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Calcinated Ferronickel Slag As Catalyst in Biodiesel Synthesis from Cooking Oil

Boy Chandra Sitanggang*, Neny Rasnyanti M. Aras

Chemical Analysis Study Program, Academy of Manufacturing Industry Community Bantaeng, Desa Nipa-Nipa, Pajukukang, Bantaeng, Indonesia

**Corresponding author: boycsitanggang@akom-bantaeng.ac.id*

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Abstract

Ferronickel slag is a byproduct of the nickel ore smelter factory that is typically dumped in an open area and is detrimental for the environment. The research objectives are to examine ferronickel slag potential as catalyst in producing biodiesel. Ferronickel slag was prepared by milling followed by sieving 200 meshes and calcinated at 900 ºC. The next step was to evaluate the calcinated slag using XRF, which revealed that the major components were, in order, Si (49.47%), Fe (36.09%), Ca (7.12%), Cr (3.01%), and Mn (2.28%). Slag that has been calcined and utilized in the transesterification of cooking oil as catalyst in three necked flask with oil to methanol ratio is 1:9, reaction times 1, 2, 3 hours and temperatures 70, 90, 110 ^oC. Then, the product were tested for water content, density, viscosity, acid number, free fatty acids, total glycerol, percent of methyl esters according to SNI 7182-2015. FTIR showed the presence of peaks at 1743.65 and 1157.29 corresponding to C=O and $O\text{-}CH_3$ functional groups.

Keywords: Slag, Ferronickel, smelter, Biodiesel, Catalyst

INTRODUCTION

The rapid development of nickel refining industry, especially in eastern Indonesia, generates a large amount of slag as a byproduct. Ferronickel slag always stored in open field, so it has the potential to be an avalanche hazard and detrimental to the ecosystem. Slag still contains valuable metals and can be utilized as secondary raw materials for metals refineries (Mikhail & Webster, 1992; Sitanggang & Abidin, 2020; Zhang, Wang, Chen, & Cheng, 2020). In addition, its utilization has generally been studied as a construction material (Wang, 2016), ceramic material Zhang, Wang, Zhu, Wu, Hu, Feng, & Jia, 2020), catalyst (Bennett, Wilson, & Lee, 2016; Kamil, Salmiaton, Hafriz, Hussien, & Omar, 2020).

On the other hand, research on catalysts in the manufacture of biodiesel or fatty acid methyl ester (FAME) has received great attention from researchers. (Chai, Tu, Lu, & Yang, 2014; Rosmawaty, Bandjar, & Gunoroso, 2015), pretreated used cooking oil and converted into biodiesel through an esterification reaction using an acid catalyst. Meanwhile (Abd Rabu, Janajreh, & Honnery, 2013; Ali & Tay, 2013) did the same thing but used an alkaline catalyst. Both acid and base catalysts used are homogeneous catalysts so it is difficult to separate and purify the produced biodiesel. Moreover, research on heterogeneous catalysts in the manufacture of biodiesel has been widely carried out. (Fattahi, Triantafyllidis, Luque, & Ramazani, 2019), using various types of zeolite as a catalyst; (Omar, Bita, Louafi, & Djouadi, 2018), using ZSM-5 zeolite; (Julianti, Wardani, & Gunardi, 2014), using a $CaO/MgO/\gamma\text{-}Al_2O_3$ catalyst; Meanwhile Barros, Coelho, Lachter, San Gil, Dahmouche, Pais da Silva, & Souza, 2013), using ZnO/SBA-15 and MgO/SBA-15; (Srilatha, Prabhavathi Devi, Lingaiah, Prasad, & Sai Prasad, 2012), using heterogeneous catalysts of tungstophosporic acid/Nb_2O_5 and ZnO/Na-Y zeolite. Then, (Awaluddin, Saryono, Nelvia, & Wahyuni, 2012), using $CaCO_3$ which is calcined at 900 ^oC with a ratio of methanol to oil is 1:9, the purpose of calcination is to activate the non-oxide to metal oxide. (Tahya, Yulius Tahya, & Kainama, 2019), synthesis CaO from chiken eggshell as catalyst in fish oil transesterification. (Bandjar, Sutapa, Rosmawaty, & Mahulau, 2014) utilise beef tallow by esterification using sulfuric acid and transesterification using CaO and give relatively high conversion results.

Therefore, the study of the use of calcinated ferronickel slag in the manufacture of biodiesel from cooking oil attracted the attention of the authors and is expected to be a new option.

METHODOLOGY

Materials and Instrumentals

Ferronickel slag obtains from PT Huadi Nickel Alloy in Bantaeng South Sulawesi. KOH, methanol, ethanol, Phenolphthalein, Kalium Hydrogen Ptalat, $Ba(OH)_2$, HCl, NaOH, $K_2Cr_2O_7$, Natrium Thiosulfate, Chloroform are pro analysis grade and used without further purification. Instrumentation of analysis used are ARL-QUANT'X EDXRF Analyzer and FTIR Shimadzu.

