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OPTIMIZATION OF PROCESS PARAMETERS FOR THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL IN THE PRESENCE OF BIFUNCTIONAL γ-Al_2O_3-CeO_2 SUPPORTED CATALYSTS

(Pengoptimuman Parameter Pemprosesan untuk Penghasilan Biodesel daripada Sisa Minyak Masak dengan Menggunakan Mangkin Dwifungsi Berpenyokong γ-Al_2O_3-CeO_2)

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Abstract

Huge quantities of waste cooking oils are produced all over the world every day, especially in the developed countries with 0.5 million ton per year waste cooking oil are being generated in Malaysia alone. Such large amount of waste cooking oil production can create disposal problems and contamination to water and land resources if not disposed properly. The use of waste cooking oil as feedstock for biodiesel production will not only avoid the competition of the same oil resources for food and fuel but will also overcome the waste cooking oil disposal problems. However, waste cooking oil has high acid value, thus would require the oil to undergo esterification with an acid catalyst prior to transesterification with a base catalyst. Therefore, in this study, bifunctional catalyst supports were developed for one-step esterification-transesterification of waste cooking oil by varying the CeO_2 loading on γ-Al_2O_3. The bifunctional supports were then impregnated with 5 wt% Mo and characterized using N_2 adsorption-desorption isotherm to determine the surface area of the catalysts while temperature programmed desorption with NH_3 and CO_2 as adsorbents were used to determine the acidity and basicity of the catalysts. Results show that the γ-Al_2O_3-CeO_2 supported Mo catalysts are active for the one-step esterification-transesterification of waste cooking oil to produce biodiesel with the Mo/γ-Al_2O_3-20 wt% CeO_2 as the most active catalyst. Optimization of process parameters for the production of biodiesel from waste cooking oil in the presence of this catalyst show that 81.1% biodiesel yield was produced at 110^{o}C with catalyst loading of 7 wt%, agitation speed of 600 rpm, methanol to oil ratio of 30:1 and reaction period of 270 minutes.

Keywords: biodiesel, waste cooking oil, bifunctional catalysts, γ-Al_2O_3-CeO_2

Abstrak

Sisa minyak masak dihasilkan dalam kuantiti yang amat besar di seluruh dunia setiap hari terutamanya di negara membangun di mana Malaysia sahaja menghasilkan sebanyak 0.5 juta tan sisa minyak masak setahun. Kuantiti yang sangat besar ini menimbulkan masalah dari segi pelupusannya dan boleh mengakibatkan pencemaran tanah dan air jika tidak dilupuskan dengan baik. Penggunaan sisa minyak masak sebagai bahan mentah untuk penghasilan biodesel bukan sahaja dapat menghindari persaingan terhadap sumber minyak yang sama bagi sumber makanan dan bahan bakar, tetapi juga dapat menyelesaikan masalah berkaitan pelupusan sisa minyak masak yang sempurna. Walau bagaimanapun, sisa minyak masak mempunyai nilai asid yang tinggi yang memerlukan minyak itu melalui proses esterifikasi terlebih dahulu menggunakan mangkin asid sebelum proses esterifikasi menggunakan mangkin alkali. Oleh itu, dalam kajian ini, penyokong bersifat dwifungsi telah dibangunkan bagi tindak balas serentak esterifikasi-tranesterifikasi sisa minyak masak dengan pelbagai muatan CeO_2 di atas γ-Al_2O_3. Penyokong dwifungsi itu kemudian diimpregnasi dengan 5% Mo dan dicirikan menggunakan isoterma jerapan-nyahjerapan menggunakan N_2 untuk penentuan jumlah luas permukaan mangkin manakala nyahjerapan berpengatur suhu menggunakan NH_3 dan CO_2 sebagai bahan penjerap digunakan untuk penentuan sifat keasidan dan kealkalian mangkin. Keputusan kajian menunjukkan bahawa mangkin Mo berpenyokong γ-Al_2O_3-CeO_2 adalah aktif di dalam tindak balas serentak esterifikasi-tranesterifikasi sisa minyak masak untuk penghasilan biodesel dengan Mo/γ-Al_2O_3-20 wt% CeO_2 merupakan mangkin yang paling aktif. Pengoptimuman parameter pemprosesan untuk penghasilan biodesel daripada sisa minyak masak menggunakan mangkin ini mendapati 81.1% biodesel dapat dihasilkan pada suhu 110°C dengan muatan mangkin sebanyak 7%, kelajuan pengacauan setinggi 600 rpm, nisbah methanol kepada minyak sebanyak 30:1 dan masa tindak balas selama 270 minit.

