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Transesterification of Vegetable Oil to Biodiesel using a Heteropolyacid Solid Catalyst

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Abstract: A clean, facile, and ecologically friendly method for the production of biodiesel has been developed. A solid acid, namely the heteropolyacid (HPA) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, has been used as a heterogeneous catalyst for the production of biodiesel from *Eruca sativa* Gars. oils (ESG oil) with methanol at a certain temperature. A study for optimizing the reaction conditions such as the reaction time, temperature, the oil to methanol ratio, the amount of catalyst, and the usage times of the catalyst, has been performed. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heterogeneous acid catalyst shows almost the same activity under the optimized reaction conditions as compared to a conventional homogeneous catalyst such as sodium hydroxide or sulfuric acid, and can easily be separated from the products and can be used for several more runs. The most important features of this catalyst are that the catalytic activity is not effected by the content of free fatty acids and content of water in the vegetable oil and that the esterification can occur at a lower temperature (room temperature) and be finished within a shorter time. The results illustrate that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an excellent, water-tolerant and environmentally benign solid acid catalyst for the production of biodiesel. The fuel properties of ESG biodiesel were found to be in agreement with the ASTM standard.

Keywords: biodiesel; heterogeneous acid catalyst; heteropolyacids; methyl esters; transesterification; vegetable oil

Introduction

Biodiesel is a promising non-toxic and biodegradable, renewable alternative fuel compared to petroleum diesel in the light of the limited nature of fossil fuel and the environmental concerns. Biodiesel is oxygenated and essentially free of sulfur and aromatics making it a more clean burning fuel with reduced emission of SO_x, CO, unburnt hydrocarbons and particulate matter.[1] Moreover, using pure or blend biodiesel as fuel, the net production of CO_2 can be highly suppressed thus avoiding increasing the local air pollution as is the case with petroleum. Shamer et al. have estimated that in the case of using 1 kg of pure biodiesel instead of the fossil fuel, 3.2 kg of CO_2 production could be avoided.[2] So owing to the benefit for the environment, the rise in crude oil prices and the limited resources of fossil oil, there has been a renewed focus on vegetable oils to make biodiesel fuels. Biodiesel has been produced from vegetable oils, animal fat, and recycled greases from the food industry which are composed of C_{14}–C_{20} fatty acid triglycerides.[3] They are converted into the respective fatty acid esters and glycerol by transesterification with short-chain alcohols, using homogeneous basic catalysts including sodium or potassium hydroxides, carbonates or alkoxides.[4,5] These alkaline catalysts show higher performance for obtaining biodiesel. But, these homogeneous alkaline catalysts are corrosive to equipment and also react with free fatty acids to form unwanted soap by-products, requiring expensive separation, so they cannot directly be used due to the presence of large amounts of free fatty acids (FFA). Another route to produce fatty esters is catalyzed by homogeneous acids, such as H_2SO_4, H_3PO_4, HCl, *p*-toluenesulfuric acid, $BuSn(OH)_3$, $Al(OR)_3$ etc., however they are toxic, corrosive, and produce many by-products which are difficult to separate from the reaction medium.[6] For example, in the case of sulfuric acid,[7] it slowly catalyzes the transesterification of triglycerides and requires temperatures typically above 100 °C and a higher alcohol to oil ratio. And this is followed by a distillation process for water removal, recycling of excess alcohol and ester purification. For homogeneous catalysts, the problem is the high consumption of energy and costly separation of the homogeneous catalyst from the homogeneous reaction mixture which generates more waste water.[8,9] In view of environmental concerns, there needs to be a concerted effort to replace the conventional catalysts by solid catalysts which are easily separated from the products, less toxic and recyclable. So the production of biodiesel from vegetable oil calls for an efficient solid catalyst to make the process fully environmentally and ecologically friendly. During the last decade, many industrial processes have shifted towards using solid acid catalysts.[10,11] Compared to the liquid acid, solid acids contain a variety of acid sites.[12] They exhibit Brønsted or Lewis acidity with different strengths and number of sites, different properties such as porosity and surface area. Some recyclable solid acids, such as Nafion[13,14] make better catalysts, but they are expensive and their activity is less than that of liquid acids. Some solid oxides such as Al_2O_3, SiO_2, ZrO_2 and their sulfated forms, mixed oxides ZrO_2–Al_2O_3, ZrO_2–SiO_2, Mo/ZrO_2 showed some certain activity.[6] Rothenberg's group has screened and evaluated various solid acids such as zeolites, ion-exchange resins, and mixed metal oxides as catalysts in the esterification of dodecanoic acid with 2-ethylhexanol, 1-propanol, and methanol at 130-180 °C, finding that sulfated zirconia is a promising candidate.[15] Recently, Hara's group reported a recyclable solid acid catalyst generated from sugar.[16] The activity of this new solid sulfonated carbon catalyst is more than half that of a liquid sulfuric acid catalyst and much higher than that of some conventional solid acid catalysts.

