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Optimization of biodiesel production by alkali-catalyzed transesterification of used frying oil

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ABSTRACT

Biodiesel as an alternative fuel for fossil diesel has many benefits such as reducing regulated air pollutants emissions, reducing greenhouse gases emissions, being renewable, biodegradable and non-toxic. In this study, used frying oil was applied as a low cost feedstock for biodiesel production by alkali-catalyzed transesterification. The design of experiments was performed using a double 5-level-4-factor central composite design coupled with response surface methodology in order to study the effect of factors on the yield of biodiesel and optimizing the reaction conditions. The factors studied were: reaction temperature, molar ratio of methanol to oil, catalyst concentration, reaction time and catalyst type (NaOH and KOH). A quadratic model was suggested for the prediction of the ester yield. The *p*-value for the model fell below 0.01 (*F*-value of 27.55). Also, the R^2 value of the model was 0.8831 which indicates the acceptable accuracy of the model. The optimum conditions were obtained as follows: reaction temperature of 65 °C, methanol to oil molar ratio of 9, NaOH concentration of 0.72% w/w, reaction time of 45 min and NaOH as the more effective catalyst. In these conditions the predicted and observed ester yields were 93.56% and 92.05%, respectively, which experimentally verified the accuracy of the model. The fuel properties of the biodiesel produced under optimum conditions, including density, kinetic viscosity, flash point, cloud and pour points were measured according to ASTM standard methods and found to be within specifications of EN 14214 and ASTM 6751 biodiesel standards.

Keywords: Biodiesel; Used frying oil; Design of experiments; Optimization; Response surface methodology

1. Introduction

Since fossil fuel resources are finite and nonrenewable, using renewable sources of energy such as biodiesel is increasing in different countries. Chemically, biodiesel is a mixture of mono-alkyl esters of long chain fatty acids (Meher et al., 2006). It is an ecological fuel because of its qualitative composition (Tomasevic and Siler-Marinkovic, 2003). Biodiesel has many environmental benefits such as reducing regulated air pollutants emissions (Dorado et al., 2003), reducing greenhouse gases emissions (Bouaid et al., 2007), together with being biodegradable and non-toxic in nature (Murugesan et al., 2009) over petroleum diesel. Biodiesel can be utilized in diesel engines because of having fuel properties close to petroleum diesel (Dorado, 2008). However, the high cost of produced biodiesel mainly because of the cost of raw material i.e. vegetable oil, is the main obstacle for its commercialization. Therefore, using a low cost feedstock such as non-edible oils, low-cost edible oils, by products of the refining vegetable oils, soap stocks and animal fats, restaurant greases and used frying oil (UFO) is necessary (Canakci and Sanli, 2008). Enormous amount of UFO is generated in the world which may lead to environmental and health problems if not properly managed. On the other hand, using UFO as raw material for biodiesel production can significantly reduce the total biodiesel production cost. Therefore, production of biodiesel from UFO and other greasy wastes has the advantage of recycling waste materials without competing with the food market. However, UFO might include food remaining, particles and other impurities that requires pretreatment before being utilized as raw material for biodiesel production. Also, some properties of UFO such as viscosity, acid value, sulfur content and heating value are different with those of virgin vegetable oils. (Dias et al., 2008; Lam et al., 2010; Marchetti, 2012).

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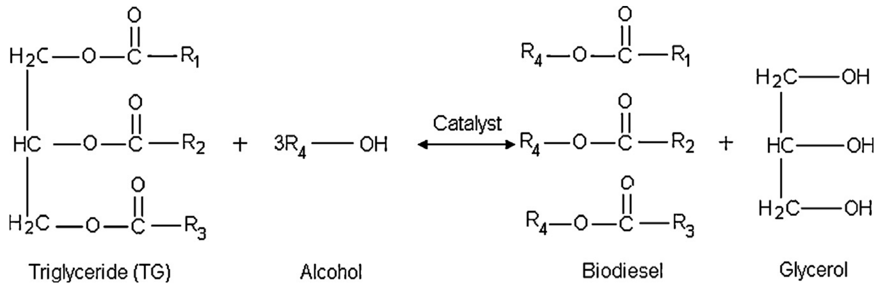

Fig. 1 – Stoichiometric transesterification reaction.

Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol, also known as glycerin (Encinar et al., 2005). The transesterification reaction is represented in Fig. 1. The stoichiometric molar ratio of alcohol to triglycerides is 3:1 in this reaction. Amongst alchols, methanol is the most common used alcohol because of being more reactive and least expensive one (Knothe, 2001). In the transesterification reaction, an alkaline, acid or enzyme catalyst is often used to promote the reaction rate and product yield. Alkaline catalysts such as sodium hydroxide and potassium hydroxide have been found more effective (Meher et al., 2006). Different operational and process conditions such as reaction time and temperature, molar ratio of alcohol to oil and catalyst concentration are among the important factors affecting biodiesel production (Leung and Guo, 2006).

The purpose of the current study was to investigate the biodiesel production from UFO, which was originally a mixture of different fatty acids of vegetables, domestically produced in Iran. In this research, the effect of reaction temperature, molar ratio of methanol to oil, catalyst concentration, reaction time and catalyst type (NaOH and KOH) were investigated. The major purpose of the current study was to optimize the factors for maximizing biodiesel yield and quality using design of experiments.

2. Materials and methods

2.1. Materials

The UFO was collected from Sharif University of Technology restaurant, Tehran, Iran. Physical and chemical properties of UFO are presented in Table 1. Various methyl esters used as standards for analysis of samples by gas chromatography were obtained from Wako Pure Chemical Industries, Japan. All other chemicals and solvents used during biodiesel production, purification and analysis were prepared form Merck and Co. Inc., Germany. This includes methanol with 99.5% purity, sodium hydroxide pellets with 98% purity, potassium hydroxide pellets with 85% purity, anhydrous magnesium sulfate powder with 98% purity, *n*-hexane with 99% purity and hydrochloric acid with 37% purity.

Table 1 – Physical and chemical properties of the UFO.

Property	Value
Acid value, mg KOH/g	0.24
Density at 15 °C, g/cm^3	0.918
Kinematic viscosity at 40 °C, mm^2/s	39.78
Fatty acid composition, wt.%	
Lauric acid (C12:0)	0.2
Myristic acid (C14:0)	0.7
Palmitic acid (C16:0)	28.9
Palmitoleic acid (C16:1)	0.2
Stearic acid (C18:0)	4.0
Oleic acid (C18:1)	37.3
Linoleic acid (C18:2)	26.8
Linolenic acid (C18:3)	1.1
Arachidic acid (C20:0)	0.3
Mean molecular weight, g/mol	854.2

2.2. *Design of experiments*

A double 5-level 4-factor (5 levels for 4 numerical factors and 2 levels for 1 categorical factor) central composite design (CCD) coupled with response surface methodology (RSM) provided in the Design-Expert 7.1.4 (Stat-Ease, Inc) software was employed to design the experiments and fit a quadratic response surface to experimental data. This led to 60 runs with 16 axial points, 32 factorial points and 12 center points. Selection of the factors was based on the fact that for a given used frying oil (i.e. for used frying oil with certain properties such as free fatty acid and moisture content), parameters including reaction temperature, molar ratio of methanol to oil, catalyst concentration, reaction time and catalyst type are the influencing factors affecting transesterification reaction, according to previous works (Dias et al., 2008; Meher et al., 2006). The ester yield as defined before was selected as response. The coded and real levels of the independent factors are given in Table 2. The standard design matrix, experimental and predicted results are represented in Table 3. All experimental runs were carried out at random to minimize systematic errors.

2.3. *Pretreatment of the UFO*

Pretreatment of the used frying oil was completed in three-steps. First the UFO was filtered under vacuum conditions to remove food remaining and other suspended particles. Then, it was dried using anhydrous sodium sulfate and filtered under vacuum again, prior to transesterification.

2.4. *Transesterification procedure*

A 500 ml glass made three-neck flat-bottom batch reactor equipped with a thermometer, a magnetic stirrer and a reflux condenser (60 cm height) was used for biodiesel production. The reactor containing of 100 g of the UFO (0.117 mol) was placed in a water bath heated by a hot plate. Under agitation condition, the reactor and its content was heated up to a desired temperature, first. Defined amount of the catalyst previously dissolved in methanol was added into the reactor; the reaction started and proceeded for a specific time.