Kata kunci: biodesel, sisa minyak masak, mangkin dwifungsi, γ-Al_2O_3-CeO_2

Introduction

Biodiesel is a fuel made up by mono-alkyl-esters of long chain fatty acids, derived from a renewable lipid feedstock, such as vegetable oil or animal fat [1]. Biodiesel is renewable, biodegradable, highly oxygenated, generates lower emission gases from combustion such as CO_2, NO_x, hydrocarbon particles, non-toxic and essentially free of sulfur and aromatics which give it edge over the conventional petroleum derived diesel [2,3].

The energy content and the physiochemical properties of biodiesel are almost similar to conventional diesel fuel, therefore it can be used either as such on its own or mixed with conventional diesel in existing conventional compression-ignition engines without any engine modifications [4]. Compared to petroleum-derived diesel fuel, biodiesel offers several advantages, including renewability, biodegradability, negligible toxicity, environmental friendly emission profile, higher combustion efficiency, higher cetane number, higher flash point, contains higher oxygen contents (10–12% by weight) than petroleum diesel which results in lower pollution emission and has higher lubricity [2,5].

However, the high cost of biodiesel is the major obstacle for its commercialization. The feedstocks contribute to a major portion in the cost of biodiesel production. It has been reported that approximately 70-95% of the total biodiesel production cost is related to the cost of the raw materials (vegetable oil or animal fates) [6]. In this context, waste cooking oil is considered to be a promising feedstock for low cost biodiesel production. It has been reported that the biodiesel production cost can be reduced effectively to 60 to 70% by using waste cooking oil [7]. Since waste oil is easily available at a relatively low price, therefore can be a workable feedstock for biodiesel production to make the biodiesel competitive in price with petroleum based diesel. Moreover, the production of biodiesel from waste cooking oil will not only avoid the competition of the same oil resources for food and fuel but will also overcome the WCO disposal problems.

The transesterification reaction is carried out in the presence of a catalyst in order to obtain reasonable conversion rates. Generally, homogeneous bas/acid catalysts are used in biodiesel production via transesterification process. Traditional homogeneous catalysts (basic or acid) possess several advantages such as high catalytic activity (reaction complete within 1 h) and mild reaction conditions (from 40 to 65 °C and atmospheric pressure). However, the use of homogeneous catalysts lead to serious contamination problems that require the implementation of nearly perfect separation and product purification processes, resulting in increased production costs.

Heterogeneous catalysis is promising technology for biodiesel production from vegetable oils and other feedstocks. Heterogeneous catalysts have a number of advantages such as noncorrosive, environmentally benign, present fewer disposal problems. In addition, they are also much easier to separate from final reaction products and can be designed to give higher activity, selectivity, and longer catalyst lifetimes as compared to homogeneous catalysts [8].

Currently, new trends are oriented toward the search for new solid bifunctional heterogeneous catalysts that can simultaneously carry out esterification of FFA and transesterification of triglycerides to make the biodiesel production technology sustainable. Bifunctional heterogeneous catalysts having both acidic and basic sites may be a promising alternative to overcome the problems encountered with other catalysts. These bifunctional catalysts act as acidic and basic catalysts at the same time thereby, carry out simultaneously the esterification and transesterification reaction. More importantly, bifunctional heterogeneous catalyst can easily be modified to introduce desired physiochemical properties so that the presence of FFAs or water does not adversely affect the reaction steps during transesterification process [9].

In the present study, we have focused on the biodiesel production from waste cocking oil (WCO) using bifunctional heterogeneous solid catalysts prepared by modified impregnation method. Moreover, the biodiesel production process was optimized in terms of reaction temperature, reaction time, methanol to oil molar ratio, catalyst amount and agitation speed to get maximum biodiesel yield.

Materials and Methods

Catalyst preparation

The bifunctional heterogeneous catalysts were prepared by modified wet impregnation method. The γ-Al_2O_3-CeO_2 mixed oxides with different CeO_2 loadings (5, 10, 15 and 20 with respect to γ-Al_2O_3) were prepared by impregnated method as reported in our previous work [10]. The supports were further impregnated with aqueous solution of $(NH_4)_6\ Mo_7O_{24}.4H_2O$ with constant stirring to avoid the formation of a thick paste. During the impregnation few drops of 0.01 M HNO_3 solution were added to attain maximum adsorption of ions on support.

