

Effect of Addition of CaO and ZrO₂ on the Performance of MgO/AC Catalyst for the Synthesis of New Bio-Diesel (HiBD) from Waste Cooking Oil

Paweesuda Natewong^{a*}, Natthawan Prasongthum^b, Yayoi Murakami^c, Haruki Tani^d, Kenji Asami^e

^{a,e}Faculty of Environmental Engineering, The University of Kitakyushu, Kitakyushu 808-0135, Japan

^bFaculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^cHiBD Research Institute, The University of Kitakyushu, Kitakyushu 808-0135, Japan

^dGraduate of School of Engineering, Nagoya University, Nagoya 464-8601, Japan

^aEmail: u3daa401@eng.kitakyu-u.ac.jp

^bEmail: natthawan_takon@yahoo.com

^cEmail: yayoi-murakami@env.kitakyu-u.ac.jp

^dEmail: h-tani@numse.nagoya-u.ac.jp

^eEmail: asami@kitakyu-u.ac.jp

Abstract

MgO catalysts supported on activated carbon with the addition of CaO and ZrO₂ were successfully prepared by incipient wetness impregnation method used for production of high quality bio-diesel (HiBD) through catalytic-decarboxylation. The prepared catalysts were characterized by BET, XRD and CO₂-TPD. The results of XRD and BET indicated that MgO and added oxides of all of catalysts were highly dispersed on activated carbon and the addition of ZrO₂ lead to a large specific surface area and pore volume. Catalytic conversion of waste cooking oil was carried out with an agitated reactor under conditions of 430 °C in an He flow (50 ml/min). The triglycerides in the oil were converted into a mixture of hydrocarbons, CO, CO₂ and water with a very small amount of oxygenated compounds, mostly free fatty acids. CO₂ yield and acid value (AV) were used to evaluate the decarboxylation performance as indexes. The results indicated that the MgO/AC catalyst with the addition of ZrO₂ exhibited a high activity for the decarboxylation of fatty acids due to it had higher surface area and pore volume.

Keywords: High quality Bio-diesel; Deoxygenation; Decarboxylation; CaO, ZrO₂

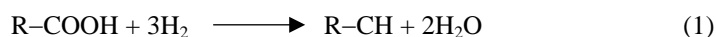
* Corresponding author.

1. Introduction

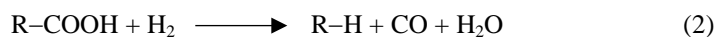
Biodiesel is one of the promising alternative liquid fuel which can be used as a substitute for petroleum diesel. It has much attention in recent years as an environmentally friendly fuel due to its biodegradability, non-toxic and low emission of green-house gas. Biodiesel can be manufactured from a variety of resources: vegetable oils, animal fats or waste cooking oils [1,2]. Currently, the most common derivative of triglycerides or fatty acids for fuel is fatty acid methyl ester (FAME), which is formed by transesterification of triglyceride with methanol in presence of alkali, acidic or enzymatic catalysts with glycerol as a by-product [3,4]. However, because of high oxygen content of FAME, oxidation stability and performance under cold weather are the major problems [5,6]. Therefore, attention has lately been shifted towards the upgrading of biodiesel by deoxygenation in which oxygen is eliminated either as H₂O or as CO_x.

Catalytic deoxygenation is another alternative technique employed to decrease oxygen content in biodiesel. It is proposed that the major reaction routes of deoxygenation can be via hydrodeoxygenation, decarbonylation and decarboxylation as the following equations below [7].

