Preparation of novel catalyst composition from natural waste for biodiesel production

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This study presents preparation of a novel, cost effective and recyclable catalyst from natural waste for production of biodiesel. Novel catalyst composition has been developed using combination of seashell and eggshell in complexation with transition metal oxide TiO\textsubscript{2} to form A-B-O type metal oxide complex, where A is alkaline metal and B is transition metal. Catalyst composition has been evaluated and a robust cost effective method for biodiesel production is proposed.

Keywords: Biodiesel, Heterogeneous catalyst, Natural waste

Introduction

Biodiesel is a clean fuel as it has almost no sulphur, no aromatics and has 10% oxygen, which helps its complete combustion in internal combustion (IC) engines. Its higher cetane number leads to improved ignition quality, even in petroleum diesel blends\textsuperscript{1-5}. For biodiesel production, non edible oil based crops (Jatropha\textsuperscript{6}, Pongamia pinnata\textsuperscript{7}, Guizota abyssinica\textsuperscript{8} etc.) can be grown on non cropped marginal lands and wastelands. Processes for producing biodiesel employ different catalysts: i) homogeneous\textsuperscript{9-13} (NaOH, KOH, NaOMe, KOMe, H\textsubscript{2}SO\textsubscript{4}) ii) biocatalysts\textsuperscript{14,15} (lipases); and iii) heterogeneous\textsuperscript{16-21} (metal hydroxides, metal complexes, metal oxides such as calcium oxide, magnesium oxide, zirconium oxide, zeolites, hydrotalcites and supported catalysts etc.). Different experimental reaction parameters while using various heterogeneous catalysts have also been reported\textsuperscript{22}. Presence of free fatty acid (FFA) is a major problem with non-edible oil, waste oil and animal fats. Using homogeneous alkaline catalysts for oils having higher FFA leads to soap formation and therefore feedstock should have less than 0.5% w/w of FFA. Ma & Hanna\textsuperscript{23} observed that use of acid catalyst for vegetable oils having FFA (>0.5%) results in esterification and transesterification of triglyceride simultaneously. However, this process has inhibition of transesterification of glycerides due to production of water along with ester, higher reaction temperature, high molar ratio of alcohol to oil, high concentration of H\textsubscript{2}SO\textsubscript{4} long reaction time and lower yields of biodiesel. Some biodiesel pilot plants in Europe applied a very fast and catalyst-free supercritical process, however due to need for high temperature and pressure, these technologies require high capital investments\textsuperscript{24-26}. Enzyme based transesterification can be carried at moderate temperature and can also tolerate FFA up to 10%. However, enzyme based transesterification processes are very slow and seldom lead to completion.

Heterogeneous solid are non-corrosive, environmentally benign catalysts (there is no need for acid or water treatment in the separation step and moreover present fewer disposal problems), and produce high purity glycerol. Common problems encountered while using heterogeneous catalysts for transesterification of triglycerides are higher catalyst cost, lower recyclability and requirement for elaborate procedures for catalyst preparation. Moreira \textit{et al}\textsuperscript{27} reported preparation of CaTiO\textsubscript{3} using TiCl\textsubscript{4}, CaCl\textsubscript{2},2H\textsubscript{2}O and KOH, which can react with each other where a microwave assisted hydrothermal method is used. Kawashima \textit{et al}\textsuperscript{28} reported preparation of a CaTiO\textsubscript{3} catalyst using pure TiO\textsubscript{2} and CaCO\textsubscript{3} and then using it for biodiesel preparation (yield, 85%) from rapeseed oil.
This study presents preparation of a transesterification catalyst of A-B-O type metal oxide (CaTiO$_3$), where A is alkaline earth metal, and B is transition metal. Study also includes evaluation of catalyst activity for transesterification of non-edible oils (jatropha oil) over repeated cycles to validate catalyst recyclability, optimization of temperature and pressure for maximum biodiesel yield, and evaluation of physico-chemical characteristics of produced biodiesel.

**Experimental Section**

**Reagents and Materials**

Non-edible grade Jatropha oil [total acid number (TAN), 6-10] was purchased from local market and used as such. Methanol (>98%) and titanium oxide (>95%) were procured in LR grade. Raw material used for preparation of catalyst (CaTiO$_3$) was derived from waste material (egg shells and sea shells), which were procured from local market, and washed in water to remove impurities or interfering materials. Washed shells were dried in an oven at 110°C for 6 h to remove traces of water.