This mixture was stirred for 3 h at room temperature after which water was slowly evaporated by gentle heating at 70^{o}C. The catalyst samples were then dried at 110^{o}C for 12 h and finally calcined at 500^{o}C in the presence of air in muffle furnace for 5 h. The catalysts were further treated with enough aqueous solution of 0.02 M KOH, dried at 110^{o}C and then calcined at 500 ^{o}C in the presence of air in muffle furnace for 3 h. The synthesized bifunctional heterogeneous catalysts were further modified with Mn metal oxide (5 wt%) using wet impregnation method. The synthesized catalysts were impregnated with aqueous solution of $Mn(NO_3)_2.6H_2O$ at room temperature. However, during preparation of Mn modified bifunctional heterogeneous catalyst the impregnation was carried out slightly in basic medium using KOH solution to achieve the maximum adsorption of Mn onto supports. The mixture was stirred for 3 h at room temperature. After removal of the water from the mixture by heating gently at 70^{o}C, the as prepared samples were than dried at 110^{o}C for 12 h. Subsequently, the catalysts were calcined at 500^{o}C in the presence of air in muffle furnace for 5 h. Finally, the catalysts were stored in desiccators prior to activity testing.

Catalyst characterization

The physiochemical properties of synthesized bifunctional heterogeneous catalysts were studied by various characterization techniques such as N_2 adsorption-desorption (BET), X-ray diffraction (XRD), temperature programmed desorption temperature programmed desorption of NH_3 (TPD-NH_3) and CO_2 (TPD-CO_2).

Feedstock characterization

The waste cooking oil (WCO) was collected from the Universiti Teknologi PETRONAS cafeteria. Prior to use, the waste cooking oil was filtered using fine cloth to remove all insoluble impurities and washed several times with hot distilled water to remove salt and other soluble materials. Water was removed by mixing WCO with 10 wt% silica gel followed by stirring the mixture and vacuum filtration using Whatman filter paper (No. 40 Quantitative) for the removal of silica gel [11]. This step was performed three times to ensure complete removal of the water present in the WCO. The oil was dried at 110^{o}C for 24 h in oven and then stored in air tight bottle for further studies.

The key physical and chemical characteristics of waste cooking oil such as acid value, saponification value, flash point, specific gravity viscosity and calorific value were determined experimentally following standard test methods (Table 1).

Catalyst screening and catalytic activity testing

The waste cooking was transesterified in a 250 ml three-naked round bottom glass batch reactor fitted with a water-cooled condenser and thermometer. The transesterification reaction was carried out with methanol and different bifunctional heterogeneous catalysts under different reaction conditions such as reaction time, reaction temperature, catalyst amount, methanol to oil molar ratio and agitation speed to obtain optimum reaction conditions for biodiesel production. Prior to test reaction, each catalyst was dried in oven at 80°C for 1 h and then activated by dispersing it in methanol at 50°C with constant stirring for 30 min. After catalyst activation, required amount of WCO (heated at 100^{o}C for 12 h) was added to the reactor and reaction was carried out under identified reaction conditions. After reaction completion, the reaction mixture was filtered through a Whatman 42 filter paper (125 mm diameter and a pore size of 2.5 µm) and further centrifuged to separate the catalyst. The mixture was then transferred to a separating funnel and allowed to stand for approximately 24 h. The bottom layer (glycerol and methanol) was drained out and the upper layer consisted of biodiesel (methyl esters) was washed with hot deionized water several times. Finally, the biodiesel was dried at 80^{o}C in vacuum oven for 24 h and stored in air tight bottle for further investigations. The biodiesel yield was calculated by the following formula (1) as reported elsewhere in the literature [12-13]:

$$Biodiesel\ \ yield = \frac{Weight\ \ of\ \ biodiesel}{Weight\ \ of\ \ oil} \times 100 \tag{1}$$

Table 1. Physicochemical properties of selected WCO.

Property	Unit	Value
Acid value	mg KOH/g	2.19
Calorific value	J/g	38462
Kinematic viscosity at 40 ºC	(cSt)	41.17
Specific gravity at 30 ºC	-	0.903
Saponification value	mg KOH/g	186.12
Flash point	^oC	274
Moisture content	%	0.02
Mean molecular weight	g/mol	915.02

Physiochemical properties of synthesized biodiesel

Various important physiochemical properties of synthesized biodiesel such as viscosity, density, acid value, flash point, moisture content and calorific value were determined by following well established methods.

Results and Discussion

Catalyst characterization

The N_2-adsorption-desorption analysis results showed that surface area, pore diameter and pore volume of different synthesized heterogeneous catalysts decreased slightly depending on the CeO_2 loading (Table 2). This decrease in the surface area, pore volume and pore diameter could be the result of pore blockage after the metal oxide impregnation on the support. However, the decrease in the surface area was very small, suggesting that the active metal species were highly dispersed on the support surface as supported by the XRD results. The isotherms of all synthesized catalysts exhibited IV type isotherms and well developed H_2 type hysteresis loops, showing the characteristics of mesoporous materials according to IUPAC classification [14].