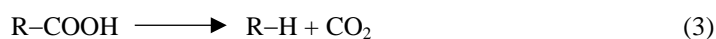
Hydrodeoxygenation



Decarbonylation



Decarboxylation



In principle, the decarbonylation (-CO, eq. (2)) and decarboxylation (-CO₂, eq. (3)) routes are more applicable than the hydrodeoxygenation pathway (eq. (1)), due to less or no hydrogen is required and their higher selectivity to the aliphatic hydrocarbons for diesel applications, respectively, and therefore the production cost is less expensive. Most of the research on decarboxylation of fatty acids as feedstock was carried out over noble metal oxides. Murzin et al. [9-12] have investigated deoxygenation of triglycerides and fatty acids over palladium (Pd) supported on activated carbon catalyst, and the results revealed that Pd/C catalyst displayed as the promising catalyst in the deoxygenation. In addition, Do et al. [13] have reported that alumina-supported Pt (Pt/Al₂O₃) can also be effectively in this reaction. However, considering the high cost of above noble metals, it is more practical in industrial standpoint to develop the catalysts showing similar performance and stability. Zhang et al. [14] investigated the decarboxylation of naphthoic acid over the following series of alkaline-earth metal oxides: CaO, MgO, BaO and SrO. All of these oxides showed high decarboxylation activity for naphthoic acid compound, from which the acid conversion, CO₂ yield and naphthalene yield reached 93.9%, 96.9% and 66.2%, respectively. Watanabe et al. [15] have studied the catalytic decarboxylation of stearic acid with alkaline hydroxide (KOH and NaOH) and metal oxides (CeO₂, Y₂O₃ and ZrO₂) in supercritical water. The major

products of this reaction were n-heptadecane, n-hexadecane and CO₂. As a consequence, ZrO₂ showed the highest activity with approximately 68% and 9% for conversion of stearic acid and yield of CO₂, respectively.

Recently, we have developed a new biodiesel process which give a mixture of hydrocarbons in the diesel fraction oils of C₁₀-C₂₀ aliphatic hydrocarbons as a major products, without using any sub-raw material. We named this fuel as High quality Bio-Diesel (HiBD). HiBD is expected as the second generation diesel fuel which fits the next generation diesel engine due to the physical properties of HiBD is similar to the conventional diesel fuel and exhibits an excellent low temperature fluidity which enables to use in cold weather as are presented in Table 1. HiBD can be obtained by catalytic cracking decarboxylation of triglycerides and fatty acids as reaction intermediates over the basic catalyst (MgO/SiO₂) at 400-470 °C and LHSV = 0.3 h⁻¹ with releasing oxygen by forming CO₂ [16-20].

In this study, magnesium oxide catalyst supported on active carbon (MgO/AC) is selected as a basic catalyst. However, MgO exhibited a poor CO₂ adsorption properties due to its low surface area and pore volume. This study mainly focuses on improving the performance of MgO/AC catalyst for decarboxylation reaction by the addition of CaO and ZrO₂ to synthesis a new hydrocarbon biodiesel (HiBD) from waste cooking oil, and investigated the CO₂ formation to know the decarboxylation efficiency. Its catalytic activity was evaluated by catalytic cracking and decarboxylation in an agitated reactor.

Table 1: Physical properties of high quality bio-diesel (HiBD)

Properties	HiBD (WCO)	JIS Gas oil regulation
Density at 15 °C (g/cm ³)	0.83	0.86 ≥
Kinetic viscosity at 30 °C (mm ² /s)	1.9	≥ 2.5
10% residual carbon	0.1	0.1 ≥
Flash point (°C)	47.5	≥ 50
Cetane number	46.6	≥ 45
Pour point (°C)	-15.0	-7.5 ≥
Blocking point (°C)	-17.0	-5 ≥

2. Experimental

2.1 Catalyst preparation

MgO/AC catalysts with addition of CaO and ZrO₂ were prepared by the incipient wetness impregnation with a commercially active carbon (SA 862 m²/g; PV 0.565 cm³/g) as a support. Precursor materials used for this synthesis were magnesium nitrate hexahydrate (Mg(NO₃)₂.6H₂O, 99.0% purity, Wako, Japan), calcium nitrate

tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98.5% purity, Wako, Japan) and zirconyl nitrate dihydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 97.0% purity, Wako, Japan). After impregnation, they were dried in an oven at 110 °C and then calcined in N_2 at 500 °C for 3 h. Names of the catalyst samples were abbreviated with the loadings; for example, a catalyst containing 5 wt%-MgO, 5 wt%-CaO, and 5 wt%- ZrO_2 on AC was expressed as 5M5C5Z/AC.