But, for solid acid catalysts, the water in the aqueous phase may easily cause deactivation and often lead to phase segregation, so a water-tolerant catalyst is required.[15] In order to obtain water-tolerant solid acid catalysts for making biodiesel from vegetable oil, we explored as solid acid catalyst some heteropolyacids (HPAs). HPAs are known to be active catalysts for both homogeneous and heterogeneous acid-catalyzed reactions.[17] Owing to their inherent advantages like ease of handling and removal, reusability, fewer side reactions, strong Brønsted acidity approaching the superacid region, high proton mobility, stability and catalytic activity, heteropolyacids are valued as environmentally benign and economically feasible solid catalysts.[18,19] Among the heteropolyacids, dodecatungstophosphoric acid, $H_3PW_{12}O_{40}$, is characterized by its strong acidity, being classified as a superacid,[20] which has been used as a commercial catalyst for the hydration of olefins.[21] An acidic cesium salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}PW$) with strong acidity,[22] is insoluble in water and organic solvents and has micro- and mesopores with a high surface area (around 130 $m^2 \cdot g^{-1}$).[23,24] $Cs_{2.5}PW$ has been reported as a water-tolerant solid acid catalyst which may be desirable for environmentally benign or green industrial processes.[25] Various acid-catalyzed reactions such as alkylation,[26] acylation,[27] Diels–Alder reactions,[28] skeletal isomerization of *n*-butane,[24,29] ester decomposition[30–32] and hydration of esters or olefins in the presence of excess water[33] have been reported to proceed on $Cs_{2.5}H_{0.5}PW_{12}O_{40.}$ In ester hydrolysis or esterification, the catalytic activity (per unit weight) of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was much higher than those of other inorganic solid acids like H-ZSM-5, SO_4^{2-}/ZrO_2, and Nb_2O_5. The acidity per unit acid site of $Cs_{2.5}PW$ was superior to those of Amberlyst-15, Nafion-H, H_2SO_4, $H_3W_{12}O_{40}$ and *p*-toluenesulfonic acid. These facts demonstrate that $Cs_{2.5}PW$ is a promising candidate for a water-tolerant catalyst owing to its strong acidity and hydrophobic nature.[25]

For the purpose of seeking a new catalyst with high activity, water-tolerance, reusability and that is environmentally benign for biodiesel production, the heteropolyacid $Cs_{2.5}PW$ has been used as a catalyst in transesterification of vegetable oil to produce biodiesel. The experimental results demonstrate that $Cs_{2.5}PW$ exhibits a higher catalytic activity at low temperature than does H_2SO_4, and also enables an easy separation from the mixture. The catalyst was not effected by the free fatty acid content of and moisture in the vegetable oil, so it is a promising candidate for the production of biodiesel.

Eruca sativa Gars. (ESG) is a kind of crucifer plant which is an important oil crop in the drought regions and half drought regions of the world and has attracted more and more attention because of its excellent resistance to drought climate, poor soil conditions and diseases. The freshly extracted ESG oil is yellowish orange with a disagreeable taste which is not suitable for eating. The seed of ESG contains 35 % oil which is suitable for the production of biodiesel. Although ESG oil is important for oil production, the transesterification of ESG oil has received much less attention. Moreover, the commercial use of biodiesel is strongly dependent on the price of the feedstocks so lower cost feedstocks are needed. The price of ESG oil in northwest China is about $ 0.15 per kg, i.e., much cheaper than soybean oil. Thus, ESG oil is a good choice for the production of biodiesel. So the aim of our paper is to report on the transesterification of ESG oil with methanol under heterogeneous acid ($Cs_{2.5}PW$) catalyzed conditions. A preliminary evaluation of some properties of methyl ESG oil as a diesel fuel (viscosity, density, pour point, calorific value, cetane number) is also reported.

Results and Discussion

Characterization of Vegetable Oil

The vegetable oil used in this study was *Eruca sativa* Gars. (ESG) oil. Some of its properties such as density at 27 °C, kinematic viscosity, free fatty acid and moisture contents were determined as 0.8990 g/mL, 27.73 mm^2s, 3.65 % and 0.077 %, respectively.

Influence of Temperature

Alcoholysis of vegetable oils is normally performed near the boiling point of the alcohol. We studied the methanolysis of the ESG oil at 20 °C, 25 °C, 40 °C, and 60 °C in order to determine the effect of the reaction temperature on the methyl ester formation. In all experiments, a methanol/oil ratio of 5.3:1 and 0.02 mmol of catalyst were used and the reaction was carried out for 1 h. Figure 1 shows the temporal evaluation of the results and it can be seen that under $Cs_{2.5}PW$ catalysis, the transesterification of ESG oil to fatty acid esters can occurr at lower temperature, the conversion being more than 96% at 60 °C for 1 h. When the reaction had finished, the mixture was allowed to separate into two layers, and the solid catalyst decanted in the bottom of the reactors which is easily recovered. At 20 °C (room temperature), the conversion of oil is about 40 % in 1 h, with a prolonged reaction time, the transesterification reaction could reach 96 % at 4 h. This fact shows that the catalyst $Cs_{2.5}PW$ exhibited a higher activity owing to its pretreatment at 300–400 °C to acquire super acid sites[34] stronger than 100 % H_2SO_4 and allowed the reaction to occur at a lower temperature.

