Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

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To cite this article: A Simanjuntak *et al* 2019 *J. Phys.: Conf. Ser.* **1338** 012013

The Effect of Sugarcane Bagasse to Rubber Seed Oil Ratios on The Chemical Composition of Liquid Fuels Produced by Zeolite-Y Catalyzed Pyrolysis

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Abstract. In this research, co-pyrolysis of sugarcane bagasse and rubber seed oil using zeolite-Y as catalyst was carried out, with the main purpose to study the effect of raw material compositions on chemical composition of liquid fuel produced. For this purpose, the mixture of sugarcane bagasse and rubber seed oil with different mass ratios of bagasse to oil of 1 : 1; 1: 2; 1: 3: and 1: 4 was subjected to pyrolysis at 450 ° C in the presence of zeolite-Y as catalyst, and the liquid fuels were analyzed by GC-MS. The results show that liquid fuel contains hydrocarbons as main components, with several additional components include alcohols, esters, ketones, aldehydes, and acids. The liquid fuel produced from the raw material with the ratio of 1 : 3 was found to contain hydrocarbon with the highest relative percentage (87.91%), and consists of gasoline fraction (42.60%), kerosene fraction (43.59%), and residual fraction (1.72%).

1. Introduction

Depletion of fossil fuels has encouraged researchers to research and develop about alternative and renewable sources of energy that is easily obtained and a environment friendly, one of which is the development of fuel such as liquid fuel. Liquid fuel is alternative sources of energy can be obtained from the organic raw materials (biomass) of agriculture waste, the unused and not consumed plant.

To obtain the liquid fuel from biomass, pyrolysis method is one of the effective method in cracking carbon bond from organic material contained in biomass. The product can be obtained from pyrolysis are gases, liquid and charcoal [1]. There are several types of pyrolysis methods one of which is co-pyrolysis. The co-pyrolysis technique is one of the techniques chosen to produce a more optimum liquid fuel derived from biomass mixed with other hydrogen rich ingredients, can help increase the quantity and quality of the oil produced [2]. Co-pyrolysis method has been applied to several researches such as liquid fuel produced from water hyacinth and polyethylene plastic [3], liquid fuel from pyrolysis of bagasse and plastic waste, raw material from municipal waste or environmental waste and walnut seeds [4].

To optimize the pyrolysis product in the formation of liquid product, solid biomass can be added with the catalyst. There are several catalysts that have been used for co-pyrolysis processes such as Ni and nitrate catalyst, alkali and metal oxides of the alkaline and carbonate, and zeolite [5]. In the development of synthetic zeolite, silica be one of the raw materials used in its manufacture. Rice husk is one of the most abundant sources of silica. The results of research showed that in rice husks contained 18-20% silica [6]. Rice husk silica is amorphous and has high reactivity with alumina. The silica in the rice husk can be utilized as one of the raw materials to produce zeolite as a catalyst which will help in the pyrolysis process of a mixture of biomass materials to produce liquid fuel.

Research was carried out to get liquid fuel from various types of biomass materials such as bagasse [7] and rubber seed oil [8] through pyrolysis method. In addition to the previously mentioned single biomass raw materials, the processing of a mixture of bagasse and rubber seed oil by pyrolysis method has been done and obtained by optimum liquid fuel yield [9]. In pyrolysis method, the mixture is added catalyst such as zeolite synthetic zeolites A, X and Y each of which are zeolites calcined at four different temperatures at 600, 700, 800 and 900 ^{o}C.

In addition to the effect of adding zeolite to the obtained liquid fuel yield, the composition of the raw material affects the chemical composition of the liquid fuel obtained. This experiment was done by comparison of the raw material mixture as follows 50 grams of bagasse and 50 mL of rubber seed oil (1:1), 50 grams of bagasse and 100 mL of rubber seed oil (1:2), 50 grams of bagasse and 150 mL of rubber seed oil (1:3) and 50 grams of bagasse, and 200 mL of rubber seed oil (1: 4). Of all synthetic zeolites used as catalysts it was found that liqud fuel with calcined zeolite Y catalyst at 700 °C had the highest hydrocarbon content. From the results of this study, the next will be studied and researched some aspects that have not previously done is to study the effect of raw material composition on the chemical composition of liquid fuel produced, and next, liquid fuel will be fractionated to know about the chemical composition in it and will be studying about up-grading of liquid fuel to increase the amount and quality of liquid fuel be biogasoline category.