The XRD patterns of different heterogeneous catalysts are presented in Figure 1. The XRD patterns showed characteristic diffraction peaks at $2\theta = 37.54, 45.60$ and 66.89^o corresponding to γ-Al_2O_3 [15], and diffraction peaks at $2\theta = 28.76, 33.22, 47.67, 56.46, 59.29, 69.56, 76.86$ and 79.25^o corresponding to crystalline CeO_2 [16].The intensities of crystalline CeO_2 increased as the CeO_2 loading was increased in catalysts. However, no remarkable peaks were found in the XRD patterns for metallic Mo and Mn in monometallic and bimetallic heterogeneous solid catalysts showing that metal oxides were highly dispersed on the surface of all supports, forming small size crystallite metal particles which didn’t give clear diffraction peaks due to the lack of sufficient degree of order [17].

The acid-base properties of the γ-Al_2O_3-CeO_2 supported monometallic Mo catalysts were evaluated by the temperature-programmed desorption (TPD) of ammonia and carbon dioxide. The CO_2-TPD results of the γ-Al_2O_3-CeO_2 supported monometallic Mo catalysts are depicted in Figure 2. The CO_2-TPD results of the γ-Al_2O_3, CeO_2 and Mo/γ-Al_2O_3 catalysts are also presented for comparison. It is observed that the γ-Al_2O_3, CeO_2 and Mo/γ-Al_2O_3 catalysts possess only weak basic sites. On the other hand, the basic sites of medium strength also appear at about 334 °C along with the weak basic sites upon introduction of the CeO_2 into the γ-Al_2O_3.

Table 2. Textural properties of the synthesized bifunctional catalysts

Catalyst	Total Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Mo/γ-Al_2O_3-5 wt% CeO_2	165	0.169	7.1
Mo/γ-Al_2O_3-10 wt% CeO_2	149	0.160	6.6
Mo/γ-Al_2O_3-15 wt% CeO_2	140	0.149	5.9
Mo/γ-Al_2O_3-20 wt% CeO_2	131	0.138	4.8

The results further demonstrate that the percentage of basic sites of medium strength increases with increasing the CeO_2 loading into the monometallic Mo catalysts. Among different catalysts, the Mo/γ-Al_2O_3-20 wt% CeO_2 shows high percentage of medium strength basic sites as clear from the peak intensity. Gutiérrez-Ortiz et al. [18] reported that the chemical addition of one metal oxide into another significantly changes the acid-base properties of the mixed oxides. The appearance of the basic sites of medium strength on the γ-Al_2O_3-CeO_2 supported monometallic catalysts may be attributed to the redistribution of the charges upon introduction of the CeO_2 into the monometallic Mo catalysts.

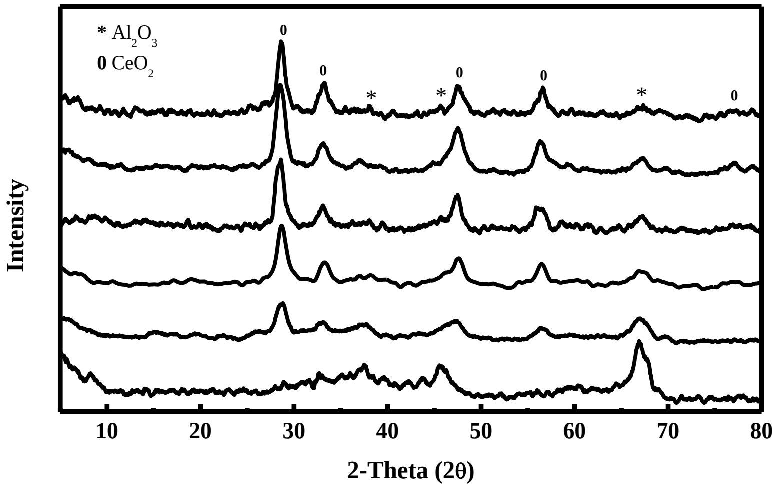

Figure 1. XRD profile of (a) Mo/γ-Al_2O_3, (b) Mo/γ-Al_2O_3- 5 wt % CeO_2 (c) Mo/γ-Al_2O_3-10 wt % CeO_2 (d) Mo/γ-Al_2O_3-15 wt % CeO_2 (e) Mo/γ-Al_2O_3-20 wt % CeO_2 (f) Mo-Mn/γ-Al_2O_3-15 wt % CeO_2 catalysts.