Influence of Methanol/Oil Molar Ratio

Another important variable with an effect on the yield of methyl ester is the molar ratio of alcohol to vegetable oil. As noted in the literature,[35] the reaction stoichiometry requires three moles of alcohol per mole of triglyceride to yield three moles of fatty esters and one mole of glycerin. But in practice a higher alcohol/oil ratio is employed in order to obtain a higher yield of ester production. However, the high molar ratio interferes with the separation of glycerin because there is an increase in solubility.[36] We selected molars ratio of methanol to oil between 3:1 and 9:1 (Figure 2). The molar ratio 5.3:1 is suitable for obtaining high yields of products as summarized in Figure 2.

It can be seen in Figure 2 that with a stoichiometric amount of methanol, the conversion to esters was only 68 % after 1 h. The oil conversion increased with the increases of the methanol/oil ratio and reached a maximum at 5.3:1, with a ratio of less than 5.3:1, the reaction was incomplete. When the methanol/oil ratio was higher than 5.3:1, the conversion decreased. So the molar ratio 5.3:1 is suitable for obtaining high yields of products.

Influence of the Free Fatty Acids in Virgin Vegetable Oil

In general, virgin vegetable oils contain free fatty acids (1–5 %), phospholipids, carotenes, tocopherols and traces of water.[37] And the type and percentage of fatty acids contained in an oil depends on the plant species and on the growth conditions of the plant. As for alkaline catalysts, vegetable oils with high free fatty acid (FFA) contents suffer from soap formation

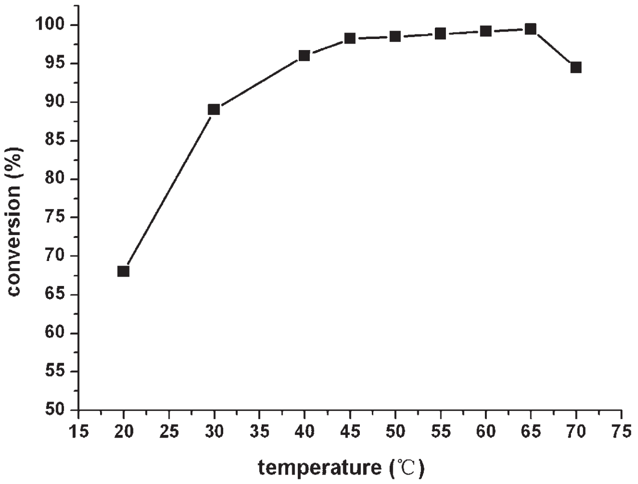

Figure 1. Transesterification of ESG oil at different temperatures (ratio of methanol to oil = 5.3:1, in the presence of $Cs_{2.5}PW$ in 1 h).

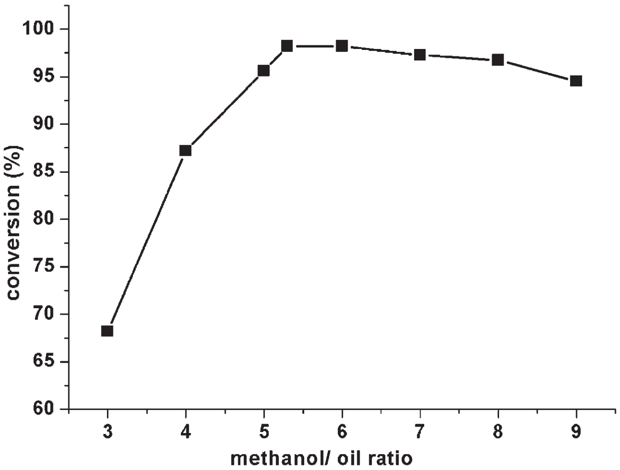

Figure 2. Transesterification of ESG oil with different molar ratios of methanol to oil at 60 °C in the presence of $Cs_{2.5}PW$ in 1 h.

Table 1. Conversion of oils with different FFA.[a]

FFA (%)	1.67	3.8	7.5	10.8
Conversion[b] (%)	98	98	97	96

[a] *Conditions:* methanol/oil ratio = 5.3:1, temperature 60 °C, time = 1 h, catalyst = 0.02 mmol.