2.2 Catalyst characterization

The specific surface area of the fresh catalysts was measured by nitrogen adsorption-desorption isotherms at -196 °C. Prior to the BET measurement, the catalysts were preheated at 200 °C for 2 h to remove the adsorbed water. The BET surface areas were determined by a multi-point Brunauer, Emmett and Teller (BET) method at the relative pressures of nitrogen in range of 10^{-6} to 0.99 and pore volume was calculated by applying Barrett, Joyner, and Halenda (BJH) method (BELSORP-mini II, Japan Bel Inc.).

The crystalline structure of the fresh and spent catalysts were determined by X-ray diffraction (XRD) with a RIGAKU, XRD-DSC-XII diffractometer using $\text{Cu } K_\alpha$ as the radiation source with $\lambda = 1.54 \text{ \AA}$ and Ni as the filter in the range of 2θ from 10° to 80°. The X-ray tube was operated at 40 kV and 20 mA at room temperature.

The basicity of the active catalysts were characterized by using temperature-programmed desorption of CO_2 (CO_2 -TPD) on a BELCAT (Japan Bel Inc.). The catalyst (0.05 g) was heated at 10 °C/min under a flow of helium (He) from room temperature to 500 °C and then held at this temperature for 60 min. After cooling to 50 °C and saturated with 50 ml/min CO_2 for 60 min. Subsequently, the catalyst was purge with He by flowing 50 ml/min for 1 h in order to eliminate any physically adsorbed and/or weakly bond species at 10 °C/min up to 900 °C.

The amount of CO_2 , which was adsorbed or reacted with the oxides on the spent catalysts was measured using the thermogravimetric (TG) technique. Around 5 mg of spent catalyst was placed in a platinum crucible that was introduced in a RIGAKU TG 8210. The sample was heated under N_2 flow (100 ml/min) from room temperature up to 900 °C at heating rate of 10 °C/min.

2.3 Catalyst testing

The catalytic decarboxylation of waste cooking oil was carried out at 430 °C under atmospheric pressure in an agitated reactor, as shown in **Figure 1**. The oil was supplied from the university restaurant. Typically, 25 g of catalyst was charged into the reactor and then it was heated up to the reaction temperature in carrier gas He flow rate = 50 ml/min. It was pumped continuously into the reactor by liquid pump at a rate of 0.25 ml/min. During the reaction, the gaseous products were analyzed every 30 min using an on-line gas chromatograph (Shimadzu GC-14A) with thermal conductivity detector and flame ionization detector. The liquid products were collected by a trap at 0 °C and then analyzed by GC-MS (Agilent GC-7890A). Potentiometric titration methods (JIS 2501-2003 and JIS K0070-1992) were employed to measure total acid value (AV) and iodine value (IV) of the cracking oil.

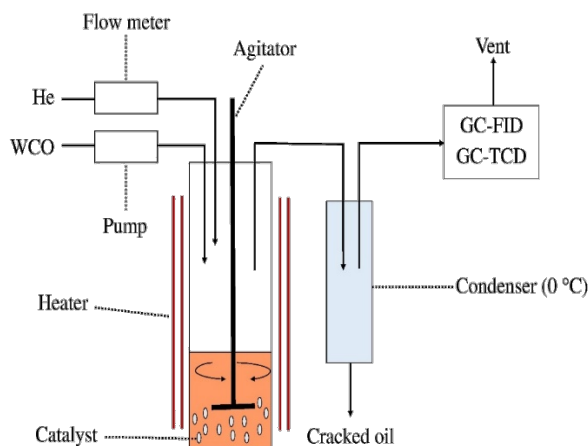


Figure 1: Experimental apparatus for catalytic cracking decarboxylation

3. Results and discussion

3.1 Catalyst characterization

Table 2: Textural properties and basicity of the prepared catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Total basicity (mmol/g)	
				Fresh	Spent
AC	813	187	3.14	0.537	0.286
10M/AC	549	126	3.21	0.857	0.285
5M5Z/AC	599	138	3.12	0.706	0.350
5M5C/AC	530	122	2.67	0.818	0.537
5M5C5Z/AC	466	102	3.21	0.975	0.640

