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Abstract. In this study, cassava root was subjected to torrefaction pretreatment prior to catalytic pyrolysis, with the main objective to investigate the effect of torrefaction time on chemical composition of bio crude oil (BCO) distillate resulted. For this purpose, the root was torrefied at $200^{o}C$ for 30, 60, 90, and 120 minutes. The torrefied samples were then mixed with palm oil and then pyrolyzed at 450 ^{o}C in the presence of zeolite-A, prepared from rice husk silica (RHS) and food grade aluminum foil, as catalyst. A sample without torrefaction was pyrolyzed in a similar condition for comparison. The bio-crude oil (BCO) obtained was distilled at 150 ^{o}C, and the chemical composition of the distillate was determined using gas chromatography-mass spectrometry (GC-MS) method. The components of the distillates produced from torrefied samples are composed of mainly C_6-C_{13} hydrocarbons, which are considered as biogasoline, while that produced from the sample without torrefaction was found to contain ketone in addition to hydrocarbon. The experimental results also demonstrate that the chemical compositions of the BCO distillates produced from the samples torrefied at 30, 60, and 90 minutes are not significantly different, but significantly different composition was observed for the sample torrefied at 120 ^{o}C.

Keywords: torrefaction, cassava root, pyrolysis, zeolite-A, bio-crude oil, biogasoline.

1. Introduction
Growing interest in renewable energy sources (RES) as an anticipative response to depletion of petroleum reserves, together with increased awareness of environmental impacts arises from fossil fuels combustion, have led to invention of various technologies, which enable the production of different forms of energy source from various renewable feedstocks. In the light of RES, development of biomass based fuels (biofuels) have gained important position as the focus of intensive studies around the globe.   Biofuels are now considered as prospective energy sources in the future acknowledging the availability and renewability of biomass, as well as continuous improvement of biomass to energy conversion technologies.

Among the biomass to energy conversion processes, for production of liquid fuel in particular, pyrolysis continuous to attract growing interest [1-3], because this method offers several advantages.

From raw material point of view, pyrolysis is a flexible method since it can be applied to process any type of biomass for production of liquid fuel, also known as bio-crude oil (BCO). Simplicity of the process, the applicability of the BCO for various applications, such as for boilers and turbines [4], and the possibility to improve the quality of the BCO into fuel which suites the application with more stringent requirements [5,6] are other advantages offered by pyrolysis. Production of BCO from various biomass raw materials has been reported in literatures, such as wild reed [7], rice husk [8], Napier grass [9], palm oil [10], coconut oil [11], and agricultural wastes [12].

The general feature of BCO is complex composition, in which large number of compounds belongs to various classes of organic such as hydrocarbon, acid, phenolic, alcohol, and other oxygenates are present [7, 9, 13]. Out of these components, biogasoline, which is the BCO fraction that composed of C_5-C_{12} hydrocarbons, is of particular interest for its similar characteristics with fossil originated gasoline. For this reason, optimizing the formation of biogasoline is continuously searched. One approach that has been developed in recent years is torrefaction of raw material prior to pyrolysis. Torrefaction is simply a heat treatment of biomass at temperature range of 200-300℃, depending on the type of biomass, during which the moisture content of the biomass is significantly reduced while the biomass is retained as densificated solid. The mass of torrefied solid was reduced down to 70% of the initial mass, while 90% of the initial energy content was maintained [14]. In addition, torrefaction was reported to improve the quality of the biomass for pyrolysis by reducing the oxygen content and increasing the bulk density of biomass [15]. Taking advantages offered by this pretreatment process, pyrolysis of torrefied biomass has been reported in a number of previous studies [4, 16, 17].

One of attractive biomass feedstocks for development of biogasoline is cassava roots. This agriculture commodity is available in large quantity in Indonesia and mostly is cultivated by traditional farmers. The traditional utilization of this agriculture product is for production of starch known as cassava floor, used as foodstuff or bioethanol production. The rest of the root, includes solid residue and peel, is not considered by the company purchasing the cassava, therefore, no economic benefit gained by the farmer. Most of these residues are practically unutilized and cause environmental concern due to their disposal. In this respect utilization of the root as a whole will improve the economic gain of the farmers as well as alleviate the environmental problem to significant extent.

