelling. The following problem based on rapidly growing market which will be arrived soon are related to the amount of biodiesel feedstocks which has not been identification and quantification locally or regionally available, and picked up the oils from restaurants by unlicensed handlers. Some modern plants are also now looking for alternative feedstocks, and an effort to add value to commodities and gain additional income from by-products. Although there are available many processing problems, trading is also a highly competitive subject, and must be considered all parameters to create too small amounts of by-products and to reduce the level of emissions.

Consequently, although an extensive work has been done on transesterification with different vegetable oils [8-10] in the literature, this work reviews transesterification method relating to experimental design. To evaluate the reaction of waste frying oils in treatment of KOH and methanol, which has economical, physical and chemical advantages, three parameters and three levels are selected.

2. EXPERIMENTAL STUDY

2.1. Materials

Waste frying oils including olive oil, corn oil and sunflower oil were used in the experiments. To avoid negatively impacting the biodiesel production process, the waste frying oils were subject to clean-up process which consists of a series of steps such as filtering through a screen to remove large particles (Fig. 1), washing with water, then heating the oil to remove the water content and dried in the anhydrous sodium sulphate. Then, the waste frying oils were stored individually at room temperature, and evaluated about FFA content and fatty acid composition. The results of testing showed that the FFA content for olive, sunflower and corn oils changes 2.120, 0.937 and 0.664%, respectively. All other reagents used were of the highest purity available from commercial suppliers.

2.2.Experimental Design

Experiments were carried out based on experimental design in constant temperature of 65°C, the oil amount of 120 mL and agitation speed of 1000 rpm. An experimental design at three levels was employed to evaluate the effects of the kinds of oil selected (x_1), the amount of catalyst (x_2) and the volumetric ratio of alcohol to oil (x_3) on the methyl esters formation, and coded as -1, 0 and +1, and required a total of 15 runs. The range of operating conditions was clearly demonstrated in Table 2 and 3.

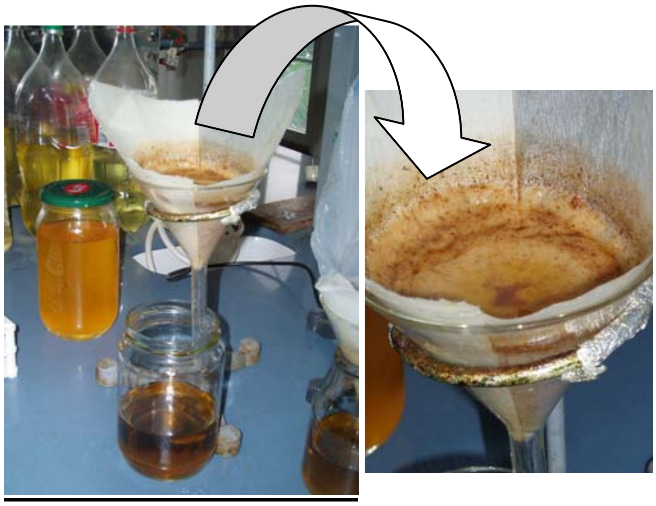

Figure 1. The pre-treatments of waste frying oils [11]

Table 2. Experimental design layout in coded variables [11]

process variables	-1	0	1
kind of waste frying oils, x_1	sunflower	corn	olive
amounts of catalyst, x_2	0.7	0.9	1.1
the volumetric ratio of alcohol to oil, x_3	1:3	1:2	1:1

The dependent variable, $y_{conversion}$, was taken as the conversion percentage of transesterification (%), which was determined as the amount of free glycerol product, and yield, y_{yield}, was also calculated as the amount of biodiesel which was obtained after a series of washing and drying treatments.

The second order polynomial model was used to describe the influence of these effects on the conversion percentage of transesterification or the yield.

$$y = \beta_0 + \sum_{k=1}^{n} \beta_k x_k + \sum_{k=1}^{n} \beta_{kk} x_k^2 + \sum_{k=1}^{n} \sum_{\ell=1}^{n} \beta_{k\ell} x_k x_\ell \qquad (1)$$

Here, y, x_k and $x_k x_\ell$ represent the dependent variable, the main effects, and the interaction terms, which are the effects between variables, respectively. Consequently, if interaction or main effect term(s) drop from the final model, this implies that they have no effect on the response. If the term has positive (negative) value, this indicates that as x_k increases (decreases), y increases (decreases) as well. The detailed description of experimental design and the relationship between the coded and the real values of the variables (Eq. 2) were given by Box and Draper (1987).