The catalyst surface area, pore volume and pore diameter are given in **Table 2**. It can be seen that the highest surface area was found on the binary 5M5Z/AC catalyst, and the lowest surface area was observed in ternary catalyst, 5M5C5Z/AC. Probably due to the blockage of pore of support by increasing of number of other metals as indicated by the pore volume data.

In order to get information about the strength of basic sites temperature-programmed desorption of CO₂ was carried out. The CO₂-TPD profiles over the fresh and spent catalysts are presented in **Figure 2**. The spent catalysts was collected after runs of decarboxy-cracking at 430 °C for 7 h. Oil remained in the catalyst was removed by heating in N₂ flow at 250 °C for 4 h. The fresh catalysts showed a similar patterns with two types of

CO₂ desorption sites: the 1st peak centered at lower temperature near 160 °C is assigned to the weak basic sites and the 2nd peak centered at relatively higher temperature (around 500-800 °C) is assigned to the strong basic sites, and contains CO₂ decomposition of activated carbon that the surface contains many oxygen functional groups: carboxylic, ketone, lactone, phenol. All of these oxygen groups are benefit to adsorb CO₂. The low temperature CO₂ peak at 160 °C of all spent catalysts was very broad or absent, but a sharp CO₂ peak at 675 °C was observed with 5M5C/AC and 5M5C5Z/AC catalysts related to the decomposition of adsorbed CO₂ during the reaction due to CaCO₃ requires a high temperature to remove CO₂ [21,22], as evidenced by XRD results (**Figure 3.**). Moreover a broad peak at 800 °C probably causing CO₂ desorption of activated carbon.

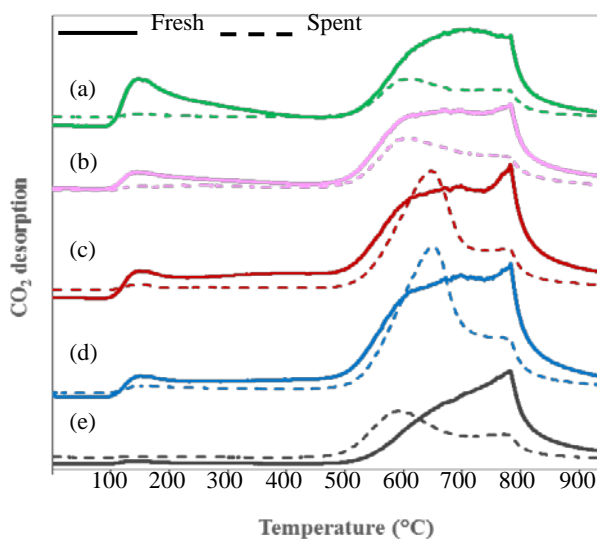


Figure 2: CO₂-TPD profiles of the fresh and spent catalysts (a) 10M/AC; (b) 5M5Z/AC; (c) 5M5C/AC; (d) 5M5C5Z/AC; (e) Activated carbon.

The total basicity of the fresh and spent catalysts is summarized in **Table 2**. On the basis of TPD profiles the basicity of the fresh catalysts can be arranged in the following order: 5M5C5Z > 5M5C > 10M > 5M5Z. Based on these basicity properties of the metal oxide. It has been reported that basic catalysts could improve the adsorption of CO₂ in decarboxylation reaction that supplies more surface oxygen species on the catalyst surface. However, it is quite difficult to estimate the catalyst activity because the catalytic performance also depend on several other important factors including the active surface site, particle size and metal dispersion [23].