In present work, cassava root was subjected to torrefaction pretreatment prior to pyrolysis, with the main objective to assess the effect of torrefaction time on the production and chemical composition of the biogasoline resulted from pyrolysis of mixed root and palm oil. Torrefaction was carried out fixed temperature of 200 ^{o}C, with varied time of 30, 60, 90, and 120 minutes and then the torrefied roots was mixed with palm oil for pyrolysis experiment. The BCO produced was distilled at 150 ^{o}C and the distillate was analyzed using GC-MS technique.

Pyrolysis experiment was undertaken in the presence of zeolite-A prepared from RHS and food grade aluminum as catalyst. This catalyst was chosen since zeolites, including zeolite-A, are the most widely used catalyst in biomass pyrolysis due to their acidic nature and the ability to enhance deoxygenation during pyrolysis. As a result, the formation of oxygen-containing substances is limited, leading to more effective formation of hydrocarbons [18; 19].

2. Materials and methods

2.1. Materials and Instruments

Reagent grade sodium hydroxide and nitric acid used in this work were purchased from Aldrich. Rice husk silica (RHS) was extracted from rice husk (RH) obtained from local rice milling company, food grade aluminium foil was purchased from local supplier, and cassava root was purchased from local market. Polytetrafluoroethylene (PTFE) lined stainless steel autoclave was used as crystallization chamber for zeolite preparation, and a Nabertherm electrical furnace (Lilienthal, Germany) for zeolite calcination. Pyrolysis experiment was carried out using bench scale pyrolysis unit, equipped with thermocouple for temperature control, enabling the pyrolysis to be carried out at specified temperature, and connected to water cooled condenser for liquid product collection. Heating mantle, Favoirite Model MS-E104 was used for BCO distillation process. GC-MS analysis was conducted using the GCMS-QP2010 SE SHIMADZU. The chemical components of distillate was tentatively identified with the aid of MS Library system NIST12.LIB and WILEY229.LIB.

2.2. Procedures

RHS was obtained using an alkali extraction according to the method reported in previous study [20]. Typically, a sample of 50 g dried RH was mixed with 500 mL of 1.5% NaOH solution in a beaker glass. The mixture was boiled for 30 min, and then allowed to cool to room temperature and left for 24 h, and finally filtered to separate the filtrate which contains silica (silica sol) and residual husk. Acidification of the sol to neutral condition (pH of 6.8-7.0) for conversion of the sol into gel was carried out using 10% nitric acid solution. The gel was aged for 24 hours, and then rinsed repeatedly with distilled water to remove the excess of acid. Solid RHS was obtained by oven drying of the gel at 110 ^{o}C for eight hours. Finally, the solid RHS was ground into powder and sieved with 250 mesh sieve to obtain the sample with relatively homogeneous sizes.

Zeolite-A was prepared from raw materials according to the general formula of ($Na_2O.Al_2O_3.2SiO_2.xH_2O$). Typical preparation was conducted by dissolving 40 g NaOH in 350 mL of distilled water, and the solution was divided into two parts. The first part with the volume of 100 mL was used as a solvent to dissolve 27 g of Al metal, and the second part, with the volume of 250 mL, to dissolve 60 g of rice husk silica. The silica and aluminum solutions were then thoroughly mixed using a laboratory blender, and then transferred into a teflon lined autoclave for 24 hour aging process. The autoclave was placed in an oven set at 100 ^{o}C for 72 hours for crystallization. After completion of crystallization process, the solid zeolite produced was filtered to remove the excess of water, and then subjected to calcination at 550 ^{o}C for eight hours, and then ground into powder.

For torrefaction pretreatment, the outer skin (epidermis) of fresh cassava root was removed. The roots were washed with water to remove natural dirt, and then chopped into small pieces, and then placed in an oven set at 200 ^{o}C for different time of 30, 60, 90, and 120 minutes. Using mortar, the torrefied samples were ground into powder for pyrolysis experiments. To commence the pyrolysis experiment, 100 g of root sample was mixed with 100 mL of palm oil, and 10 g of catalyst, and the mixture was transferred into pyrolysis unit. The pyrolysis temperature was set at peak temperature of 450 ^{o}C, and pyrolysis was run by heating the reactor until the peak temperature was reached at which the pyrolysis process was allowed to proceed for 60 minutes. The liquid product was collected and then transferred into separatory funnel to allow the separation of the liquid to two layers. The bottom layer, which is water phase, was discarded and the organic phase (BCO) was collected. To obtain the biogasoline fraction, 100 mL of the BCO was distilled at 150 ^{o}C and the distillate was anaylzed by GC-MS.