Methods

Hard granule and metallic gray ferronickel slag prepared by grind in ball mill and sieve to 200 mesh continued by calcination at 900 ºC for one hour and ready to use. 150 mL oil pours into three necked flask and heated (Figure 1) to 60 ºC. Calcinated slag and methanol mixed in other flask, then the mixture dropped to the three necked flask, oil to methanol ratio is 9:1. The reaction conducted at stir rate 400 rpm, temperatures 70, 90, 110 ºC and reaction times 1, 2, 3 hours. The mixture poured into separation funnel and let stand for 16 hours. The resulted biodiesel was collected and dried in oven at 105 ºC for one hour. Then, water content, density, , acid number, free fatty acids, total glycerol, percent of methyl esters were tested according to SNI 7182-2015 (Badan Standarisasi Nasional, 2015). Viscosity examines by viscometer Ostwald and yield calculated according to formula (Equation 1).

$$\%\ yield = \frac{Mass\ of\ biodiesel}{mass\ of\ cooking\ oil}\ X\ 100 \quad (1)$$

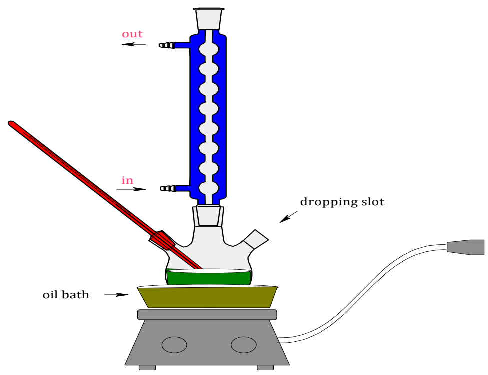

Figure 1 Tools assembly.

RESULTS AND DISCUSSION

XRF analysis

The composition of ferronickel slag and catalyst calcinated slag are shown in Table 1. The major metal component consist of Fe, Ca, Cr, Mn and also Si as nonmetallic. The elements of slag are determined by the ore used and the manufacturing process, this kind of ferronickel slag is a secondary product generated from electric arc furnace (Kamil, Salmiaton, Hafriz, Hussien, & Omar, 2020). the calcination temperature affect the composition of slag, silica decreased while metal oxides increased and considerably enhance acidity of slag hence increased catalytic activity (L. Wang, Li, Xin, & Li, 2014).

FTIR Analysis

The FTIR spectra shown by Figure 2, it's appear slightly differences between cooking oil and biodiesel spectra and very similar to each other due to essentially chemical similarity of triglycerides and fatty acid methyl ester. However, Figure 2 show peaks seem to be different in % transmittance and intensity but peaks still exist. The comparison of functional groups of biodeiesel and cooking oil given in Table 2. The visible difference seen at 1157.29 in biodiesel which associated to $O\text{-}CH_3$, meanwhile no such wavenumber for cooking oil. The biodiesel confirmed with the presence of three significance peak which are 1157.29; 1373.72; 1460.11 cm^{-1} (Kamaronzaman, Kahar, Hassan, Hanafi, & Sapawe, 2020).

Chemical and physical analysis

The chemical properties water content, acid number, FFA, methyl ester, total glycerol and physical properties density were tested according to SNI 7182-2015 while viscosity determined by Ostwald viscometer. All measurement conducted in Duplo. In general, the influence of various reaction times gives slightly different results for all parameters as well as various reaction temperatures. Noticeable influence of vaious reaction times and temperatures is percent of yield, where as the optimum results at 2 hour reaction time and 90 ^{o}C. Density and viscosity of biodiesel are complying to SNI specification at various reaction times and temperatures. Water content and free fatty acid

Table 1. Result of Elemental and Oxide Analysis (%)

Sample	Si	Fe	Ca	Cr	Mn	SiO_2	Fe_2O_3	CaO	Cr_2O_3	MnO
Slag	51.66	34.45	6.97	2.99	2.20	68.34	21.94	4.98	2.09	1.32
Calcinated Slag	49.47	36.09	7.12	3.01	2.28	66.00	23.94	5.27	2.18	1.42

also follow SNI. Meanwhile, acid number as oleic acid doesn't comply, it is because of the factor that used to calculate as oleic acid, if palmitic acid used as factor the results fulfill the SNI specification. The transesterification reaction suspected doesn't complete due to reaction time that is why methyl ester gives low results. In comparison, our research give higher yields compare to (Ishola, Adelekan, Mamudu, Aboudunrin, Aworinde, Olatunji, Akinlabi, 2020).