The XRD patterns of the fresh and spent catalysts are shown in **Figure 3**. All of catalysts exhibit a broad diffraction peaks around $2\theta = 25^\circ$ and 42° , which suggests an amorphous structure of active carbon. No obvious diffraction peaks of MgO, CaO and ZrO₂, implying that most of MgO, CaO and ZrO₂ species are highly dispersed on the active carbon surface [24]. On the other hand, for the spent catalysts, two typical diffraction lines at around 42° and 62° due to MgO were observable, showing a strong sintering of MgO species. In the

cases of catalyst with adding CaO, the XRD peaks assigned to CaCO_3 were appeared. This compound was formed by chemical reaction between CaO and CO_2 during the process. In the case of ZrO_2 added catalyst, no clear diffraction line due to Zr species was observed. It is supposed that the t- ZrO_2 crystal size was extremely small [25]. In these results it can be confirmed the presence of MgO and CaO species in the fresh catalyst.

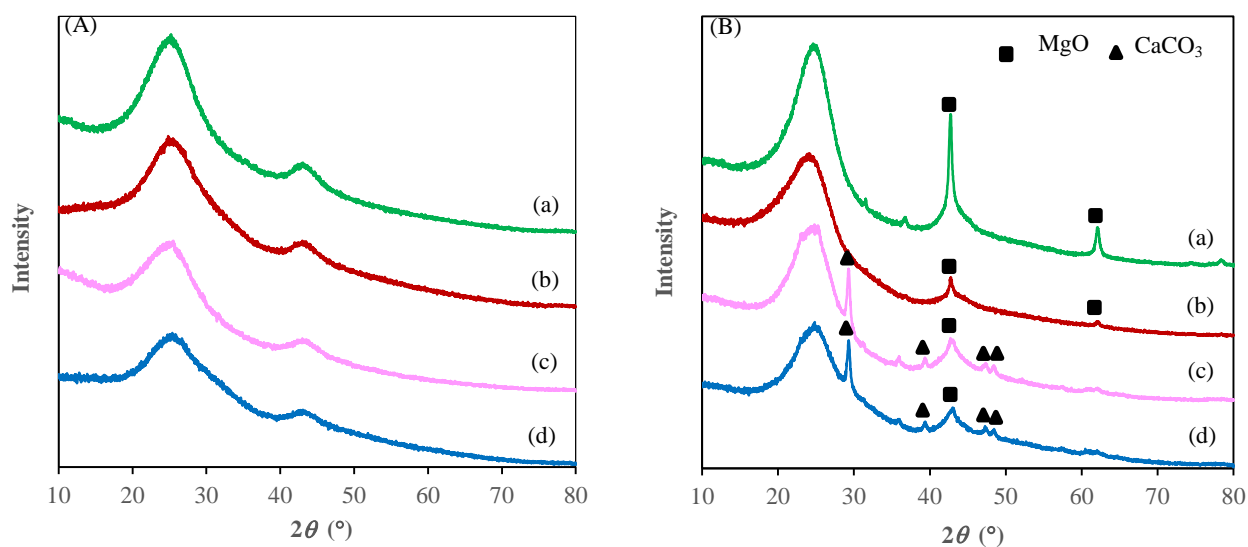


Figure 3: XRD patterns of the fresh (A) and (B) spent catalysts. (a) 10M/AC; (b) 5M5Z/AC; (c) 5M5C/AC; (d) 5M5C5Z/AC.

3.2 Catalyst performance

The effect of the addition of metal oxide to MgO/AC catalyst on decarboxylation reaction of waste cooking oil was investigated. For all the catalysts in the study, the major products from this reaction were a mixture of liquid aliphatic hydrocarbons, dry gases (C_1 - C_4 hydrocarbons), CO, CO_2 , water and residue as presented in **Table 3**. The probable reaction pathway of the catalytic decarboxylation of triglycerides is based on three main reactions as shown in **Figure 4**. The glycerine formed would then be converted to gaseous hydrocarbons and water by dehydration, while, free fatty acids would be cracked into hydrocarbons and CO_2 by decarboxylation. Moreover, two molecules of the free fatty acids can be dehydrocondensed to produce long chain ketones, which can be further decomposed into hydrocarbons and CO [16,17].