[b] The conversion of oil = total conversion − conversion of FFA which is determined by measuring the residual FFA concentration by titration.[39]

leading to less product and problems with product separation and purification. Canakci and Van Gerpan reported that transesterification would not occur if the free fatty acid content in the oil was about 3 %.[38] In fact, for the use of alkaline catalysts the FFA concentration should be less than 0.5 %.[39] Otherwise, prior neutralization of the virgin oil is needed. As for acid catalysts, the transesterification is not effective because of free fatty acids. The heteropolyacid $Cs_{2.5}PW$, which is a superacid, can act as acid catalyst not only in transesterification of the triglyceride into methyl esters, but also in the esterification of free fatty acids into esters as well. The free fatty acid content of the ESG oil we used was about 1.67 % that is, an acid value 3.3 which is not suitable for alkaline catalysts. In order to assess the activity of $Cs_{2.5}PW$ in different FFA containing vegetable oil, the effect of the free fatty acid was carried out by adding some oleic acid to the ESG oil to form different FFA contents (w/w) of 1.67, 3.8, 7.5, 10.8 %. Table 1 gives the results of methyl ester conversion of these ESG oils with various FFA contents.

This shows that at 60 °C, the free fatty acid present in the oils did not decrease the catalytic activity of HPAs because the HPAs could catalyze the free fatty acid and react with methanol to generate the fatty acid methyl ester.

Influence of Water Content

It is known that the transesterification of the vegetable oil is inhibited by the presence of water in the oil phase. In the above esterification reaction of a free fatty acid into an ester an excess of water is obtained. So water-tolerant catalysts needed to be explored. the Heteropolyacid salt $Cs_{2.5}PW$ was found to be water-tolerant[25] and could be used as a solid acid catalyst for the hydrolysis of ethyl acetate and for the esterification of acetic acid with ethanol, whereby it is much more active than zeolite H-ZSM-5.[41]

The water content in the ESG oil was 0.077 %. Komer et al. reported that the transesterification should be water-free[42] and Ma thought that the water content must be kept below 0.06 %.[43] To investigate the effect of water on catalytic activity, the experiment was carried out by adding some excess water to the mixture under the same conditions (methanol/oil = 5.3:1, temperature 60 °C, catalyst 0.02 mmol, 1 h) and the results are shown in Figure 3.

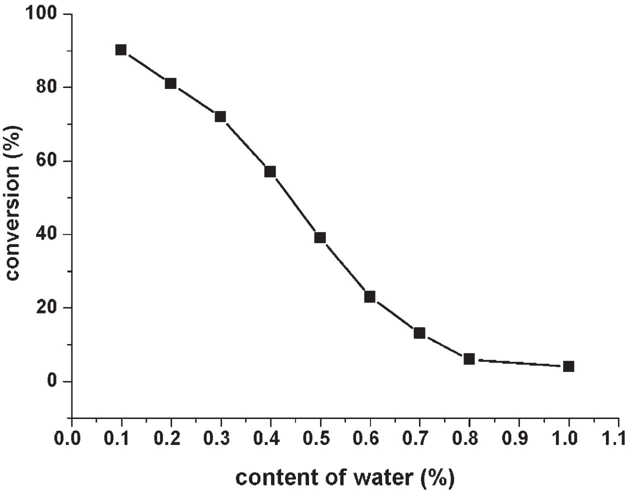

Figure 3. Effects of water on the catalytic activity. *Conditions:* molar ratio of methanol/oil = 5.3:1, temperature 60 °C, time = 1 h, catalyst = 0.02 mmol.

It can be seen that the effect of water on the catalytic activity is related to its content. When the water content was below 0.5 %, the conversion was slightly reduced to 80 % but the conversion was significantly reduced to 4 % when 1 % of water was added. So our catalyst is relatively more tolerant of water than other acid catalyst such as H_2SO_4,[44] SO_4^{2-}/ZrO_2.[45]

Effect of Catalyst Weight

Experiments were carried out by varying the amount of the catalyst between 0.05 to 1.5 g keeping methanol/oil ratio at 5.3:1 for 1 h at 60 °C. The effect of the catalyst amount on the vegetable oil conversion is shown in Figure 4. It can be seen that an increase in the conversion of vegetable oil from 47 % to 94 % was noticed when the amount of the $Cs_{2.5}PW$ was increased from 0.05 to 1.5 g and the acid-catalyst process attains a maximum conversion at 0.1 g of the catalyst $Cs_{2.5}PW$. The increase in the conversion with an increase in the catalyst weight can be attributed to an increase in the availability and number of catalytically active sites.