Similarly, the NH_3-TPD patterns of different γ-Al_2O_3-CeO_2 supported monometallic Mo catalysts are presented in Figure 3. The NH_3-TPD patterns of the γ-Al_2O_3, CeO_2 and Mo/γ-Al_2O_3 catalysts are also shown for comparison. It is observed that the strong acid sites of γ-Al_2O_3 disappear when molybdenum and ceria are added into the γ-Al_2O_3, generating weak and medium acid sites on the surface of all monometallic catalysts. The results further demonstrate that the percentage of weak acid sites increases with increasing of CeO_2 loading into the γ-Al_2O_3. On the other hand the percentage of acid sites of medium strength decreases with increasing of CeO_2 loading into the catalyst composition. Among different catalysts analyzed, the Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst shows maximum NH_3 uptake at lower temperature, showing greater number of weak acid sites on the surface of catalyst. Kumar et al. [19] reported that the acidity of a catalyst depends upon the average electronegativity of the ions present. Therefore, the change in the acid sites of different strength on the surface of monometallic Mo catalysts may be attributed to the redistribution of charges upon the addition of different CeO_2 loadings which may cause change in the structure of catalyst.

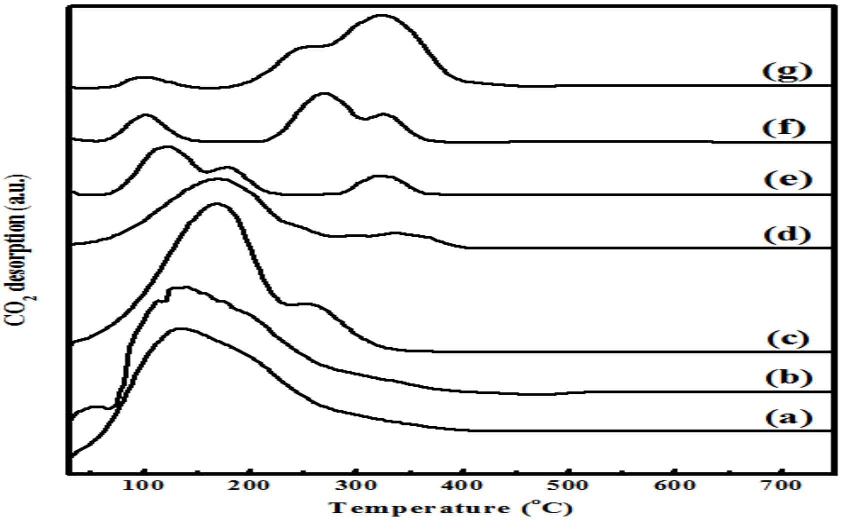

Figure 2. CO_2-TPD patterns of (a) γ-Al_2O_3 (b) Mo/γ-Al_2O_3 (c) CeO_2 (d) Mo/γ-Al_2O_3-5 wt% CeO_2 (e) Mo/γ-Al_2O_3-10 wt% CeO_2 (f) Mo/γ-Al_2O_3-15 wt% CeO_2 (g) Mo/γ-Al_2O_3-20 wt% CeO_2 catalysts.

Catalyst screening and catalytic activity tests

The synthesized bifunctional heterogeneous catalysts were tested in the transesterification reaction of waste cooking oil at identified reaction conditions such as reaction temperature of 95°C, methanol to oil molar ratio of 15:1, reaction time of 30-270 min, agitator speed of 500 rpm and catalyst loading of 5 wt%. Among different bifunctional heterogeneous catalysts, Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst showed improved transesterification activity and provided maximum biodiesel yield of 69.5% at reaction time of 270 min. The improved catalytic behaviour of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst could be due to the presence of optimal strength of active acidic and basic sites for the given reaction. Moreover, no soap formation was found during the course of reaction as esterification of FFA and transesterification of triglycerides were carried out simultaneously due to the presence of optimal strength of active acidic and basic sites on the surface of bifunctional heterogeneous solid catalyst required to catalyze the biodiesel reaction as compared to other synthesized catalysts. Among different bifunctional heterogeneous catalysts, Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst showed the most optimal active sites strength for biodiesel reaction. Based upon the experimental results, this catalyst was selected for further studies to optimize the biodiesel production process from waste cooking oil.

Effect of catalyst loading

Catalyst amount is one of the most important factors that affect the biodiesel yield during the transesterification reaction, therefore it is essential to optimize the catalyst amount for efficient biodiesel production. The biodiesel yield obtained over varying loading of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst at identified reaction conditions is depicted in Figure 4. The results showed that biodiesel yield increased as the catalyst loading was increased due to an increase in the number of active sites. Maximum biodiesel yield (73.2%) was obtained at 7 wt% catalyst loading. This suggested that at 7 wt% catalyst loading contact between the reactants and solid catalyst was maximum which directly influenced the forward transesterification reaction speed, thus provided maximum biodiesel yield. However, as the catalyst loading was increased above 7 wt% the biodiesel yield started to decrease at similar reaction conditions. This is due to the mixing problems of the reaction mixture involving reactants, products and solid catalyst. Therefore, the optimum catalyst amount of 7 wt% was chosen in this study.