Figure 5 shows the effect of the addition of ZrO_2 and CaO on the production of hydrocarbons. All of catalysts gave high yield of hydrocarbons with diesel fraction (C_{10} - C_{20}), while the compounds with carbon number higher than 21 were not observed. In the cases over the catalysts with CaO, the yield of C_1 - C_9 increased, indicating that catalytic cracking of aliphatic groups in the triglycerides into lighter hydrocarbons was promoted by the addition of the compound. C_{21} compounds were found to be ketones as described above such as methyl ketone and ethyl ketone. Yield of these compounds increased by adding oxides, especially ZrO_2 [20, 26,27].

Table 3: Material balance of waste cooking oil by decarboxy-cracking

Catalyst	Product yield (% wt)					
	Cracked oil	Dry gas	CO	CO ₂	H ₂ O	Residue
10M/AC	64.8	6.0	0.9	5.9	4.4	11.9
5M5Z/AC	65.2	6.8	1.3	6.9	4.3	10.7
5M5C/AC	62.1	7.3	1.2	5.5	4.6	13.4
5M5C5Z/AC	64.6	6.5	1.2	5.1	3.4	12.1

Reaction conditions: He = 50 ml/min, oil feed flow rate = 0.25 ml/min, reaction temperature 430 °C.

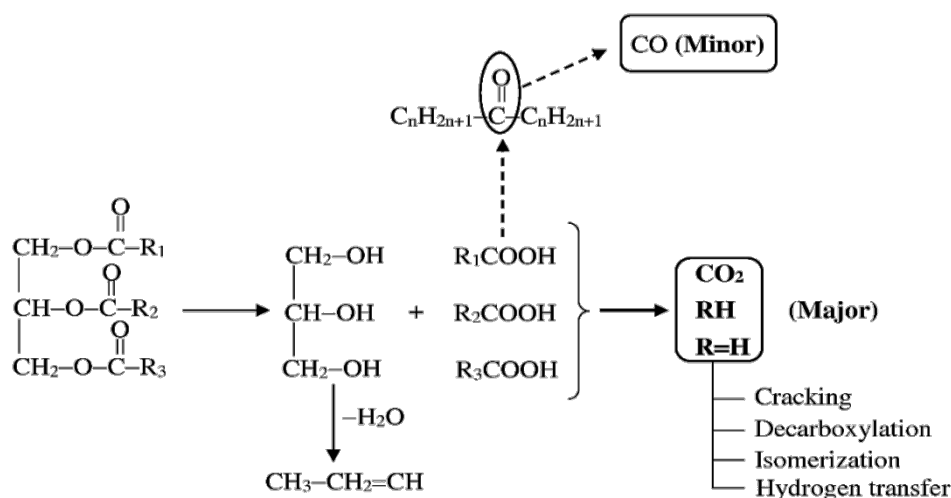


Figure 4: Reaction pathway of catalytic decarboxylation of triglycerides.

According to literature, decarbonylation and decarboxylation are essential reactions in the deoxygenation of carboxylic acids, therefore, removal of CO and H₂O can take place in the deoxygenation step [28]. The decarboxylation activity over four catalysts is presented in **Figure 6**. When all the ester groups in the parent oil are converted to CO₂, its yield comes to about 17 wt%, assuming the average formula of the triglycerides as C₃H₅(OCOC₁₇H₃₄)₃. The results indicated that about half and 10% of molar fraction of the ester groups were converted to CO₂ and CO, respectively. The rest of them would probably be converted to carbon (coke) and water, and a small amount was transformed to other oxygen containing compounds such as FFA's. Binary 5M5Z/AC catalyst gave highest CO₂ yield due to its high surface area and can reduce carboxylic acids selectively by the interaction between oxygen in the acid groups and oxygen vacancies on ZrO₂ surface and easily removed or desorbed by heating for a short while. In contrast, the low yield of CO₂ over the catalyst with low surface areas (10M/AC, 5M5C/AC and 5M5C5Z/AC catalysts) might be due to diffusion limitation between the reactants and the active sites. Moreover, the addition of CaO could impact on yield of CO₂ since CaO can react with CO₂ to form CaCO₃, and its decomposition reaction requires a thermal activation to remove the adsorbed CO₂ [29]. These results are in accordance with TGA analysis of the spent catalysts, though not