Effect of Reaction Time

In order to determine the effect of reaction time on the conversion of vegetable oil, the reactions were carried out for different reaction times with a methanol/oil ratio 5.3:1 at 60 °C. It was found (Figure 5)

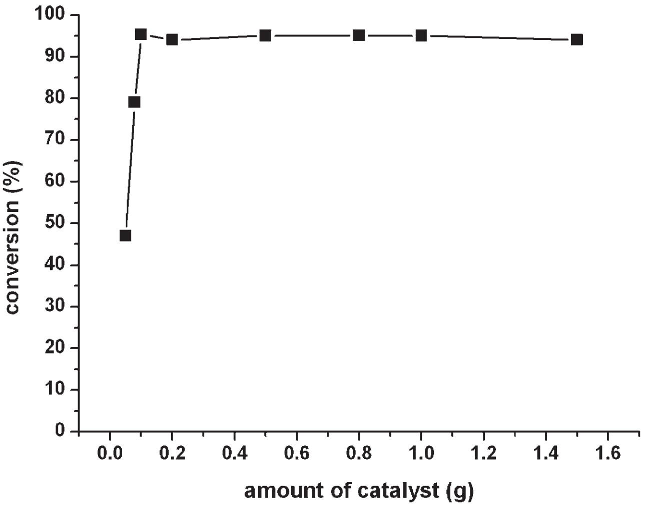

Figure 4. Effect of catalyst weight. *Conditions:* molar ratio of methanol/oil = 5.3:1, temperature 60 °C, time = 1 h.

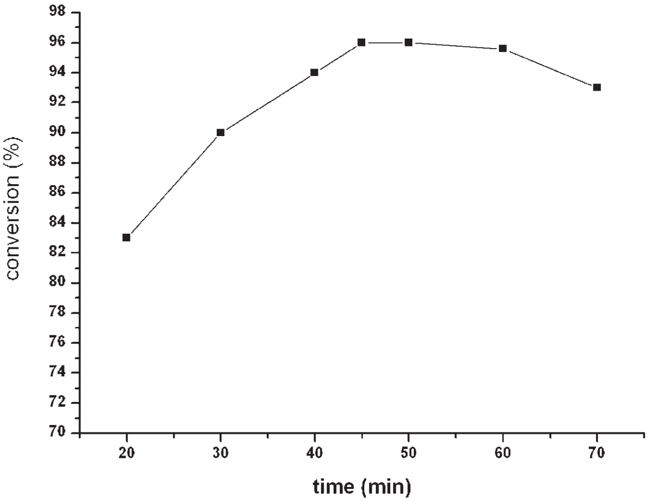

Figure 5. Ester conversion *vs.* different reaction times at temperature 60 °C (methanol/oil = 5.3:1, catalyst 0.02 mmol).

that the conversion of vegetable oil increased with the increase of time and reached a maximum of 94 % at 45 min. After 45 min, the conversion remained almost the same.

It is known that the transesterification process for solid catalysts is usually carried out in three phases. In order to conduct the reaction in a single phase, cosolvents like tetrahydrofuran (THF), 1,4-dioxane are used. Here THF was selected as a cosolvent because its boiling point of 67 °C is only two degrees higher than that of methanol, and at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled.[46] The mixture of ESG oil (20 mL), MeOH (5 mL) and THF (2 mL) in the presence of 0.1 g of $Cs_{2.5}PW$ catalyst took 45 min to reach 99 % conversion to fatty acid methyl esters as can be seen from the ^1H NMR spectra (Figure 6).

Reusability of the Catalyst

As mentioned above, the catalyst was easily separated from the production mixture, because at the end of the reaction, the catalyst settled at the bottom of the reactor, and was used one more time without any treatment. As the catalyst $Cs_{2.5}PW_{12}$ was able to settle from the mixture of fatty acid methyl ester and glycerin into the bottom of the reactor, the upper phase consisting of fatty acid methyl ester did not contain any $Cs_{2.5}PW$ solid. (This can be determined from the IR spectra of the fatty acid methyl ester: in Figure 7, the IR spectra do not exhibit the four characteristics $W{-}O_d$, $W{-}O_b{-}W$, $W{-}O_c{-}W$ and $P{-}O_a$ asymmetric stretching vibrational peaks of heteropolyanions, indicating that no $Cs_{2.5}PW$ exists in the biodiesel). Hence, the product did not need any washing treatment by base-water, i.e., this process did not generate any waste water and is environmentally benign. The experiments were repeated six times by the same transesterification procedure and the conversions to fatty acid methyl esters are given in Figure 8. This shows that there is no considerable change in the catalytic activity of the catalysts even after six reaction cycles.

To test for leaching of the $Cs_{2.5}PW$ catalyst,[47] the catalyst was filtered hot after a reaction time of 20 min (*ca.* 83 % fatty acid methyl ester conversion) and the filtrate allowed reacting over further 1 h at the same temperature of 60 °C. From the results, it can be seen that the conversion of fatty acid methanol ester is only 83.4 %, which shows a very slight leaching of $Cs_{2.5}PW$ into the mixture. The UV spectrum of the mixture exhibited two absorption bands near 200 nm and 265 nm, which are attributed to the Keggin-type $PW_{12}O_{40}^{3-}$ ion. The total amount of $Cs_{2.5}PW$ leaching through six runs of the reaction reached 5.6 % of the starting amount of $Cs_{2.5}PW$ (Figure 8).