$$x_k = \frac{\text{value of variable k - midpoint value of variable k}}{\text{range of values of variable k}} \qquad (2)$$

Table 3. Design matrix for the experimental design [11]

no	x_1	x_2	x_3	kind of waste frying oils	consumed amount of alcohol (mL)	consumed amount of catalyst (g)
1	-1	-1	-1	sunflower	40	0.756
2	1	-1	-1	olive oil	40	0.756
3	-1	1	-1	sunflower	120	0.756
4	1	1	-1	olive oil	120	0.756
5	-1	-1	1	sunflower	40	1.188
6	1	-1	1	olive oil	40	1.188
7	-1	1	1	sunflower	120	1.188
8	1	1	1	olive oil	120	1.188
9	-1	0	0	sunflower	60	0.972
10	1	0	0	olive oil	60	0.972
11	0	-1	0	corn oil	40	0.972
12	0	1	0	corn oil	120	0.972
13	0	0	-1	corn oil	60	0.756
14	0	0	1	corn oil	60	1.188
15	0	0	0	corn oil	60	0.972

2.3. Method

Transesterification experiments were carried out by a magnetic stirred in a closed reaction vessel of 250 mL volume, and provided with a reflux condenser to avoid methanol losses (Fig. 2). Certain amounts of alcohol and catalyst were stirred to ensure that the mixture was uniformity, and reaction was initiated by adding vegetable oil of 120 mL. Vigorous mixing was significant during the reaction due to phases of oil and methoxide, and controlled to 1000 rpm. After the reaction time was completed, the solution was neutralized by an acid under the pH-meter control, then transferred into a separatory funnel, following the waiting at room temperature to separate overnight. The top layer is the biodiesel (methyl ester), and the bottom layer contains unreacted methanol, salts, glycerine and impurities. The impurities and salts were discarded after the filtration step. Excess methanol was recovered by using a vacuum rotary evaporator. The bottom layer was weighed as crude glycerol, $y_{glycerol}$. The methyl ester phase was also sequentially rinsed with hot water, and washing was completed when a clear water layer observed. Then, the ester was filtered over anhydrous sodium sulphate, weighed as the yield of biodiesel (y_{yield}), and stored in glass containers.

Figure 2. Experimental set-up [11]

3. RESULTS AND DISCUSSION

Glycerol is produced as a by-product of the transesterification, and in a crude form which is mixed with varying amounts of alcohol, catalyst and water. Generally, since the overall transesterification process does not include neutralization step in Türkiye, the properties of glycerol are changed in the range of texture from a liquid to gel form and in the range of color from transparent-light yellow to opaque-dark brown. On the contrary, the results of the experiments show that the neutralization step causes to a shorter processing, and purification steps decreased since the settling step was occurred faster. Additionally, not only the separation of glycerol from biodiesel is simpler but also its amount is reduced.

Experimental results showed that it was possible to obtain high yields of methyl ester from waste frying oils, though somewhat lower than refined oils. Nevertheless, transesterification of waste olive oil gave much lower yields, due to the high levels of FFA in the oil. Since higher the values of FFA is formed soap with the metal ion from the alkali catalysts, the reaction mixture is tend to solidify at ambient temperatures, and the problems is associated with glycerol separation and decreasing of yield (Fig. 3) . Moreover, while olive oil has fatty acid composition based oleic, the others are based linoleic. It is common knowledge that vegetable oils based linoleic are much faster reacted which could be monitored via changing color with yellowish pink, and simple washing step. Yet, olive oil is showed cloudy greenish yellow in the beginning of reaction and trouble washing step.

Quantitative analysis of methyl esters (ME) was also performed on a Thermo DSQ model gas chromatograph equipped with ZB-5 (30mx0.25mmx0.25μm) capillary column and FID detector. Figure 4 shows that the composition consists of methyl esters about 90% in both corn and sunflower oils. Therefore, an alternative-environmental approach may be design a blending model among oils with lower FFA and oils with higher FFA, and dry-washing with magnesol instead of water should be preferred in further cleaning step. As a result of this, biodiesel produced from waste frying oils can give Cold Filter Plug Point (CFPP) values close to what would be needed in the Türkiye climate.