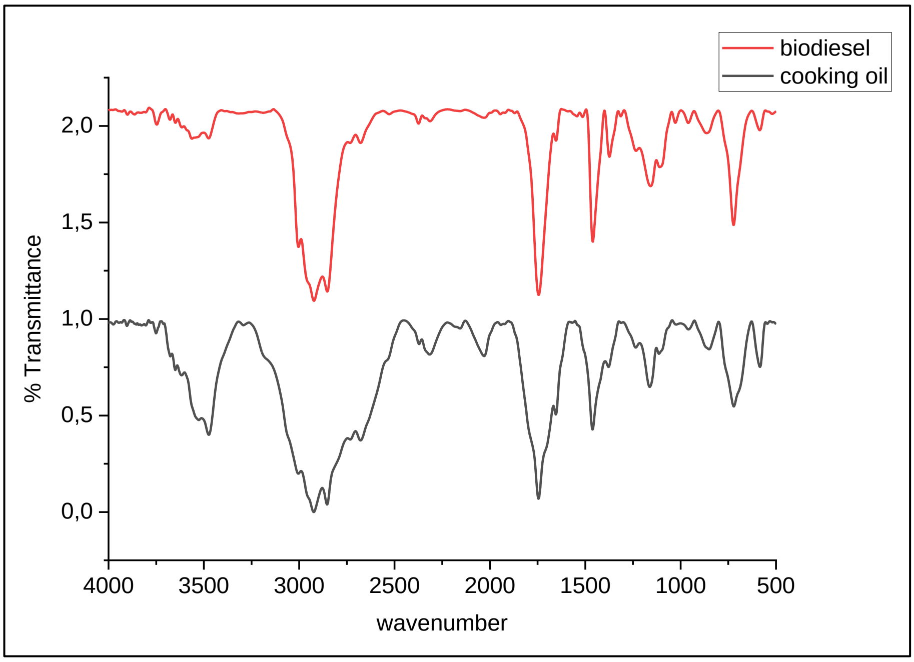

Figure 2. FTIR Spectrum of biodiesel and cooking oil

Table 2. The comparison FTIR spectra of biodiesel and cooking oil

Wavenumber (cm^{-1})	Biodiesel	Wavenumber (cm^{-1})	Cooking Oil
3475.73	N-H strecth	3473.80	N-H strecth
2924.09	C-H metilen	2924.09	C-H metilen
2852.72	C-H strecth	2854.85	C-H strecth
2679.13	O-H stretch	2733.13	C-H strecth
1743.65	C=O strecth	2679.13	O-H stretch
1653.00	C=C aromatic	1743.58	C=O strecth
		1654.92	C=C aromatic
1460.11	$-CH_3$	1462.04	$-CH_3$
1373.72	$O-CH_2$	1377.17	$O-CH_2$
1234.44	C-N strecth	1236.37	C-N strecth
1157.29	**$O-CH_3$**		
1109.07	C-O strecth	1112.93	C-O strecth

(Bhikuning & Senda, 2020; Farooq, Ramli, & Subbarao, 2013; Fattahi, Triantafyllidis, Luque, & Ramazani, 2019, 2019; Ishola, Adelekan, Mamudu, Aboudunrin, Aworinde, Olatunji, Akinlabi, 2020; Kamaronzaman, Kahar, Hassan, Hanafi, Sapawe, 2020; Oliveira, Montalvão, Daher, Suarez, & Rubim, 2006; Rosset & Perez-Lopez, 2019)

Table 3. Chemical and physical properties of biodiesel produced at various reaction time and temperature

Parameters	Reaction time (hour)			Temperature (ºC)			SNI 7182-2015
	1	2	3	70	90	110	
Water content (%)	0.03	0.04	0.03	0.03	0.03	0.04	< 0.05
Density (kg/m^3)	883.6	882.2	883.8	883.5	883.1	882.1	850-890
Viscosity (cSt)	4.59	4.61	4.61	4.61	4.62	4.62	2.3-6.0
Acid number (mg-KOH/g)	0.59	0.59	0.58	0.59	0.59	0.59	< 0.5
Free Fatty Acid (mg/g)	0.3	0.3	0.29	0.3	0.3	0.3	< 2
Total Glycerol (%)	0.32	0.32	0.32	0.32	0.31	0.32	< 0.24
Methyl ester (%)	83.18	83.18	83.22	83.24	83.18	83.21	> 96.5
Yield (%)	79.3	82	80	76	80	75.3	-

CONCLUSION

The utilization of ferronickel slag as catalyst in transesterification of cooking oil is promising enough. Major metals in ferronickel slag are Si. Fe. Ca. Cr. Mn. The biodiesel convertion gives promising results. optimum yield of biodiesel convertion at 2 hours and temperature 90 ^{o}C. However, ester formation of biodiesel confirmed by gained it at peak 1157.29; 1373.72; 1460.11 cm^{-1}.

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