Thus, our solid acid catalyst is stable and can be reused up to a minimum of six reaction cycles.

Properties of the Methyl Ester of ESG Oil

The gas chromatographic-mass spectroscopic (GC-MS) analysis (Figure 9) showed that the ESG biodiesel contained a large amount of C_{18} species, and that the C, H, O composition of ESG methyl ester is 77.15 %, 11.58 % and 10.75 %, respectively. Based on GC-MS analysis, the fatty acid methyl ester content in the product is about 94 %, and there was no glycerin remaining. The elementary analytical results showed that the content of sulfur is about 0.04 %, a level in

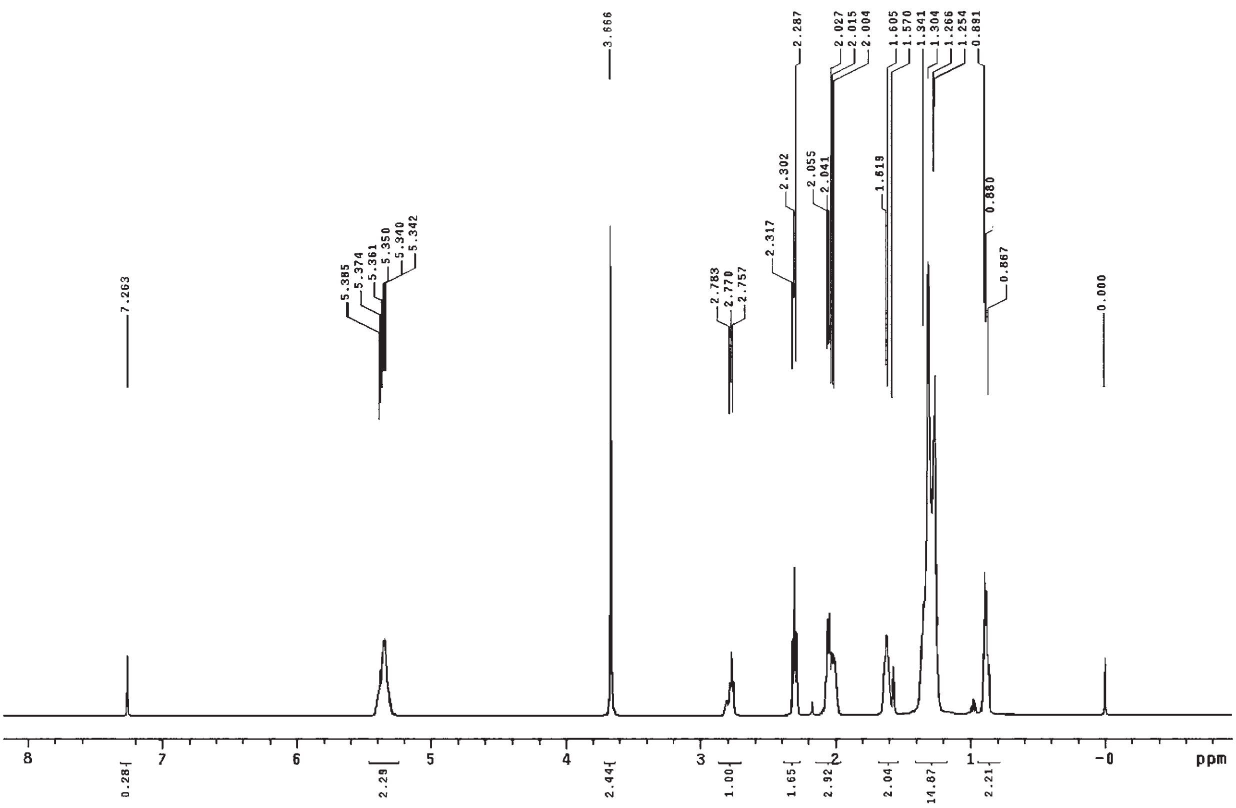

Figure 6. ^{1}H NMR spectrum of the ESG biodiesel.

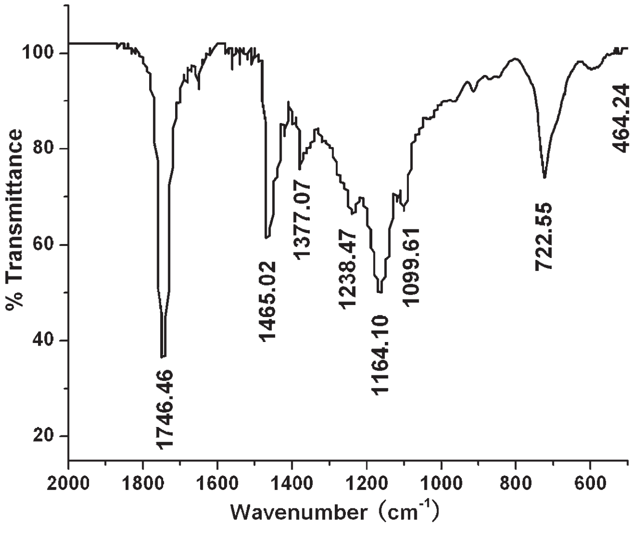

Figure 7. IR spectrum of the ESG biodiesel.