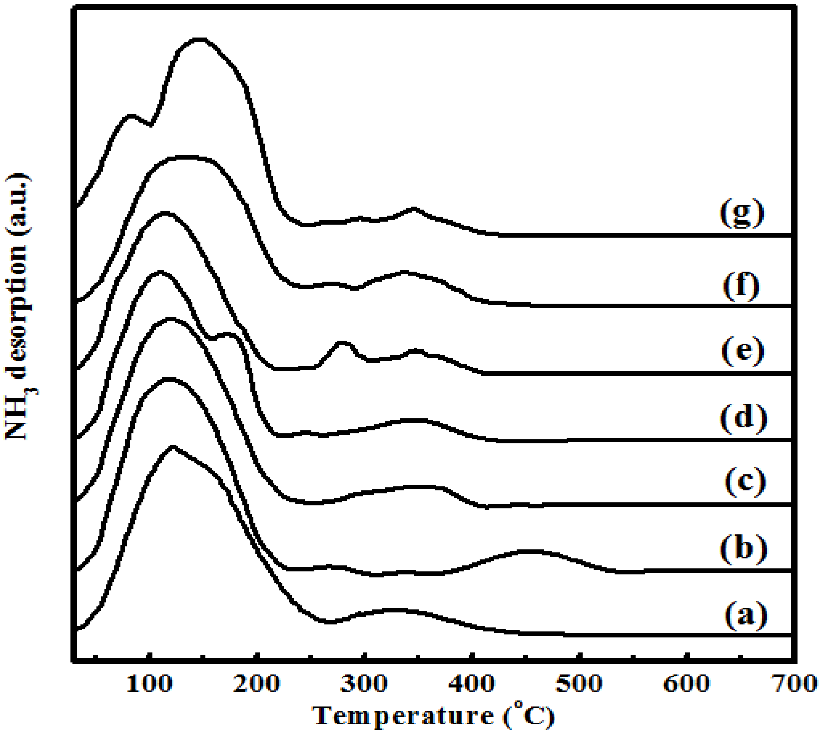

Figure 3. NH_3-TPD patterns of (a) CeO_2 (b) γ-Al_2O_3 (c) Mo/γ-Al_2O_3 (d) Mo/γ-Al_2O_3-5 wt% CeO_2 (e) Mo/γ-Al_2O_3-10 wt% CeO_2 (f) Mo/γ-Al_2O_3-15 wt% CeO_2 (g) Mo/γ-Al_2O_3-20 wt% CeO_2 catalysts.

Effect of methanol/oil molar ratio

The effect of methanol to oil molar ratio on biodiesel yield from transesterification reaction of WCO in the presence of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst is illustrated in Figure 5. It was noted that biodiesel yield increased as the amount of methanol was increased, and maximum biodiesel yield of 79.7% was obtained at methanol to oil molar ratio of 30:1.

However, it was observed that beyond the optimum molar ratio, there was no significant increase in the biodiesel yield and remained almost constant. The maximum biodiesel yield at optimum methanol to oil molar ratio (30:1) was due to the formation of methoxy species on the active sites present on the surface of solid heterogeneous catalyst, pushing the transesterification reaction in the forward direction to produce maximum biodiesel [20]. Moreover, the results showed that this optimum methanol concentration provided suitable contact between the reactants and, thereby provided maximum biodiesel yield. In the present work, the optimum methanol to oil molar ratio was found to be 30:1 for transesterification reaction of WCO. This optimum methanol to oil molar ratio was used for optimization of other parameters during the experimental work.

