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Production of biodiesel from waste vegetable oil using impregnated diatomite as heterogeneous catalyst

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ABSTRACT

In this study, biodiesel was produced from waste vegetable oil using a heterogeneous base catalyst synthesized by impregnating potassium hydroxide (KOH) onto diatomite. Response surface methodology based on a central composite design was used to optimize four transesterification variables: temperature (30–120 °C), reaction time (2–6 h), methanol to oil mass ratio (10%–50%) and catalyst to oil mass ratio (2.1%–7.9%). A quadratic polynomial equation was obtained to correlate biodiesel yield to the transesterification variables. The diatomite–KOH catalyst was characterized using X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR) and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector (EDS). A maximum biodiesel yield of 90%(by mass) was obtained. The reaction conditions were as follows: methanol to oil mass ratio 30%, catalyst to oil mass ratio 5%, reaction time 4 h, and reaction temperature 75 °C. The XRD, FTIR and SEM (EDS) results confirm that the addition of KOH modifies the structure of diatomite. During impregnation and calcination of the diatomite catalyst the K_2O phase forms in the diatomite structural matrix and the active basicity of this compound facilitates the transesterification process. It is possible to recycle the diatomite–KOH catalyst up to three times. The crucial biodiesel properties from waste vegetable oil are within the American Standard Test Method specifications.

1. Introduction

Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [1]. Most of biodiesel production feedstocks come from edible oils and non-edibles. Non-edibles that have been used to produce biodiesel include animal fats, rice bran, and yellow grease [2–4]. Edible vegetable oils such as canola, soybean and corn have been used for biodiesel production and found to be good as a diesel substitute [5]. The production of biodiesel is performed through transesterification of triglycerides using alcohol in the presence of a catalyst [6].

Different catalysts have been explored and used for biodiesel production from seed oils using homogenous bases such as potassium hydroxide and sodium hydroxide and homogenous acids such as sulfuric acid [7]. However, homogeneous base catalysts such as sodium hydroxide for the production of biodiesel cannot be recovered or regenerated after the reaction and produce toxic wastewater. Heterogeneous solid catalysts from egg shell, tungstated zirconia, activated lime, calcium oxide and zeolites have been used [8–13]. Heterogeneous catalysts, for example, can be prepared by impregnating a homogeneous catalyst on bentonite surface structure [14]. Heterogeneous solid catalysts have been studied as substitutes for homogeneous catalysts, with the advantage of being easy to recover and reuse, and they also offer the major advantages of easy separation and purification of the final product.

Diatomite is a siliceous, porous and low density [15,16] material, which has been used as a filter aid [17], insulating material [18], insecticide, catalyst support, *etc.* [19]. Diatomite is normally calcined at temperature about 900 °C for its industrial application. Diatomite can also be chemically treated or activated to modify its porous surface structure for several applications in water treatment. Diatomite contains traces of K_2O and NaO so that it can be used as a catalyst in biodiesel production. Diatomite as a siliceous material can undergo a pozzolanic reaction to form hydrated silicates [20].

Optimizations using surface response methodology have been applied in the production of biodiesel from manketti oil, rapeseed oil and palm oil [21–23]. The main objective of this work is to produce biodiesel from waste vegetable oil using impregnated diatomite with KOH as a heterogeneous catalyst. Surface response methodology technique is applied using a central composite design (CCD) to optimize the process. The reaction process variables under investigation are the methanol to oil ratio and catalyst to oil ratio, reaction time and reaction temperature. A mathematical model is developed to correlate the yield of methyl esters (biodiesel) to the transesterification process variables.

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2. Materials and Methods

2.1. Materials

The waste vegetable oil was obtained from the Vaal University of Technology cafeteria and calcined diatomite was supplied by Infigro Pty South Africa. Potassium hydroxide, isopropanol, methanol and phenolphthalein indicator were supplied by Rochelle Chemical, a local chemical supplier.

Reference standards of fatty acid methyl esters (FAMEs), including palmitic, stearic, palmitoleic, linoleic, oleic, alpha linolenic, icosnoic, iconsenoic and docosenoic methyl ester, all with purity greater than 99%, were purchased from the Sigma Chemical Co. Ltd. The X-ray fluorescence (XRF) analysis of the diatomite shows that the chemical composition of diatomite is as follows in mass percentage: SiO_2 88.02%, Fe_2O_3 1.5%, CaO 0.3%, Na_2O 2.22%, Al_2O_3 3.68%, TiO_2 0.01%, MgO 0.28%, K_2O 2.79% and loss on ignition 1.2%.

2.2. Experimental design

The experimental design selected for this study was CCD, which helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables independently on the yield of biodiesel (response) [24]. The four transesterification process variables studied were methanol to oil ratio (X_1), catalyst to oil ratio (X_2), reaction time (X_3) and reaction temperature (X_4), with each variable being considered as two levels: low (−2) and high (+2). Table 1 shows the range and the levels of the four transesterification variables. For each categorical variable, a 2^4 full factorial CCD for the four variables, consisting of 16 non-center points and 5 replicates at the center points is used. A full experimental design matrix is shown in Table 2.

