Bioresource Technology 102 (2011) 9749–9754

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Synthesis of methyl esters from palm (*Elaeis guineensis*) oil using cobalt doped MgO as solid oxide catalyst

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ARTICLE INFO

Article history:
Received 30 March 2011
Received in revised form 3 July 2011
Accepted 11 July 2011
Available online 22 July 2011

Keywords:
Methyl ester
Solid oxide catalyst
Transesterification
Palm oil

ABSTRACT

The potential of $Mg_xCo_{2-x}O_2$ as heterogeneous reusable catalyst in transesterification of palm oil to methyl ester was investigated. The catalyst was prepared via co-precipitation of the metal hydroxides at different Mg–Co ratios. $Mg_{1.7}Co_{0.3}O_2$ catalyst was more active than $Mg_{0.3}Co_{1.7}O_2$ in the transesterification of palm oil with methanol. The catalysts calcined at temperature 300 °C for 4 h resulted in highly active oxides and the highest transesterification of 90% was achieved at methanol/oil molar ratio of 9:1, catalyst loading of 5.00 wt.%, reaction temperature of 150 °C and reaction time of 2 h. The catalyst could easily be removed from reaction mixture, but showed 50% decrease in activity when reused due to leaching of active sites.

1. Introduction

Biodiesel or fatty acid methyl esters can be synthesized by transesterification of vegetable oils or animal fat by reacting with lower molecular weight alcohol such as methanol in the presence of a catalyst. Various edible and non-edible oils such as sunflower oil (Granados et al., 2007; Dizge et al., 2009; Li et al., 2009), canola oil (Issariyakul et al., 2008), jatropha oil (Sahoo and Das, 2009), soybean oil (Dizge et al., 2009) and palm oil (Olutoye and Hameed, 2009) have been used as feedstock for biodiesel production. Conventional biodiesel production is based on homogeneous base-catalyzed processes in which sodium and potassium hydroxides are preferred (Hameed et al., 2009a,b). Unfortunately, the separation and purification processes of these catalysts from the final products are time-consuming and produce caustic wastewater (Ngamcharussrivichai et al., 2010). Vegetable oils and animal fats may also contain small amounts of water and free fatty acids (FFA) which will cause soap formation which reduces the yield of the biodiesel.

Recently, heterogeneous catalysts have been studied for use in biodiesel production processes since they would simplify separation and purification processes, avoid the production of soaps through free fatty acid neutralization (Albuquerque et al., 2008; Sharma et al., 2008), and are reusable (Sree et al., 2009). Three types of catalysts can be used in transesterification, alkalis, acids and enzymes (Kaya et al., 2009). Transesterification of edible and non-edible oils at room temperature catalyzed by Mg/Zr (2:1 wt/wt.%) has been reported (Albuquerque et al., 2008) as was the use of a Mg_2CoAl catalyst (Li et al., 2009). At a loading of 2%, this catalyst gave a yield of 96–97% at 473 K with a molar ratio of ethanol to oil of 16:1. Wen et al. (2010) investigated the catalysis performance of TiO_2–MgO in transesterification of waste cooking oil to biodiesel and found that the activity of MT-1-923 catalyst slightly increased compared with that of the fresh catalyst after the catalyst was regenerated.

In the present study, MgCoO catalyst was developed and its transesterification performance was investigated. The effects of methanol to oil molar ratio, catalyst loading, reaction temperature and reaction time were studied using design of experiment and response surface methodology (RSM).

2. Methods

2.1. Materials

Commercial edible grade palm oil was purchased from a supermarket at Nibong Tebal, Malaysia. Methanol (⩾99.9%, HPLC gradient grade) used for transesterification process was purchased from Merck (Malaysia). Analytical grade of $Mg(NO_3)_2{\cdot}6H_2O$ (⩾99.5%) and $CoN_2O_6{\cdot}6H_2O$ (⩾98%) were purchased from Sigma–Aldrich (Malaysia). KOH (⩾85%) used to synthesize the catalysts was purchased from Merck (Malaysia). Methyl heptadecanoate (99.5%) used as internal standard for gas chromatography (GC) analysis was purchased from Sigma–Aldrich (Malaysia) and *n*-hexane (96%) as solvent for GC analysis was purchased from Merck (Malaysia).

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doi:10.1016/j.biortech.2011.07.023

Table 1
Factors and corresponding levels for the response surface design.

