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Biodiesel production from Eruca Sativa Gars vegetable oil and motor, emissions properties

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ABSTRACT

An integrated, clean, facile and ecologically friendly approach of biodiesel production from Eruca Sativa Gars (ESG) vegetable oil focused on lab scaling up was reported in this study. Transesterification of ESG oil was heterogeneously catalyzed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid salt. The properties of biodiesel from ESG were comparable to conventional diesel fuel and comply with the US Standard for Biodiesel (ASTM 6751). Using ESG biodiesel instead of conventional diesel fuel reduces emissions. The results illustrate that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an environmentally benign solid acid catalyst and ESG biodiesel is a kind of nontoxic and biodegradable renewable alternative fuel.

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1. Introduction

Biodiesel is a promising nontoxic and biodegradable renewable alternative fuel compared to petroleum diesel in the light of the limited nature of fossil fuel and the environmental concerns. Biodiesel has been put into use in many areas, especially in the US and Europe. Annual USA production was estimated at 57–67 million liters, while Europe produced 500 million to 1 billion liters annually [1]. Moreover, the commercial use of biodiesel is strongly dependent on the price of the feedstocks so lower cost feedstocks are needed. The high cost of biodiesel, which is mainly due to the high costs of oil feedstock, is the main obstacle to its broader commercialization [2]. So there have been many research efforts on ways to minimize oil feedstock costs [3–8]. In China, the use of edible vegetable oils such as soybean oil, rapeseed oil limits the application of biodiesel because of vegetable oils' high price and national safety of food. So the use of inedible oils or other oils from growing natural plants as feedstocks are necessary. It is known that Eruca Sativa Gars is a kind of crucifer plant which is an important oil crop in the drought regions and half-drought regions in the world and it attracted more attention because of its excellent resistance to drought climate, poor soil conditions and diseases. The freshly extracted ESG oil is yellowish orange with disagreeable taste which is not suitable for eating. The seed of ESG contains 35% oil which is suitable for production of biodiesel. The price of ESG oil in northwest of China is about $ 0.15 per kg much cheaper than soybean oil. ESG oil is a good choice for production of biodiesel.

It is known that there are several factories that used heteropolyacids (HPAs) as catalysts which produce chemicals in industrial large-scale until now [9]. HPAs possess unique physiochemical properties such as very strong BrÖnested acidity, with their structural mobility and multifunctional the most important fro catalysis [10]. Our group first reported biodiesel production that from Eruca Sativa Gars (ESG) vegetable oil [11]. This technology involved heterogeneously catalyzed by heteropolyacid salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and put forward a novel pathway to produce raw oil feedbacks for biodiesel production. However, it is still unknown if this technology is possible to be applied in large-scale industrial production.

The biodiesel is reported to be sulfur-free, nontoxic, biodegradable oxygenated and renewable. And the characteristics of biodiesel are very close to diesel fuel [12,13] and some are better than diesel such as higher cetane number, no aromatics, almost no sulfur, and more than 10% oxygen by weight, which reduce the emission of carbon monoxide (CO), hydrocarbon (HC), particulate matter sulfur oxides (SO_x) and volatile organic compounds (VOCs) [14–19]. Although there are some advantages of using biodiesel instead of petroleum-based diesel, the engine manufactures association (EMA) reported that if higher percentage blends of biodiesel are desired, the engine manufacturers should be consulted, because

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biodiesel blends up to a maximum of 5% should not cause engine and fuel system problems since the consortium of diesel fuel injection equipment manufacturers state that blends greater than 5% can cause reduced product service life and injection equipment failures. So it can be seen that the properties of biodiesel can affect the engine performance and emissions, since it has different physical and chemical characteristics compared to petroleum-based diesel fuel. So some more research is required about the properties of biodiesel and its effect on the combustion and the fuel system, if biodiesel is wanted to be used on the diesel engines without any modification.

Until now, biodiesel most commonly are made from soybean oil in the United States and from rapeseed oil in Europe, and there are some reports on the biodiesel properties based on soybean or rapeseed biodiesel [14,15,19]. To the best of our knowledge, this is the first report on the combustion and emissions of ESG biodiesel in comparison with No.0 diesel fuel. In our study, all the experiments were performed without any modification on the engine.

In order to determine the feasibility of large-scale production we examine the solid acidcatalyzed transesterification of ESG vegetable oil in lab scale reactor. The process was divided into two sequential stages: flask and lab scale reactor. As a result, high biodiesel production rates in expand from flask to lab scale were obtained. And also combustion characteristics and emission properties of ESG biodiesel fuel were studied.