2. Materials and Methods

The study was carried out in the Departement of Chemistry, Faculty of Mathematics and Natural Science, Lampung University. The raw materials used in the study comes from of biomassa derived from the agricultural wastes, unused materials as rice husk, sugarcane bagasse, and rubber seed oil, other materials as aluminium foil, 1,5% NaOH solution, HNO_3 solution 1M, aquades, pH indicator and filter papers.

2.1 Extraction of silica

Preliminary of experiment carried out in a laboratory scale with the preparation of rice husk. Rice husk was obtained from local rice milling in Bandar Lampung. Extraction of silica from rice husk was carried out using alkalis extraction methods. Next process, mixing 50 gram rice husk was dried and 500 mL of 1,5 % (by weight) NaOH solution. The mixture was placed in a hot plate and boiled for 30 minutes. For optimize the dissolution of the silica from rice husk, the mixture was left for 24 hours at room temperature. filtrate which contain dissolved silica was addition of HNO_3 (10%) until pH = 8 and convert the sol into gel. The silica gel was keft for 24 hours at room temperature, and then washed and rinsed with hot distteld water until clean and the excess of acid lost, and then oven dried at 70-80^{o} C. If the silica gel was dried, mashed and filtered to produce of silica powder [10].

2.2 Synthesis of Zeolite

Synthesis of zeolite Y was used silica from rice husk silica and aluminium from aluminium foil has been cut small sized. Sodium hydroxide solution was prepared by dissolving 40 gr NaOH in 100 mL of destilled water and then the solution was divided into two part, with the same volume of 50 mL. The first part was used to prepare aluminium solution, by dissolving 27 grams of Al foil and add destilled water 150-200 mL. The second part was used to dissolve 144 gram of silica and add destilled water 150-200 mL. And then, the two solutions were then mixed using a blender, and into a place of resistance hot (polymer plastic) for crystalization process in the oven at 100 ^oC for 24 hours. Next, filtering the zeolite to separate the water which is still contained in the mixture. And then, the zeolite are dried in an oven at 80 ^oC, refining and sieveng. Dry solid was ground into powder and the Y zeolite is calcined at 700 ^oC for 6 hours.

2.3 Pyrolysis Experiment

Catalytic activity of the zeolite synthesized was tested for pyrolysis methods to produce liquid fuel from biomass such as agricultural waste. The sample of sugarcane bagasse with the different composition. For composition 1 : 1, mixing 50 mL rubber seed oil in 50 gram sugarcane bagasse. Mix 100 mL rubber seed oil in 50 gram sugarcane bagasse (1 : 2), mix 150 mL rubber seed oil in 50 gram sugarcane bagasse (1 : 3), and 200 mL rubber seed oil in 50 gram sugarcane bagasse (1 : 4) and for each sample add 5% of Y zeolite of the weight the sample respectively. Next, sample put into batch reactor. Pyrolysis at 450 ^oC for 3 hours. Sample was collected int the bottle form two layers of that will be screened and separated. The upper layer which is the organic phase (liquid fuel) and under layer which is the water phase. The liquid fuel was analyzed using GC-MS technique to identify the chemical composition of the sample.

3. Results and Discussion

The synthesized zeolite was tested on a mixture of bagasse and rubber seed oil through pyrolysis method with a temperature of 450 ^oC. Pyrolysis mixture bagasse and rubber seed oil with zeolite catalyst Y 700 ^oC to produce liquid fuel is done with composition ratio of raw materials 1: 1, 1: 2, 1: 3, 1: 4 and produced good data of GC-MS includes composition of compounds and hydrocarbon compositions contained in liquid fuel. GC chromatogram for sample of bagasse and rubber seed oil of 1: 1 ratio and chemical composition of liquid fuel identified with MS referring to library system Willey299.lib and it was grouped into groups of organic compounds of a general nature is presented in the following figure 1.