Table 1
Levels of transesterification process variables employed

Variable	Coding	Units	Levels				
			−2	−1	0	1	2
Methanol to oil mass ratio	X_1	%	10	18.1	30	41.9	50
Catalyst to oil mass ratio	X_2	%	2.1	3.3	5	6.7	7.9
Reaction time	X_3	h	2	2.8	4	5.2	6
Reaction temperature	X_4	°C	30	48.2	75	101.8	120

Table 2
Experimental design and results

Process variables					
Exp	Methanol to oil mass ratio (X_1)/%	Catalyst to oil mass ratio (X_2)/%	Reaction period (X_3)/h	Reaction temperature (X_4)/°C	Biodiesel mass yield (Y)/%
1	41.9	6.72	5.2	48.2	86.1 ± 2.2
2	41.9	6.72	2.8	48.2	71.0 ± 3.6
3	41.9	3.27	5.2	101.8	73.1 ± 4.7
4	18.1	6.72	2.8	101.8	78.7 ± 2.8
5	41.9	3.27	2.8	101.8	89.0 ± 3.9
6	18.1	3.27	5.2	48.2	69.2 ± 4.2
7	18.1	6.72	5.2	101.8	76.2 ± 3.8
8	18.1	3.27	2.8	48.2	57.2 ± 5.9
9	10.0	5.0	4.0	75.0	80.5 ± 4.7
10	50.0	5.0	4.0	75.0	58.2 ± 5.6
11	30.0	2.10	4.0	75.0	83.0 ± 5.8
12	30.0	7.89	4.0	75.0	91.2 ± 3.5
13	30.0	5.0	2.0	75.0	89.4 ± 4.6
14	30.0	5.0	6.0	75.0	87.5 ± 3.7
15	30.0	5.0	4.0	30.0	88.9 ± 4.6
16	30.0	5.0	4.0	120.0	43.6 ± 2.7
17	30.0	5.0	4.0	75.0	88.9 ± 5.8
18	30.0	5.0	4.0	75.0	88.8 ± 5.6
19	30.0	5.0	4.0	75.0	87.8 ± 3.8
20	30.0	5.0	4.0	75.0	88.0 ± 5.1
21	30.0	5.0	4.0	75.0	89.5 ± 6.1

A mathematical model is developed to correlate the yield of methyl esters (biodiesel) to the transesterification process variables through first order, second order and interaction terms according to the following third order polynomial equation:

$$Y = \beta_o + \sum_{j=1}^{4}\beta_j X_j + \sum_{i,j=1}^{4}\beta_{ij}X_iX_j + \sum_{j=1}^{4}\beta_{jj}X_j^2 + \sum_{k,i,j=1}^{4}\beta_{kij}X_kX_iX_j + \sum_{j=1}^{4}\beta_{jjj}X_j^3 \quad (1)$$

where Y is the predicted biodiesel yield, X_i and X_j represent the parameters, β_o is the offset term, β_i is the linear effect, β_{ij} is the first-order interaction effect, β_{jj} is the squared effect, and β_{jjj} is the second-order interaction effect.

2.3. Model fitting and statistical analysis

Design expert (6.0.6) software is used as a regression analytical tool to fit experimental data to the third-order polynomial regression model. The statistical significance of the model is evaluated.

2.4. Catalyst preparation

KOH/diatomite blends (catalyst) were dry-mixed according to following ratios: 1:3, 1:4, 1:5 and 1:6. An Erlenmeyer flask (500 ml) was fitted with a reflux condenser. A magnetic heating stirrer was used to heat the blend of KOH/diatomite, at 60 °C for 24 h with a stirring speed of 400 $r \cdot min^{-1}$. After the impregnation process, the slurry was dried in an oven at 500 °C for 4 h.

2.5. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted using a PANalytical Empyrean diffractometer, and PIXcel detector fixed slits with Fe filtered Co-Ka radiation. Qualitative analysis of diatomite–KOH catalyst was conducted using the KBr method with the Fourier transform infra-red spectroscopy (FTIR) technique. The FTIR analysis was carried out at a wavenumber range of 4000–500 cm^{-1} using a Shimadzu 8400s FTIR apparatus. The scanning electron microscope (SEM model JSM-7001F) equipped with an energy dispersive X-ray detector (EDS) was used to study the structural morphology and elemental composition of the catalysts.

2.6. Biodiesel production

The waste vegetable oil was heated at 100 °C to remove water. The free fatty acid content of waste vegetable oil was determined using titration, which was below 2% using the method described by Van Gerpen *et al.* [25]. Therefore, a one-step alkali transesterification was only required. Transesterification of waste vegetable oil was carried out in a temperature-controlled hot plate equipped with a reflux condenser and magnetic stirrer. The impregnated diatomite was used as a catalyst to produce biodiesel under the following conditions: temperature 60 °C, reaction time 3 h, methanol to oil mass ratio 30%, catalyst to oil mass ratio 5%, and stirring speed 400 $r \cdot min^{-1}$. The catalyst with the highest biodiesel yield was chosen for the study.

The mixture of biodiesel, methanol and glycerol was placed in a decanter for settling. The catalyst and glycerol layers were separated and the biodiesel phase was washed thoroughly with water and then heated at 100 °C to remove water and excess methanol. The experiment was conducted according the design of experiment as shown in Table 2. At the end of the reaction, the catalyst was filtered, washed with distilled water and dried in an oven at 120 °C. To test the recyclability the catalyst was reused under the conditions which gave the maximum yield of biodiesel. The fatty acid methyl