ESG biodiesel that is lower than in the American standard (0.05%, ASTM D6751). These results showed that ESG biodiesel is environmental benign and would be a suitable replacement of diesel.

The fuel properties of ESG methyl ester in comparison with those of other esters are shown in Table 2.[48–53] It can be seen that most of the properties of ESG oil methyl ester are quite comparable to those of other esters and standard biodiesel. The flash point of ESG methyl ester is lower than that of standard biodiesel but still higher than that of diesel so it

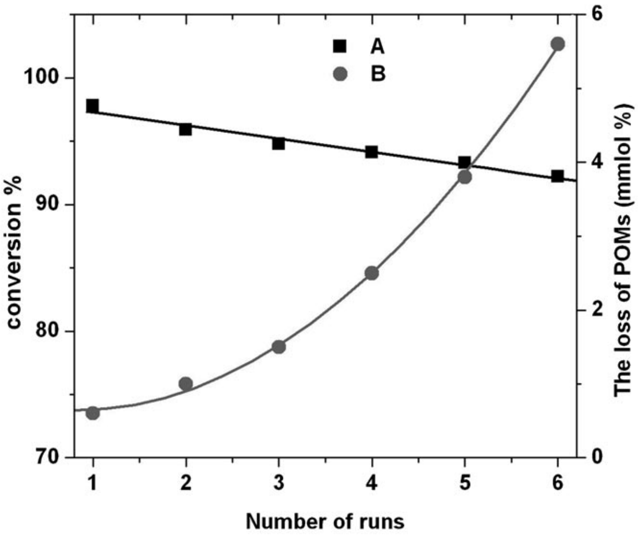

Figure 8. The catalyst activity in six reaction cycles. *Conditions:* molar ratio of methanol/oil = 5.3: 1, temperature 60 °C, time = 1 h, catalyst = 0.02 mmol (A: the conversion of ESG biodiesel; B: the loss of POMs).

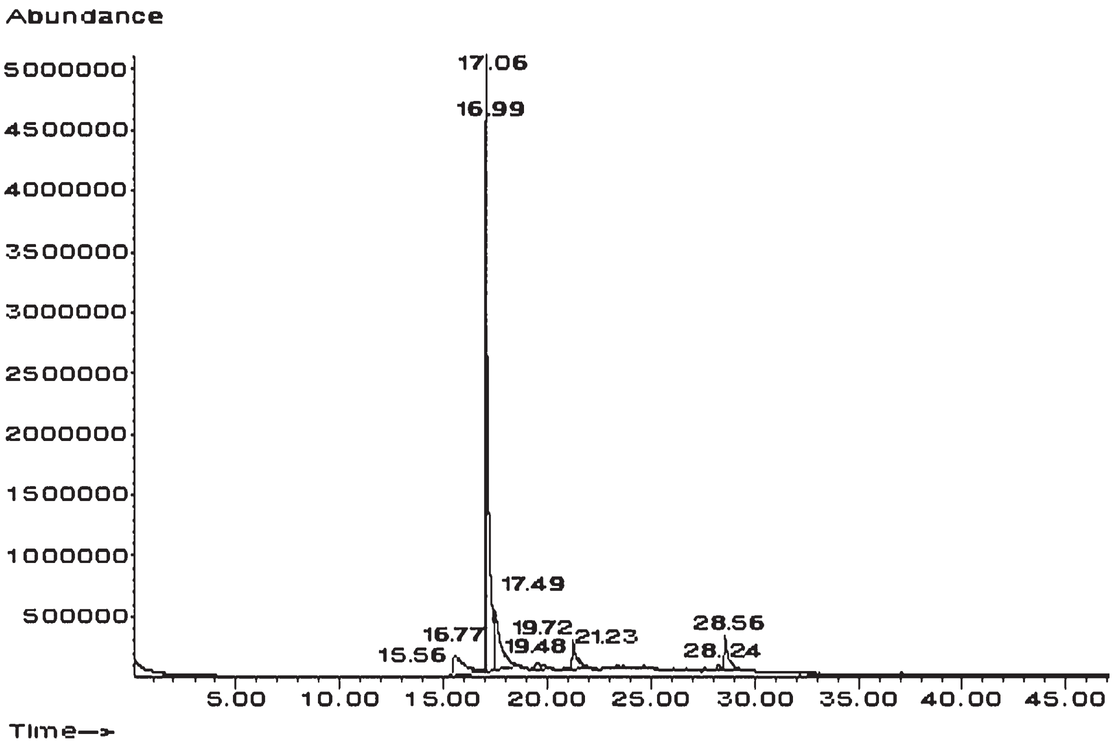

Figure 9. Composition of the fatty acid methyl esters in ESG biodiesel prepared by $Cs_{2.5}PW$ catalysis.