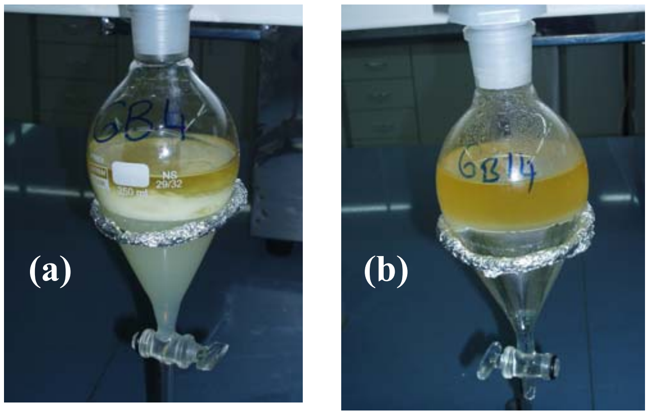

Figure 3. Washing step with water [11]
(a) biodiesel based-olive oil (b) biodiesel based corn oil

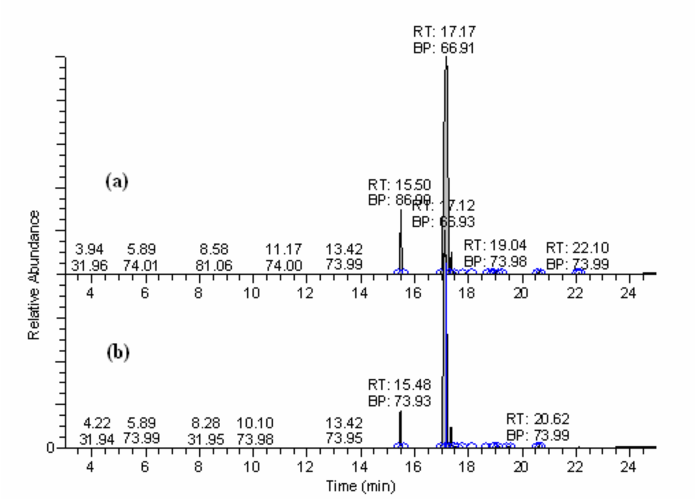

Figure 4. GC-MS results of biodiesel based waste corn oil (a) and waste sunflower oil (b) [11]

The response surface curve is described by the simplified RSM equation (p<0.05), and using the software package STATISTICA 6.0. The model obtained for the response on conversion, which is statistically significant at confidence of 95% (Table 4), is expressed as a function of the coded variables as follows:

$$y_{conversion} = 88.25 + 1.54x_2 + 2.63x_3 - 1.64x_1x_2 - 2.24x_1x_3 - 1.31x_2x_3 \quad (3)$$

Equation (3) shows that the main effect is x_3 (volumetric ratio of alcohol to oil), and its effect is positive. This indicates that excessive amount of alcohol should be added to suppress the backward reaction of methyl ester to fatty acids. However, high ratios involve high energy cost for the evaporation of the unreacted alcohol. Results were well adjusted with those of Ghadge and Raheman (2006).

Table 4. The results of ANOVA analysis [11]

	df	*SS*	*MS*	*F*
Regression	5	169.1405	33.8281	4.608056
Residual	9	66.06971	7.341078	
Total	14	235.2102		

The properties of viscosity were also determined. In particular, while the viscosity range of biodiesel based olive oil was changing extensively (4.3-7.7 cSt) depending on operating conditions, those of the others were changed in the narrower range (3-3.7 cSt).

3.1. Discussion

The rate of transesterification increases with increasing temperature however, the maximum operating temperature should be around the boiling point of the alcohol selected. It will also provide shorter settling time. On the contrary, the reaction time will not be shorter by skipping of the neutralization step. Because of the environmental point of view fuel-grade biodiesel must be produced according to specifications not to be cause of any problems, and to insure proper performance on the engines.

Moroever, depending upon climate and soil conditions, different countries are looking into different oil feedstocks for biodiesel production. For example, soybean oil in the United States and Brazil, linseed and olive oils in Spain, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), beef tallow in Ireland, lard and waste frying oil in Austria, and coconut oil in The Philippines are being considered. Researches should be continued on choosing of the best feedstock for Türkiye conditions based on price and availability. Favorable impacts such as new jobs, environmental benefits, and new markets for agricultural products may be observed based on production and consumption of biodiesel in near future.

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