**Catalyst Preparation**

Dried sea shells and egg shells were mixed in equal ratio (1:1, by wt), ground to fine powder and sieved through 150 µ mesh. Shell mixture was calcined in a muffle furnace at 550°C for 3 h before use. For preparation of CaTiO$_3$ catalyst, shell mixture and TiO$_2$ were milled in mortar (molar ratio, 1:1.2) for 15 min. Mixture was calcined at 550°C for 1 h and then at 1050°C for 3.5 h to obtain CaTiO$_3$, which was stored in a dry container and kept in desiccators. Formed catalyst was mixed with binder, pseudoboehmite or γ-aluminium oxyhydroxide (AlO(OH)) (3:1, by wt) using 2.5% (v/v) solution of nitric acid as a peptizing reagent. Final mixture was extruded through a Collin E 30 P extruder to obtain cylindrical shaped catalyst (diam, 2.5 mm).

**Catalyst Characterization**

X-ray diffraction (XRD) was carried out in a 18 KW X Ray Diffractometer (Rigaku, Japan) having copper rotating anode. XRD patterns (temp. range, 2-75°C 2θ) were recorded at 50 KV and 250 mA at a scan rate of 2°/min with a step size of 0.01°, and processed and peak search was conducted by search match to identify different phases present in the sample. XRD pattern showed CaCO$_3$ as the major peak in catalyst sample calcined at 550°C. Upon calcination at 1050°C, XRD of catalyst sample showed characteristic peaks of CaTiO$_3$ and minor peaks of TiO$_2$, indicating conversion of calcium carbonate to calcium oxide and its subsequent reaction with titanium dioxide to form desired CaTiO$_3$ complex. Some traces of calcium dialumininate; Grossite (CaAl$_2$O$_4$) were also observed (Fig. 1).

Thermogravimetric Analysis (TGA) of a milled mixture of shells and titanium oxide were recorded between 25-800°C in nitrogen at a heating rate of 10°C/ min using a Perkin Elmer, Germany instrument. TGA (Fig. 2) of synthesized CaTiO$_3$ depicted weight loss (0.5578%), possibly due to initial decomposition at 100-200°C involving loss of water. At 380-550°C, weight loss was observed due to decomposition of Ca(OH)$_2$. Weight loss observed at 500-600°C was attributed to the transformation of pseudoboehmite into γ-Al$_2$O$_3$. Between 650-800°C, the plot shows a plateau. Weight loss (1.377%) indicates thermal decomposition of CaCO$_3$ to form CaO with the loss of carbon dioxide. CaO phase can react with other active ingredient TiO$_2$ to form CaTiO$_3$.

Average particle size of catalyst was measured using a Cilas model number 1180 particle size analyzer. Accelerated surface area and porosity were measured on micrometrics instrument as per ASAP-2010 method. Average pore size of catalyst was found to be 70 Å, Brunauer, Emmett and Teller (BET) surface area was 7.59 m$^2$/g and total pore volume was 0.01 cm$^3$/g. Surface area and total pore volume of CaTiO$_3$ are small due to its high calcination temperature, however large pore size enhances the possibility of reactivity of reacting species during transesterification.

Scanning Electron Microscopy (SEM) was performed by a Hitachi S3400N scanning electron microscope. S3400N SEM utilizes an electron beam accelerated from 300V to 30 KV. SEM images show that morphology of catalyst became more regular having uniform distribution at 1050°C (Fig. 3a). While at 900°C, SEM image shows that particles are agglomerated with each other (Fig. 3b).

Basic strength of catalyst (H) was determined by using a Hammett indicator. About 0.025 g of catalyst was shaken with 5.0 ml of solution of Hammett indicator and left to equilibrate for 2 h. After equilibration, color on the catalyst was recorded. Hammett indicators used were neutral red (H =6-8), bromothymol blue (H =7.2), phenolphthalein (H =9.3), 2,4-dinitroaniline (H =15.0) and 4-dinitroaniline (H =18.4). Basic strength of CaTiO$_3$ was found to be between 6.8-7.2.
Process for Preparation of Fatty Acid Methyl Ester (FAME) or Biodiesel

Transesterification reactions were carried out in a one litre high pressure reactor (make: Amar Equipments) made of stainless steel (SS 316) and has provisions for gas inlet and outlet, sampling point, stirrer and is equipped with proportional-integral-derivative (PID) temperature and digital pressure control system circulating cold water was used to control reactor cooling.