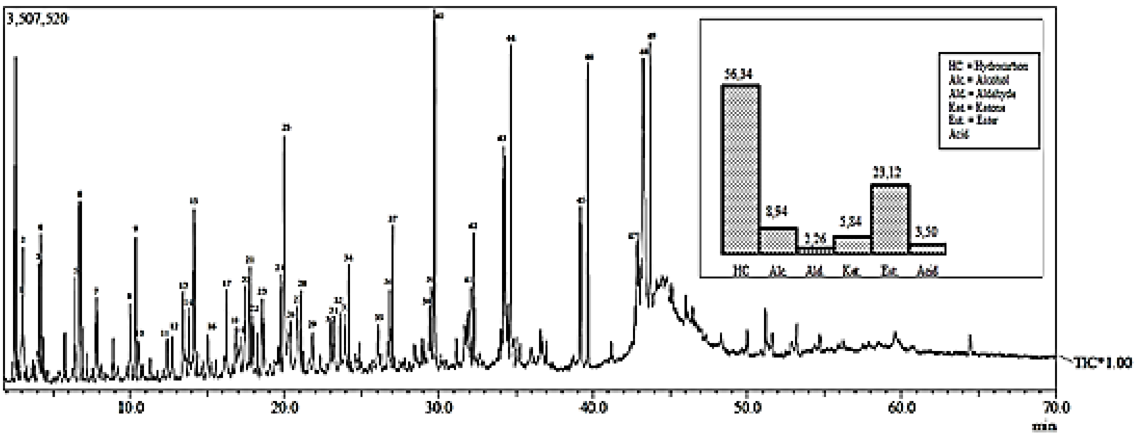

Figure 1. GC Chromatogram and chemical composition of liquid fuel pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 1 ratio using zeolite Y 700 ^oC

To know the compound of liquid fuel, identification with MS which refers to library system Willey299.lib system, and the results obtained are presented in the table GC-MS sugarcane bagasse and rubber seed oil of 1 : 1 ratio using zeolite Y 700 ^oC following table 1.

Table 1. GC-MS of sugarcane bagasse and rubber seed oil of 1: 1 ratio using zeolite Y 700 ^{o}C

Peak Number	Retention Time	Compounds Name	Molecular Name	Compounds Category	% Relative
1	3.005	1-Hexene	C_6H_{12}	Hydrocarbon	1.34
2	3.058	Hexane	C_6H_{14}	Hydrocarbon	1.33
3	4.068	1-Heptene	C_7H_{14}	Hydrocarbon	1.55
4	4.208	Heptane	C_7H_{16}	Hydrocarbon	1.39
5	6.451	1-octene	C_8H_{16}	Hydrocarbon	1.39
6	6.728	Octane	C_8H_{18}	Hydrocarbon	2.20
7	7.809	2-furaldehyde	$C_5H_4O_2$	Aldehyde	1.38
8	10.010	1-nonene	C_9H_{18}	Hydrocarbon	1.38
9	10.343	Nonane	C_9H_{20}	Hydrocarbon	1.76
10	10.516	3-methyl-2cyclopenten-1-one	C_6H_8O	Ketone	0.85
11	12.412	1-propylbenzene	C_9H_{12}	Hydrocarbon	0.74
12	12.725	Trans-trans 2.4-Heptadienal	$C_7H_{10}O$	Aldehyde	0.89
13	13.430	Phenol	C_6H_6O	Alcohol	1.89
14	13.834	1-Decene	$C_{10}H_{20}$	Hydrocarbon	1.13
15	14.155	Decane	$C_{10}H_{22}$	Hydrocarbon	2.78
16	15.043	Methyl heptanoate	$C_8H_{16}O_2$	Ester	1.03
17	16.241	1-butylbenzene	$C_{10}H_{14}$	Hydrocarbon	1.39
18	16.858	4-methyl phenol	C_7H_8O	Alcohol	1.00
19	17.145	Heptanoic acid	$C_7H_{14}O_2$	Acid	1.39
20	17.467	1-undecene	$C_{11}H_{22}$	Hydrocarbon	2.40
21	17.765	Undecane	$C_{11}H_{24}$	Hydrocarbon	1.58
22	17.942	Cis-4-Undecene	$C_{11}H_{22}$	Hydrocarbon	1.04
23	18.578	Methyl Octanoate	$C_9H_{18}O_2$	Ester	1.56
24	19.752	pentylbenzene	$C_{11}H_{16}$	Hydrocarbon	1.53
25	19.983	4-ethylphenol	$C_8H_{10}O$	Alcohol	5.06
26	20.372	Octanoic acid/Caprylic acid	$C_8H_{16}O_2$	Acid	2.11
27	20.832	1-Undecene	$C_{11}H_{22}$	Hydrocarbon	2.59
28	21.091	Dodecane	$C_{12}H_{26}$	Hydrocarbon	1.09
29	21.836	Methyl nonanoate	$C_{10}H_{20}O_2$	Ester	0.70
30	23.027	hexylbenzene	$C_{12}H_{18}$	Hydrocarbon	0.96
31	23.250	1.2.2-trimethylpropyl benzene	$C_{12}H_{18}$	Hydrocarbon	1.16
32	23.612	4-ethyl-2-methoxy phenol	$C_9H_{12}O_2$	Alcohol	0.99
33	23.928	1-Undecene	$C_{11}H_{22}$	Hydrocarbon	1.53
34	24.170	Dodecane	$C_{12}H_{26}$	Hydrocarbon	1.34
35	26.094	Heptylbenzene	$C_{13}H_{20}$	Hydrocarbon	1.14
36	26.822	1-Tetradecene	$C_{14}H_{28}$	Hydrocarbon	1.25
37	27.043	hexadecane	$C_{17}H_{34}$	Hydrocarbon	1.89
38	29.397	7-tetradecene	$C_{14}H_{28}$	Hydrocarbon	1.49
39	29.542	1-Tridecene	$C_{13}H_{26}$	Hydrocarbon	1.14
40	29.745	Hexadecane	$C_{16}H_{34}$	Hydrocarbon	5.00
41	32.096	1-Pentadecene	$C_{15}H_{30}$	Hydrocarbon	1.03

