BIODIESEL PRODUCTION USING ZnO MODIFIED BIOMASS-BASED CATALYSTS

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ABSTRACT

Biodiesel is a renewable fuel that is made with non-edible oil, animal fats, vegetable oil and waste cooking oil. Biodiesel has great advantages compared to fossil fuel such as, biodegradability, non-toxicity, and sustainability of waste management. Transesterification with vegetable oil, methanol and catalyst is proceeded for biodiesel production. Calcium oxide is derived from calcined starfish at 900℃ for 2 hours. Calcium oxide derived from starfish (SF-CaO) and zinc nitrate hexahydrate were dissolved in deionized water separately, stirring 2 hours. Then, they were mixed in a beaker with ammonia solution for 4 more hours. Transesterification proceeded under the conditions of methanol/oil of 10:1, 1 wt% catalyst loading and 4, 6, 8, 10, 12 hours reaction time. Biodiesel yield was 31.5 %, 39.8 %, 70.9 %, 94.7 %, and 95.3 %, respectively. Catalyst performance for ZnO-CaO is much better than SF-CaO.

KEY WORDS

Biodiesel, Starfish, Calcium oxide, Transition metal, Zinc oxide, Transesterification

1. INTRODUCTION

The increasing demand and rapid depletion of fossil fuel led to look for alternatives for fossil fuel. Biodiesel is well known alternative for fossil fuel for some advantages over fossil fuel. Biodiesel is biodegradable, non-toxic, sustainable for waste management. The biggest reason why biodiesel is announced as alternatives for fossil fuel is that it is properly utilized on conventional diesel engines[1-3].

This paper provides a way for waste management by biodiesel production. Starfish, considered as marine debris, is used for transesterification catalyst in the paper. Starfish indiscriminately prey on coral, high-quality fish, and shellfish such as abalone and conch so that it causes tremendous damage on fishery households[4,5]. Starfish is consisted of calcium carbonate which can be converted into calcium oxide, and it is one of the catalysts that are widely used for transesterification. Calcium oxide has many strengths to use as catalyst. It is commonly used for transesterification catalyst with non-corrosive, low toxicity, low solubility in methanol, and recyclability.

Despite these advantages of, some challenges were found on stability such as leaching Ca species in transesterification reaction. This disadvantage led lowering catalytic performance of CaO[6]. To solve the problem, some attempts with doping transition metals were proceeded. Transition metals on CaO were effective to improve stability. Furthermore, catalytic activity and basic strength were increased with transition doping which effects on catalytic performance.[7] Therefore, in this paper, Zinc oxide doped CaO is introduced for transesterification catalyst.

2. EXPERIMENTAL

2.1 Materials and catalyst preparation

Grapeseed oil was purchased from Korean local market. Methanol (99.9%) and zinc nitrate hexahydrate were purchased from Duksan General Science.

Starfish was washed with deionized water and dried in 353K for 12 hours. After drying, it is ball milled and calcined at 1173K for 2 hours to convert into calcium oxide.

ZnO-CaO was synthesized by precipitation method. 1g of calcium oxide derived from starfish and were dissolved into 60ml and 100ml respectively. They were stirred for 2 hours. Then, both stirred solutions and 6.5 ml of ammonia solution were mixed in a beaker and stirred for 4 more hours. After stirring, it was filtrated and dried at 353K for 12 hours. Lastly, calcination process was done at 1173K for 8 hours.

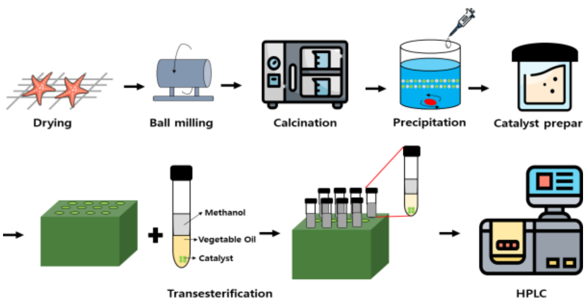

Fig.l: Catalyst preparation and experiment procedure.