Table 2. Properties of methyl esters of ESG oil in comparison with other esters.[54]

Property	Testing procedure	Biodiesel standard ASTM 6751-02	ESG oil ester	Soybean oil ester	Cotton seed oil ester
Specific gravity	ASTM D4052	0.87-0.90	0.879	0.885	0.874
Calorific value (MJ/kg)	ASTM D240	—	38.67	39.75	40.32
Viscosity at 40°C (mm^{2}s)	ASTM D445	1.9–6.0	5.0	4.08	4.0
Flash point (°C)			127	69	70
Pour point (°C)	ASTM D97	−15 to 10	−3	−15	−3
Acid value (mg KOH/g)	ASTM D974	0.8	0.09	NA[a]	NA
Cetane number	ASTM D976	$\geq$ 49	49	48.2	NA

[a] NA = not available.

is safer to store. Compared with the ASTM biodiesel standard, the fuel properties of the ESG biodiesel were found to be in reasonable agreement with those of ASTM 6751.

Biodiesel Storage Stability

One of the main criteria for the quality of biodiesel is its storage stability which is attributed by hydrolytic and oxidative reactions. The ESG biodiesel allowed to stand at room temperature without addition of any antioxidant reagent for about 7 months. The chromatographic analysis that showed no signification change had occurred during storage. Properties such as acid value, kinematic viscosity and cetane number did not show any significant change either.

Conclusions

The production of high-quality biodiesel fuel from low-cost ESG oil using the solid heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a catalyst was investigated in the present study. The solid acid $Cs_{2.5}PW$ was shown to be an efficient catalyst for the production of environmentally compatible biodiesel fuel in high yields (99%) by using a low catalyst concentration (1.85×10^{-3}:1 weight ratio of catalyst to oil), a low methanol/oil ratio (5.3:1) and some cosolvent THF in a relatively short reaction time (45 min) at a low temperature (55 °C). Significant facts are that the activity of the $Cs_{2.5}PW$ is not considerably effected by the FFA content and moisture in the ESG oil, and that the catalyst is easily separated from the production mixture and can be reused a minimum of six times. Our method is environmentally benign and economical. The viscosity of ESG biodiesel is nearer to that of diesel. The flash point (127 °C) is higher than that of diesel and the cetane value is nearer to that of standard biodiesel. These results reveal that biodiesel from unrefined ESG oil is quite suitable as an alternative to diesel. And ESG biodiesel was stored for about 7 months without any significant change. But further research and development on additional fuel properties and the effects of ESG biodiesel on the engine are necessary.

Experimental Section

Materials

ESG seed oils were obtained with the friendly support of Prof. Zhentang Wang and used without any purification. Other reagents were chemical grade and used without any treatment.

Instruments

^{1}H NMR spectroscopy was used to determine the conversions of the transesterification reaction using an INOVA 500 NMR spectrometer. The contents of the fatty acid methyl esters were confirmed by GC-MS using a GC-6890/MS-5973. Sulfur analysis was performed using a Vario EL Elementar Analysensysteme. The following parameters of biodiesel were determined using the standard procedures: density, viscosity, high heating value, cetane number, pour point. The acid value was determined by the acid-base titration technique.[55]

The solid $Cs_{2.5}PW$ was prepared from $H_3PW_{12}O_{40}$ and Cs_2CO_3 according to the literature.[23] The compound was calcined at 573 K for 3 h in air and had a surface area of 130 $m^2 g^{-1}$.

Transesterification Reaction

The typical reaction of transesterification was carried out in a 250-mL round reactor, provided with thermometer, mechanical stirring, sampling outlet, and condenser. The system was preheated to 60 °C, then, 100 g of vegetable oil were added. When the system reached 60 °C again, 28 mL of methanol, 10 mL THF and 0.02 mmol catalyst were added while stirring at 300 rpm in order to keep the system uniform in temperature and suspension.

The transesterification was performed over certain time periods and 5-mL samples were withdrawn periodically to determine the concentrations of biodiesel by ^{1}H NMR (the sample was treated according to ref.[56]). The experiment was run for about 2 h, by which time the conversion to esters was complete. After cooling, the mixture formed two layers: the upper layer consisted of methyl esters and the lower layer contained glycerin and the excess of methanol. After separating the two layers by sedimentation, the methyl esters were treated by active carbon to dehydrate and discolor them. The glycerin layer was distilled – the residual methanol being gathered at 80 °C under vacuum, and kept for reuse. The catalyst settled at the bottom of the reactor and was easily separated and reused without any further treatment.

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