42	32.280	Hexadecane	$C_{16}H_{34}$	Hydrocarbon	1.80
43	34.197	Heptadec-8-ene	$C_{17}H_{34}$	Hydrocarbon	3.51
44	34.691	Pentadecane	$C_{15}H_{32}$	Hydrocarbon	4.55
45	39.201	2-Heptdecanone	$C_{17}H_{34}O$	Ketone	2.58
46	39.680	Methyl hexadecanoate	$C_{17}H_{34}O_2$	Ester	4.20
47	42.846	4-cyclohexyl-2-butanone	$C_{10}H_{18}O$	Ketone	2.41
48	43.245	Methyl octadec-10-enoate	$C_{19}H_{36}O_2$	Ester	11.63
49	43.705	Methyl octadecanoate	$C_{19}H_{38}O_2$	Ester	4.00
					100.00

The composition of hydrocarbon content in liquid fuel from pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 1 ratio is grouped into gasoline and kerosene is shown in the following table 2.

Table 2. Group of Gasoline and kerosene from liquid fuel with 1 : 1 ratio

Gasoline	33.55
Kerosene	22.79
Hydrocarbon Total	**56,34**

GC chromatogram for sample of sugarcane bagasse and rubber seed oil of 1 : 2 ratio using zeolite Y 700 ^oC, compound of liquid fuel identified with MS referring to library system Willey299.lib system, and the results obtained are presented in table GC-MS of sugarcane bagasse and rubber seed oil of 1 : 2 ratio using zeolite Y 700 ^oC and chemical components of liquid fuel are grouped into groups of organic compounds that are common as seen in the following figure 2.