presented here. Weight loss due to CO₂ release from the catalyst occurred at over 600 °C and the amount of CO₂ formed on the catalysts is also showed in **Figure 6**. Clearly, the addition of CaO resulted in a high CO₂ weight loss. It is indicated that CaO significantly improved CO₂ capture capacity of catalyst. Furthermore, the low yield of CO was observed over each catalyst. The presence of CO would probably formed through decomposition of ketones which was formed by dimerization of fatty acids or through a reverse water- gas shift reaction [20,26,27].

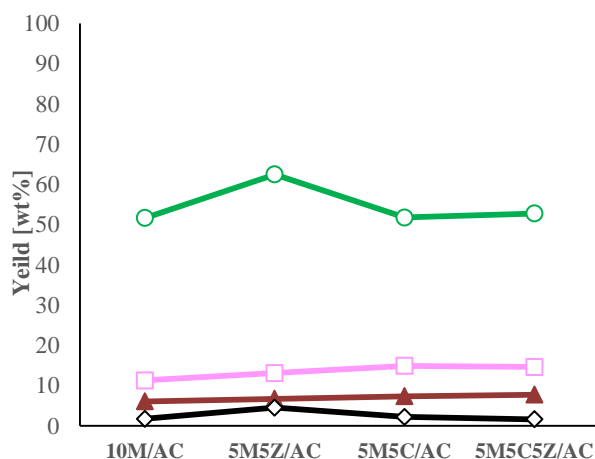


Figure 5: Effect of the addition of CaO and ZrO₂ on the production of the main fractions: (\blacktriangle) C₁-C₄; (\square) C₅-C₉; (\circ) C₁₀-C₂₀; (\diamond) C₂₁ compound.