In a typical experiment, 1 mole of jatropha oil, 20 moles of methanol and 10% catalyst w.r.t oil were placed in the reactor. Reactions were carried out at 140-190°C and at 60-80 bar. Reaction progress was monitored by thin layer chromatography using a mixture of petroleum ether, diethyl ether and glacial acetic acid (85:13.5:1.5) as eluents and by analytical techniques like GPC and $^1$H NMR spectroscopy. After completion of reaction, mixture was filtered, and catalyst removed and washed with methanol twice to remove residual ester and glycerol.
Filtrate was allowed to equilibrate to allow for separation of the two phases. Upper layer consisted of ester in methanol, and lower layer consisted of glycerol and excess methanol. After upper layer was separated, it was passed through a column of acidic alumina followed by recovery of alcohol to yield biodiesel. Optimized values (temp. 170°C and pressure 80 bar) gave maximum yield of FAME (biodiesel) in 3 h.

Characterization and Evaluation of Synthesized Biodiesel

Biodiesel was evaluated for various physico-chemical characteristics as per IS 15607/ASTM D 6751 standards. Acid value and moisture content were measured by ASTM D 974 and ASTM D 2709 methods respectively. Kinematic viscosity was determined using Cannon-Fenske viscometers following standard methods ASTM D 445. All viscosity data reported were obtained from triplicate determinations. Oxidation stability was determined by Rancimat apparatus by following EN14112 method and density at 15°C was determined by using EN14103 method (Table 1).

Results and Discussion

Effect of Catalyst Concentration on Biodiesel Yield

Effect of catalyst concentration on biodiesel yield (%) was evaluated at: oil methanol molar ratio, 1:20; reaction temperature, 170°C; and pressure, 80 bar. Catalyst concentration was varied (3-12% w/w of vegetable oils) for different reaction conditions (Fig. 4a). Maximum biodiesel yield (95%) was obtained at a catalyst concentration of 10% (w/w) for a reaction time of 3 h. At higher concentrations (> 10%), no significant increase in biodiesel yield was observed.

Table 1—Characterization of synthesized biodiesel

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Test method</th>
<th>Requirements</th>
<th>Properties of synthesized biodiesel</th>
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<tbody>
<tr>
<td>Kinematic viscosity 40°C, cSt</td>
<td>D 445</td>
<td>1.9-6.0</td>
<td>4.394</td>
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<tr>
<td>Density 15°C, kg/m³</td>
<td>EN 14103</td>
<td>800-900</td>
<td>852</td>
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<tr>
<td></td>
<td>D 4052</td>
<td></td>
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<tr>
<td>Acid value, mgKOH/g</td>
<td>D 974</td>
<td>0.50 max.</td>
<td>0.421</td>
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<tr>
<td>Water content, mg/kg</td>
<td>D 2709</td>
<td>500 max.</td>
<td>400</td>
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<tr>
<td>Carbon residue, % by mass</td>
<td>D 4530</td>
<td>0.05 max.</td>
<td>0.022</td>
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<tr>
<td>Total contamination, mg/kg</td>
<td>EN 12662</td>
<td>24 max.</td>
<td>15</td>
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<tr>
<td>Copper corrosion 50°C, 3 h</td>
<td>D 130</td>
<td>1 max.</td>
<td>1</td>
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<tr>
<td>Free Glycerol, % by mass</td>
<td>D 6584</td>
<td>0.02 max.</td>
<td>0.0078</td>
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<tr>
<td>Total glycerol, % by mass</td>
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<td>0.25 max.</td>
<td>0.0940</td>
</tr>
<tr>
<td>Na &amp; K, mg/kg</td>
<td>EN 14108 and EN 14109</td>
<td>To report</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>
Effect of Catalyst Concentration on Reaction Time at Maximum Biodiesel yield (95%)

Transesterification reactions were considered to be complete when > 95% oil was converted to FAME. With catalyst concentration at 10%, reaction completion was observed in 3 h (Fig. 4b). Thereafter no increase in biodiesel yield was observed with increase in reaction time.

Effect of Jatropha Oil to Methanol Ratio on Reaction Time

Oil: methanol molar ratio was varied from 1:5 to 1:30 with: catalyst conc., 10% w/w of oil; temp., 170°C; and pressure, 80 bar. Completion of reaction was observed in 10 h with 1:5 molar ratio of oil and methanol, whereas reaction time decreased to 3 h at molar ratio of 1:20 (Fig. 5). Thereafter, no change in reaction time was observed on increasing methanol ratio.

Catalyst Stability and Reusability

Catalyst durability was evaluated by repeating transesterification reaction of jatropha oil under optimized conditions (temp., 170°C, pressure, 80 bar; oil: methanol ratio, 1:20; catalyst conc., 10 wt%; and reaction time, 3 h). Catalyst was filtered after each cycle, washed with methanol and dried at 100°C for 1 h. XRD patterns of catalyst showed no change in structure after repeated use of 4 times, thereby establishing the durability of CaTiO₃ catalyst (Fig. 6).
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