2. Experimental section

2.1. Materials

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

2.2. Instrument

^{1}H NMR was used to determine the conversions of transesterification reaction using INOVA 500 NMR. The contents of the fatty acid methyl ester were confirmed by GC–MS using GC-6890/MS-5973. S analysis was determined using a GmbH VarioEL Elementar Analysensysteme. The following parameters of biodiesel were determined using the standard procedures such as: density, viscosity, high heating value, cetane number, pourpoint. The acid value was determined by the acid-base titration technique [20].

The solid of $Cs_{2.5}PW$ was prepared from $H_3PW_{12}O_{40}$ and Cs_2CO_3 according to Ref. [21]. The compound was calcined at 573 K for 3 h in air with surface area 130 $m^2\,g^{-1}$.

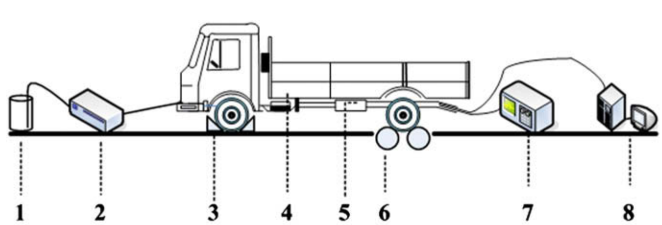

Fig. 1. Schematic diagram of experimental set up for engine test.

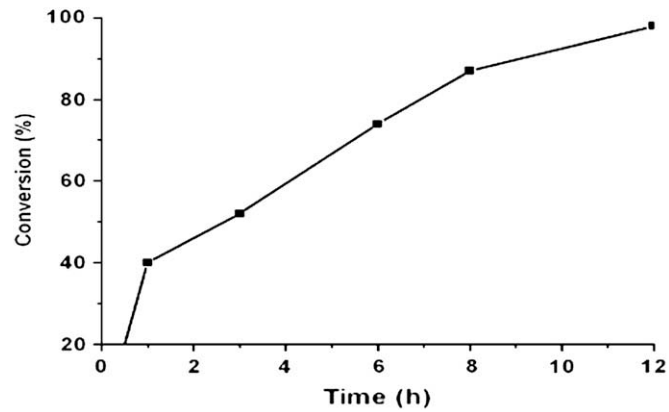

Fig. 2. Ester conversion VS different reaction time at temperature 65 °C (methanol/oil = 6:1, catalyst 0.04 mmol).

2.3. Transesterification reaction in flask

The typical reaction of transesterification was carried out in a 500 mL round reactor, provided with thermometer, mechanical stirring, sampling outlet, and condenser. The system was preheated to 65 °C, then, 200 g of vegetable oil was added. When the system reached 65 °C again, 56 mL of methanol, 10 mL THF and 0.04 mmol catalyst were added while stirring at 300 rpm in order to keep system uniform in temperature and suspension.

The experiment was prolonged for about 12 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, the excess of methanol. After separating the two layers by sedimentation, the methyl esters were treated by active carbon to dehydrate and discolor. The glycerin layer was distilled – the residual methanol being gathered at 50 °C under vacuum, and kept for reuse. The catalyst was decanted at the bottom of the reactor which was easy to be separated and reused without any further treatment.

2.4. Lab scale transesterification reaction

The typical reaction of transesterification was carried out in a 5 L reactor in which were thermometer, mechanical stirrer, sampling outlet and condenser. 2000 g of vegetable oil, 560 mL of methanol, 50 mL THF and 0.4 mmol catalyst mixture heated to 65 °C, while

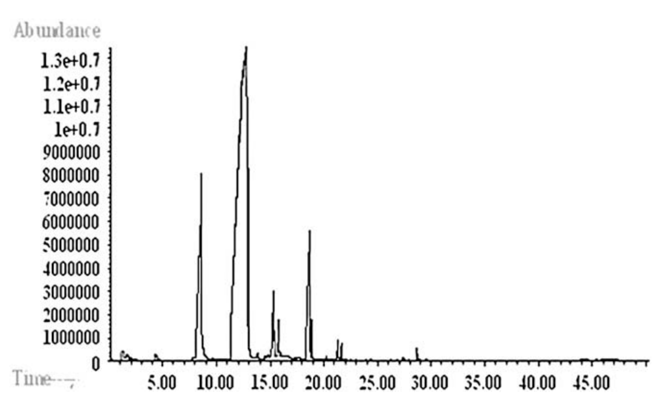

Fig. 3. Composition of the fatty acid methyl ester in ESG biodiesel over $Cs_{2.5}PW$ catalyzed.

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