2.2 Transesterification of grapeseed oil

Molar ratio of methanol/oil is 10:1, and catalyst is loaded 1wt%. They were put it in the reactor and stirred at 341K for 4, 6, 8, 10, 12 hours. The reaction for transesterification is described below.

$$\text{Vegetable Oil} + \text{Methanol} \rightarrow \text{Ester} + \text{Glycerol} \quad (1)$$

Vegetable oil is composed of triglycerides. With transesterification reaction, triglyceride reacts with methanol. Triglyceride breaks into diglycerides and monoglycerides. Lastly, monoglyceride converts into ester as transesterification product.

2.3 Characterization

X-ray diffraction (XRD, Rigaku, Ultima IV) was utilized for chemical composition analysis of catalysts.

Field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-7900F, Japan) was used to examine the surface morphology of catalysts.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD) analysis

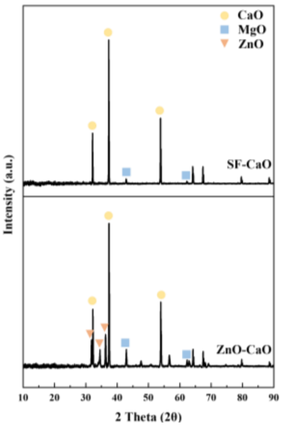

Fig.2: XRD diffractograms of the catalysts

Fig.2 shows X-ray diffractograms of Zn-CaO and CaO catalysts. Both catalysts have intensive peaks of CaO pahses. For Zn-CaO X-ray diffractogram, peaks for ZnO can be observed. As we analyze XRD of catalysts, $CaCO_3$ from starfish converted into CaO and ZnO has doped on CaO successfully.

3.2 Field emission scanning electron microscopy (FESEM) analysis

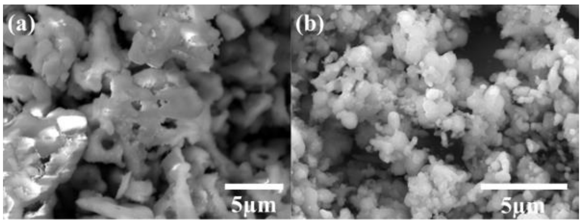

Fig.3: SEM images of (a) CaO, (b) ZnO-CaO

Table 1: Energy Dispersive Spectrometer (EDS) data for ZnO-CaO

	Ca (wt %)	Zn (wt %)	O (wt %)
ZnO-CaO	53.5	14.1	28.6

Fig.3(a) and Fig.3(b) display surface morphology of CaO and ZnO-CaO respectively. Sponge-like structure is observed on Fig.3(a) can be observed so that it has a large surface area. Thus, it is expected to influence on catalyst performance.

Fig.3 shows difference between SF-CaO and ZnO-CaO. It is assumed that ZnO is doped on SF-CaO. According to Energy Dispersive Spectrometer, Table 1, Ca, Zn, and O are detected so that Zinc is expected to be doped on CaO.

3.3 Catalytic performance

High Performance Liquid Chromatography (HPLC) was used for analysis of catalytic performance. Table 2. shows biodiesel yield of transesterification products for ZnO-CaO. Methyl ester yield for 10-hour and 12-hour reaction time are 94.7 % and 95.3 % respectively.

Although reactions got 100% conversion rate of the products, diglycerides and monoglycerides were still detected as byproducts that results have differences on ester yield.

12-hour transesterification with SF-CaO and without catalyst were proceeded to compare with ZnO-CaO. Conversion rate for product without catalyst and SF-CaO are 19.65% and 95.3 %.

Table 2: Catalyst performance

Catalyst	**Catalyst performance**	**Reaction time**	
		10 h	**12 h**
ZnO-CaO	Conversion rate (%)	100	100
	Methyl ester yield (%)	94.7	95.3

4. CONCLUSION

Starfish, marine debris, was successfully utilized as catalyst for biodiesel production. Furthermore, zinc oxide was doped on calcium oxide with precipitation method. Catalyst performance was improved about 1.5 times when zinc oxide was doped on calcium oxide. Therefore, ZnO-CaO catalyst would positively influence on biodiesel production.

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