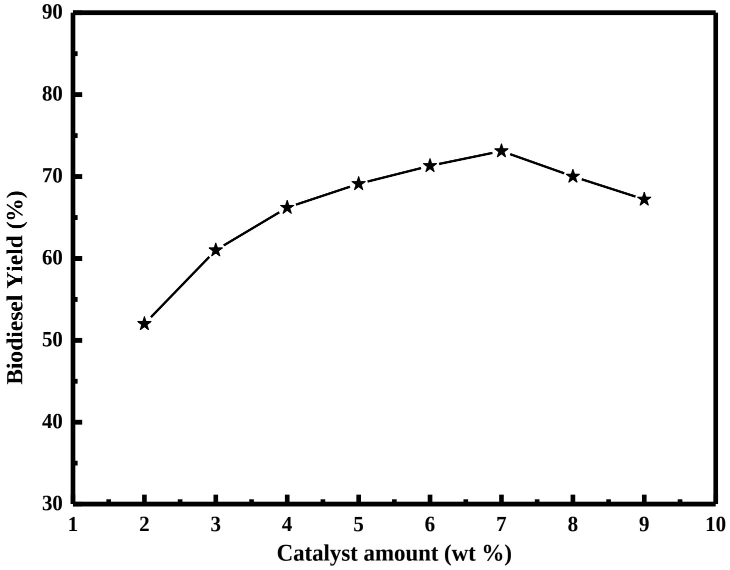

Figure 4. Effect of catalyst loading on biodiesel yield (%) in the presence of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst at methanol/oil molar ratio of 15:1, reaction temperature of 95 ^oC, reaction time of 270 min and agitator speed of 500 rpm.

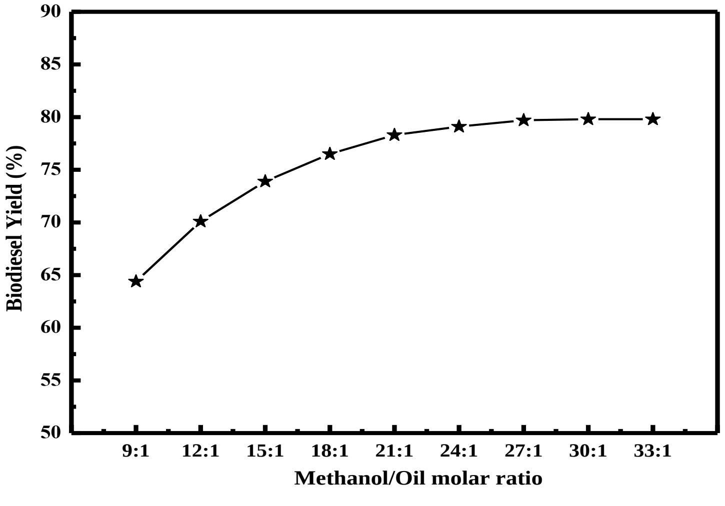

Figure 5. Effect of methanol/oil molar ratio on biodiesel yield (%) in the presence of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst at reaction temperature of 95 ^oC, reaction time of 270 min, agitator speed of 500 rpm and catalyst loading of 7 wt%.

Effect of reaction temperature

The rate of transesterification reaction is strongly influenced by the reaction temperature because of its endothermic nature [21]. As the reaction temperature increases collisions among the reactant molecules also increase by gaining kinetic energy, thereby increases the miscibility and mass transfer between the phases [22]. In the present work, the effect of reaction temperature on the biodiesel yield at given reaction conditions such as reaction time of 270 min, catalyst amount of 7 wt%, methanol to oil ratio of 30:1 was investigated as shown in Figure 6. The results showed that biodiesel yield increased as the temperature was increased and maximum biodiesel yield of 80.2% was obtained at 110 ^{o}C. This is attributed to the fact that at high temperature the carbonyl group of triglyceride molecules become more activated, thus favours the methanol nucleophillic attack on the triglyceride and pushes the transesterification reaction in the forward direction to produce higher biodiesel yield [23].

However, biodiesel yield decreased when the reaction temperature went up beyond the optimum temperature (110^{o}C). This is attributed to the fact that at high temperature the rate of vaporization becomes very high, therefore decrease the amount of methanol available for methanolysis reaction. Moreover, as the transesterification reaction is reversible, therefore high temperature can favour the backward reaction between glycerol and methyl esters on the surface of catalyst. Thus, the optimum reaction temperature for the transesterification reaction of WCO at the given reaction conditions was found to be 110^{o}C.

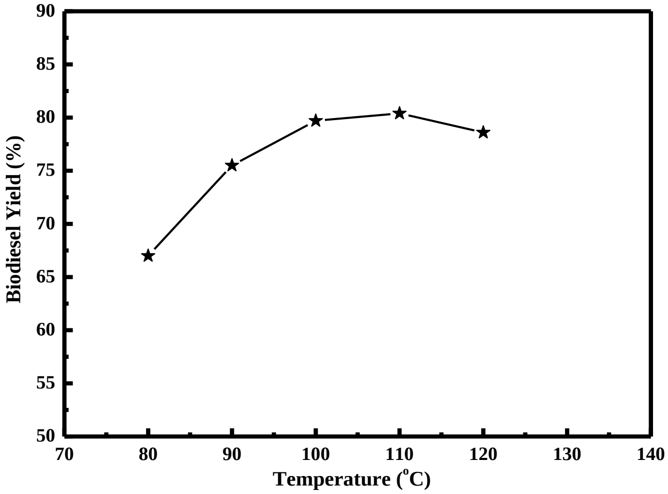

Figure 6. Effect of reaction temperature on biodiesel yield (%) in the presence of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst at methanol/oil molar ratio of 30:1, reaction time of 270 min, agitator speed of 500 rpm and catalyst loading of 7 wt%.