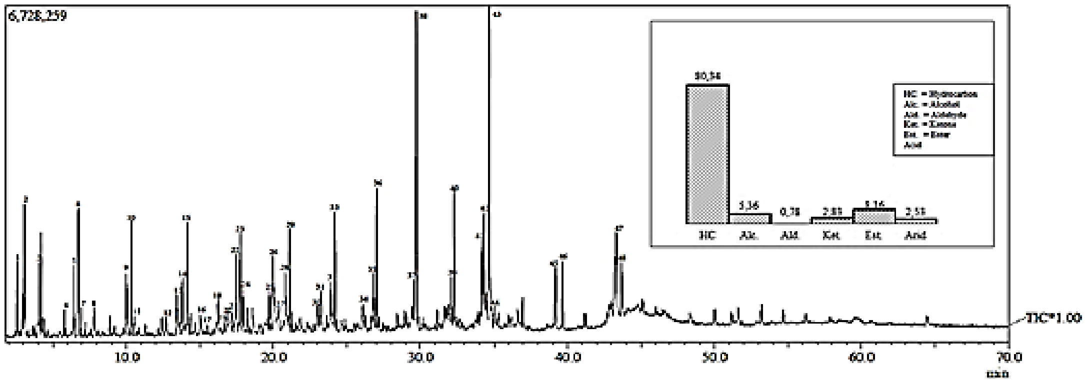

Figure 2. GC Chromatogram and chemical composition of liquid fuel pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 2 ratio using zeolite Y 700 ^oC

The composition of hydrocarbon content in liquid fuel from pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 2 ratio is grouped into gasoline and kerosene is shown in the following table 3.

Table 3. Composition of Gasoline and Kerosene in liquid fuel

Gasoline	41.62
Kerosene	38.72
Residue	0
Hydrocarbon Total	**80,34**

The pyrolysis experiment with the ratio of the raw material of bagasse and the rubber seed oil (1: 3 ratio) using the zeolite Y 700 °C, compound of liquid fuel identified with MS referring to library system Willey299.lib system, and the results obtained are presented in table GC-MS of sugarcane bagasse and rubber seed oil of 1 : 3 ratio using zeolite Y 700 °C and chemical components of liquid fuel are grouped into groups of organic compounds is presented in the following figure 3.

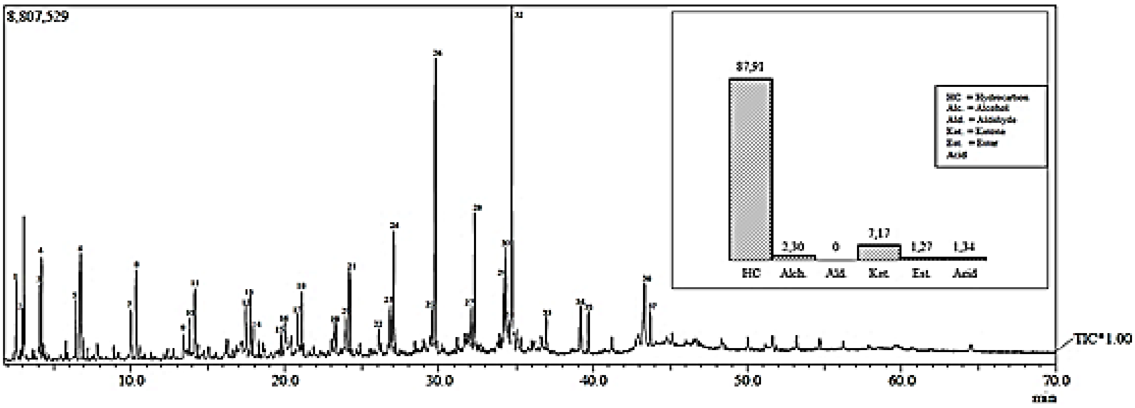

Figure 3. GC Chromatogram and chemical composition of liquid fuel pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 3 ratio using zeolite Y 700 °C

The composition of hydrocarbon content in liquid fuel from pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 3 ratio is grouped into gasoline and kerosene is shown in the following table 4.

Table 4. Composition of Gasoline and Kerosene in liquid fuel

Gasoline	42.60
Kerosene	43.59
Residue	1.72
Hydrocarbon Total	**87.91**

The pyrolysis experiment with the ratio of the raw material of bagasse and the rubber seed oil (1 : 4 ratio) using the zeolite Y 700 °C, compound of liquid fuel identified with MS referring to library system Willey299.lib system, and the results obtained are presented in table GC-MS of sugarcane bagasse and rubber seed oil of 1 : 4 ratio using zeolite Y 700 °C and chemical components of liquid fuel are grouped into groups of organic compounds is presented in the following figure 4.