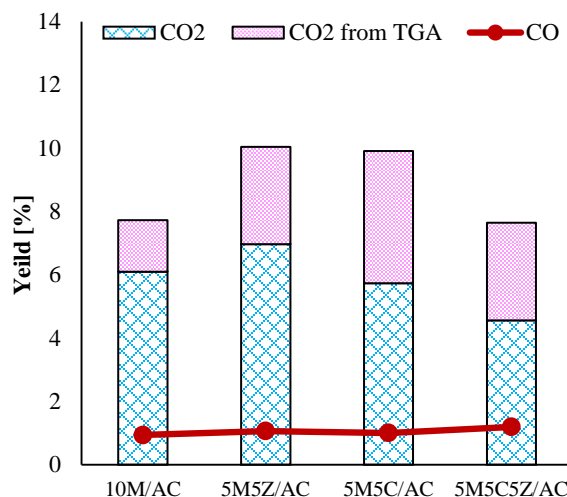


Figure 6: Decarboxylation activity of waste cooking oil over the oxide catalysts

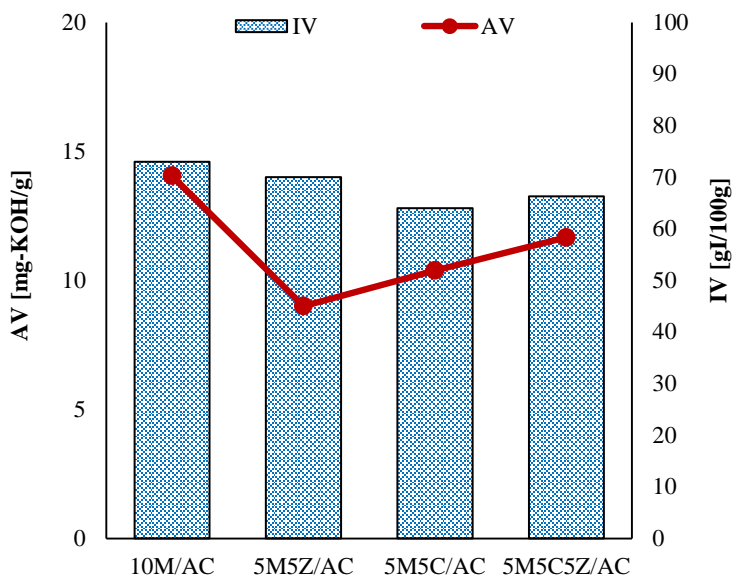


Figure 7: Effect of the addition of CaO and ZrO₂ on acid value and iodine value of the cracked oils

Figure 7 shows the acid value (AV) and iodine value (IV) of product oils. The acid values with addition of CaO and ZrO₂ were slightly lower than that with MgO alone, about 9.0-11.6 mg-KOH/g-oil. This suggested that the added CaO and ZrO₂ promote the decarboxylation reaction and ketonization of fatty acid to hydrocarbon. Although these values were slightly higher than the level of neat regulation (0.5 mg-KOH/g-oil) for the biodiesel fuel, we have already developed an adsorption technique to clear the regulation for the oils with such acid values. Iodine values of all these oils were less than 80 g-I/100g-oil and slightly lower than that obtained with MgO, indicating that the addition of CaO and ZrO₂ facilitated the cracking of C=C bonds.

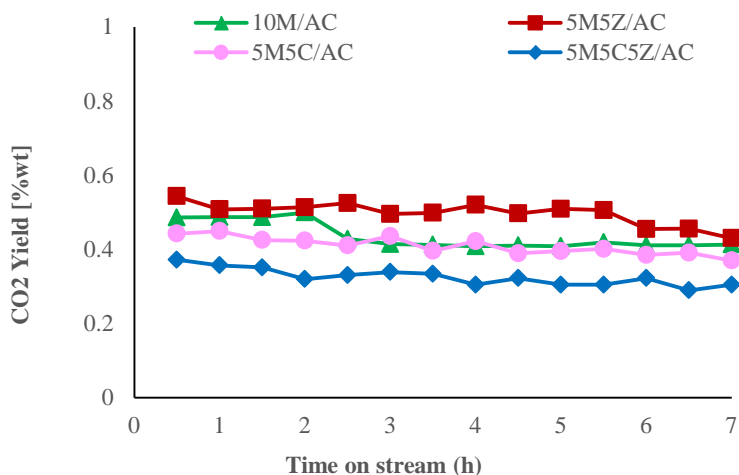


Figure 8: The time on stream stability of the oxide catalysts

The stability in term of decarboxylation of waste cooking oil over oxide catalysts, was evaluated at 430 °C for 7 h and their results are shown in **Figure 8**. Although rapid deactivation was not so significant for each catalyst, it is observable that the activity of MgO/AC catalyst decreased sharply in the first 2 h on stream and then became stable, while the binary 5M5Z/AC, 5M5C/AC and ternary 5M5C5Z/AC catalysts showed relatively stable behavior under the same conditions. These results suggest that the addition of CaO and ZrO₂ helps to improve the catalytic stability of catalyst.

4. Conclusion

MgO/AC with the addition of CaO and ZrO₂ prepared by incipient wetness impregnation method has been successfully applied in a new hydrocarbon biodiesel (HiBD) production which can substitute for petroleum diesel. The catalytic activity for the cracking and decarboxylation of triglycerides greatly depended on surface area of the catalysts. With regard to the finding results, the addition of CaO and ZrO₂ significantly improved the catalyst activity and stability. The addition of ZrO₂ was found to increase the yield in diesel fraction for the catalytic decarboxylation of waste cooking oil whereas the addition of CaO lead to the formation of increased lighter hydrocarbons (C₁-C₉) though the diesel yield was decreased.

Acknowledgements

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