Factor	ID	Unit	Low actual	High actual	Low coded	High coded
Methanol/oil molar ratio	A	–	9.00	16.00	−1.000	1.000
Temperature	B	°C	150.00	175.00	−1.000	1.000
Time	C	h	2.00	4.00	−1.000	1.000
Catalyst loading	D	wt.%	1.80	5.00	−1.000	1.000

2.2. Catalyst preparation

The heterogeneous catalyst, $Mg_xCo_{2-x}O_2$ ($0.1 \leqslant x \leqslant 0.9$) was prepared using co-precipitation and calcination of the precursors obtained by mixing 0.1326 M of $Mg(NO_3)_2$ and 0.0206 M of $Co(NO_3)_2$ in a flask and stirring at 600 rpm with a magnetic stirrer. These concentrations were selected based on preliminary trials with $x = 0.3$. The metal (Mg and Co) hydroxides were precipitated from their nitrate compounds using 4 M KOH. The mixture was stirred continuously for 6 h until the solution was homogenized. The pH of the catalyst mixture was measured by indicator strips (Olutoye and Hameed, 2009, 2010). The solution was filtered and dried at 75 °C for 24 h. The sample catalysts were calcined at 300 °C for 4 h and were employed directly for transesterification reaction.

2.3. Catalyst characterization

The specific surface area, pore volume and pore size distribution properties of the catalyst were obtained by nitrogen adsorption isotherm at 77 K in an ASAP 2020 Micromeritics instrument, using the Brunauer–Emmett–Teller (BET) method. Catalyst morphology was analyzed with a Philips XL30S model scanning electron microscope (SEM). Energy dispersive X-ray (EDX) was used to determine elemental composition of the catalyst by analyzing the microscopic image under an EDX instrument. Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups using an FTIR-2000 instrument (Perkin Elmer). The spectra were recorded in the range 4000–400 cm^{-1}.

2.4. Design of experiments

The optimization of parameter variables affecting the synthesis of methyl ester from palm oil using $Mg_xCo_{2-x}O_2$ solid oxide catalyst was carried out using the Central Composite Design (CCD) and response surface methodology (RSM). The four factors chosen were methanol to oil molar ratio, catalyst loading, reaction time and reaction temperature. Table 1 shows the factors and corresponding levels for the experimental design matrix. The complete design matrix of the experiments conducted and results are given in Table 2. The experimental sequence was randomized to avoid systematic errors.

2.5. Statistical analysis

The experimental data obtained were analyzed by the response surface methodology provided by Design-Expert software version 6.06 (Stat-Ease Inc., USA). The response was methyl ester content (Y) and the second-order polynomial equation were used as given by the following equation below:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{n} \beta_{ij} x_i x_j \quad (1)$$

where Y is the response factor (methyl ester content, wt.%), x_i and x_j are the coded independent variables, β_0 is the intercept, β_i is the first-order model coefficient, β_{ii} is the quadratic coefficient for the factor i, and β_{ij} is the linear model coefficient for the interaction between factors i and j.

Table 2
Experimental design and test results.

Standard	Experimental variables				Methyl ester content (%)	
	Methanol/oil molar ratio, A	Temperature (°C), B	Time (h), C	Catalyst loading (wt.%), D	Catalyst	
					$Mg_{1.7}Co_{0.3}O_2$	$Mg_{0.3}Co_{1.7}O_2$
1	12.50	187.50	3.00	3.40	68.77	69.51
2	9.00	150.00	2.00	5.00	90.14	87.38
3	16.00	175.00	4.00	5.00	87.50	85.29
4	12.50	162.50	3.00	3.40	75.91	87.89
5	12.50	137.50	3.00	3.40	87.58	56.52
6	16.00	150.00	2.00	5.00	84.58	89.48
7	9.00	175.00	4.00	1.80	79.37	89.50
8	12.50	162.50	3.00	3.40	68.15	66.47
9	16.00	150.00	4.00	1.80	78.50	82.00
10	12.50	162.50	1.00	3.40	69.88	69.30
11	12.50	162.50	3.00	3.40	71.56	70.68
12	16.00	150.00	2.00	1.80	67.22	81.74
13	16.00	150.00	4.00	5.00	80.04	68.47
14	9.00	150.00	4.00	1.80	74.04	64.07
15	16.00	175.00	2.00	1.80	78.31	85.44
16	9.00	175.00	2.00	5.00	90.35	78.59
17	9.00	175.00	2.00	1.80	80.90	77.23
18	16.00	175.00	4.00	1.80	66.30	74.41
19	19.50	162.50	3.00	3.40	84.96	69.41
20	5.50	162.50	3.00	3.40	85.24	85.85
21	9.00	150.00	4.00	5.00	78.47	87.58
22	9.00	175.00	4.00	5.00	81.37	78.98
23	9.00	150.00	2.00	1.80	71.00	70.83
24	12.50	162.50	3.00	6.60	86.32	84.24
25	12.50	162.50	3.00	0.20	47.39	68.60
26	12.50	162.50	5.00	3.40	76.94	83.07
27	16.00	175.00	2.00	5.00	67.13	87.67