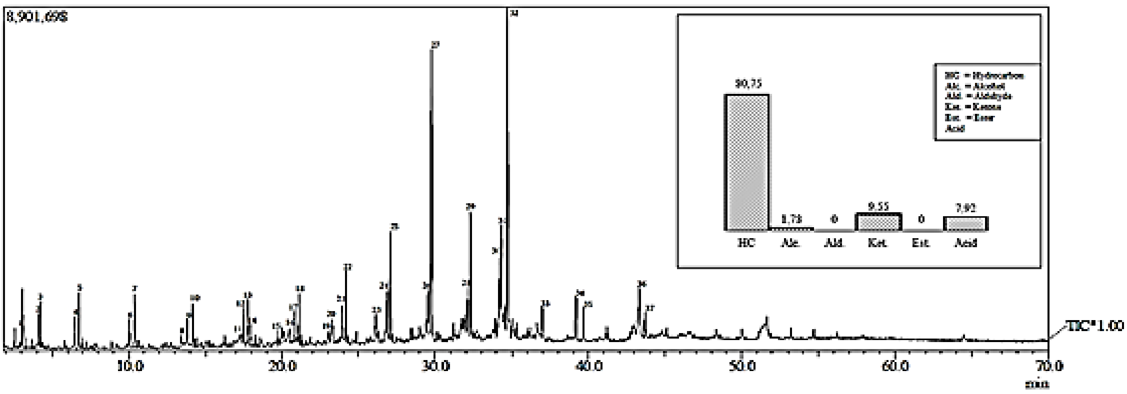

Figure 4. GC Chromatogram and chemical composition of liquid fuel pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 4 ratio using zeolite Y 700 °C

The composition of hydrocarbon content in liquid fuel from pyrolysis of sugarcane bagasse and rubber seed oil of 1 : 4 ratio is grouped into gasoline and kerosene is shown in the following table 5.

Table 5. Composition of Gasoline and Kerosene in liquid fuel

Gasoline	33.10
Kerosene	47.65
Residue	0
Hydrocarbon Total	**80.75**

From the research that was carried out with the composition of raw materials varied, obtained GC-MS data from each sample.

Table 6. Chemical composition summary of liquid fuel

No.	Ratio of raw materials	Hydrocarbon	Alcohol	Ketone	Aldehyde	Ester	Acid
1	1 : 1	56.34	8.94	5.84	2.26	23.12	3.50
2	1 : 2	80.34	5.36	2.83	0.78	8.16	2.53
3	1 : 3	87.91	2.30	7.17	0	1.27	1.34
4	1 : 4	80.75	1.78	9.55	0	0	7.92

For the chemical composition, highest hydrocarbons content are obtained from the sample with raw material ratio is 1 : 3 which is 50 grams of bagasse and 150 mL of rubber seed oil of 87.91%. The hydrocarbons were then grouped into kerosene and gasoline groups, and the kerosene content of the sample was 43.59%, gasoline 42.60% and residue 1.72%.

Table 7. The hydrocarbons from each sample grouped into kerosene and gasoline

No.	Ratio of raw materials	Gasoline	Kerosene	Residue
1	1 : 1	33.55	22.79	0
2	1 : 2	41.62	38.72	0
3	1 : 3	42.60	43.59	1.72
4	1 : 4	33.10	47.65	0

And the physical characteristic of liquid fuel with comparison raw material such as density and flash point shown on the table 8.

Table 8. Physical characteristics of liquid fuel with difference raw material composition.

No.	Ratio of raw materials	Density (g/mL)	Flash Point (°C)
1	1 : 1	0.9693	96°
2	1 : 2	0.9334	70°
3	1 : 3	0.9241	64°
4	1 : 4	0.9145	62°

4. Conclusions

The raw materials ratio of sugarcane bagasse and rubber seed oils influences the chemical composition of the liquid fuel produced. Liquid fuel with the highest hydrocarbon content (86.19%) was obtained with the raw materials ratio is 1 : 3.

Acknowledgment

The directorate of Research and Community Service Ministry of Research Technology and Higher Education for Research Grant (Hibah Berbasis Kompetensi.2018). Contact Number : 384/UN26. 21/PN/2018. Integrated Laboratory and Centre for Technology Inovation (LTSIT), Lampung University for technical assitance.

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