Effect of agitation speed

The agitation speed is also important reaction variable and affects the biodiesel yield during the transesterification reaction of triglycerides. In the case of solid heterogeneous catalyst, the reaction mixture exhibits a three-phase system i.e. oil-methanol-catalyst. The existence of three-phase system in the reaction mixture will retard the reaction rate due to strong mass transfer limitations [23].

Therefore, it is essential to investigate the influence of agitation speed on biodiesel yield in the transesterification reaction of WCO to get the optimum agitation speed. The effect of stirring speed on the biodiesel yield, while other parameters were kept at their optimal values, is depicted in Figure 7. The results showed that biodiesel yield increased as the agitation speed was increased and maximum biodiesel yield of 81.1% was achieved at agitation speed of 600 rpm. However, beyond this optimum agitation speed, no significant increase in the biodiesel yield was observed. In the present study, the agitation speed of 600 rpm was used to get maximum biodiesel yield. Moreover, this showed that agitation speed of 600 rpm was enough to minimize the mass transfer limitations in the transesterification reaction.

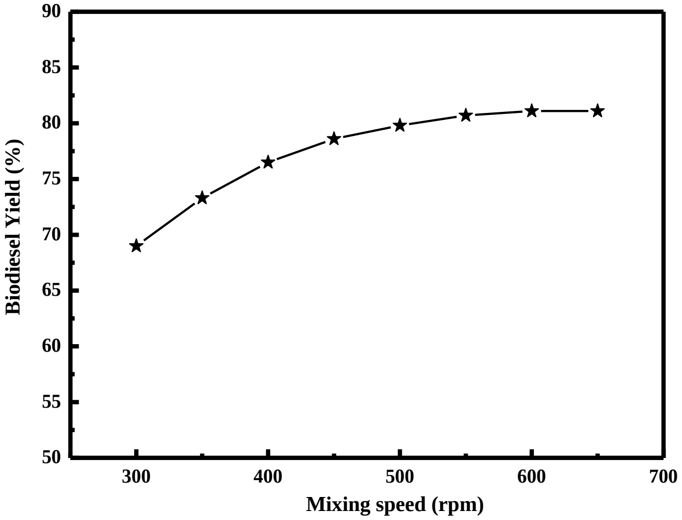

Figure 7. Effect of agitator speed on biodiesel yield (%) in the presence of Mo/γ-Al_2O_3-20 wt% CeO_2 catalyst at methanol/oil molar ratio of 30:1, reaction temperature of 110 ^oC, reaction time of 270 min and catalyst loading of 7 wt%.

Table 4. Physicochemical properties of synthesized biodiesel

Properties	**ASTM D-6751 Range**	**EN 14214 Range**	**Synthesized Biodiesel**
Kinematic viscosity at 40 ºC (mm^2/s)	1.9-6.0	3.50-5.00	4.89
Density (15 ºC) (Kg/m^3)	860-894	860-900	879
Flash point (^oC)	>120	>120	175
Moisture content (%)	< 0.05	< 0.05	0.01
Acid value (mg KOH/g)	≤ 0.5	< 0.5	0.37
Methyl ester content (%)	> 96.5	> 96.5	98.34
Calorific value (J/g)	-	-	40110
Monoglycerides (% mass)	-	< 0.8	< 0.42
Diglycerides (% mass)	-	< 0.2	< 0.06
Triglycerides (% mass)	-	< 0.2	< 0.07
Glycerol (% mass)	0.02	0.02	0.015

Physiochemical properties of synthesized biodiesel

The physiochemical properties of synthesized biodiesel were also studied by following well established methods and the results are reported in Table 4. The results showed that the properties of synthesized biodiesel were comparable to those reported in the literature and occurred within the limits prescribed by the ASTM D-6751 and European Standard EN 14214. Thus, it could be said that WCO used in this study has immense potential to be used in large scale biodiesel production with a suitable catalyst system.

Conclusion

The synthesized Mo/γ-Al_2O_3-20 wt% CeO_2 bifunctional catalyst showed improved catalytic activity in transesterification reaction of WCO at reaction temperature of 110 ^oC, reaction time of 270 min, catalyst loading of 7 wt%, methanol to oil ratio of 30:1 and agitation speed of 600 rpm. The high catalytic activity is attributed to the presence of optimum strength of active sites for the given biodiesel reaction. The present study showed that the synthesized bifunctional catalyst has immense potential to produce low cost biodiesel from low cost feedstocks for sustainable energy production.

Acknowledgement

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