3. Results and discussion

3.1. Pyrolysis of Untorrefied Cassava Root

Figure 1 is the GC chromatogram of the distillate of BCO produced from the sample without torrefaction.
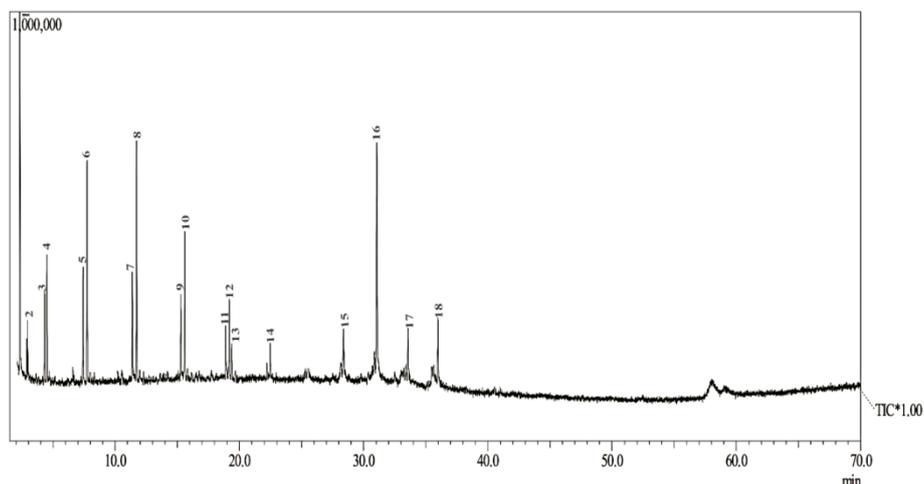
Figure 1. GC chromatogram of the distillate of BCO produced from non-torrefied cassava roots.

Table 1. The chemical composition of distillate of BCO resulted from non-torrefied cassava roots.

Peak No.	Retention Time (min)	Compounds	Molecular Formula	% Relative
1	2.321	Propanone	C_3H_6O	25.92
2	2.949	Hexane	C_6H_{14}	0.84
3	4.311	1-Heptene	C_7H_{14}	1.99
4	4.500	Heptane	C_7H_{16}	2.70
5	7.411	1-Octene	C_8H_{16}	3.09
6	7.730	Octane	C_8H_{18}	12.21
7	11.380	1-Nonene	C_9H_{18}	2.87
8	11.722	Nonane	C_9H_{20}	16.27
9	15.292	1-Decene	$C_{10}H_{20}$	2.13
10	15.610	Decane	$C_{10}H_{22}$	3.91
11	18.903	Undecene isomer	$C_{11}H_{22}$	1.46
12	19.186	Undecene isomer	$C_{11}H_{22}$	2.23
13	19.374	Undecane	$C_{11}H_{24}$	1.10
14	22.473	Dodecene isomer	$C_{12}H_{24}$	0.92
15	28.370	Dodecene isomer	$C_{12}H_{24}$	1.68
16	31.062	Dodecane	$C_{12}H_{26}$	17.33
17	33.582	Tridecane	$C_{13}H_{28}$	1.44
18	35.976	1-Tetradecene	$C_{14}H_{28}$	1.91

As many as 18 compounds were identified using the MS Library System, and they are listed in Table 1. As can be seen in Table 1, as many as 17 out of 18 compounds found are hydrocarbons with the carbon chain in the range of biogasoline. From Table 1, it can be calculated that the contribution of hydrocarbon to relative composition is around 74 %.

3.2. Pyrolysis of Torrefied Cassava Root

The GC chromatograms of the distillate of the BCO produced from the roots torrefied at 30, 60, and 90 minutes are shown in Figure 2.
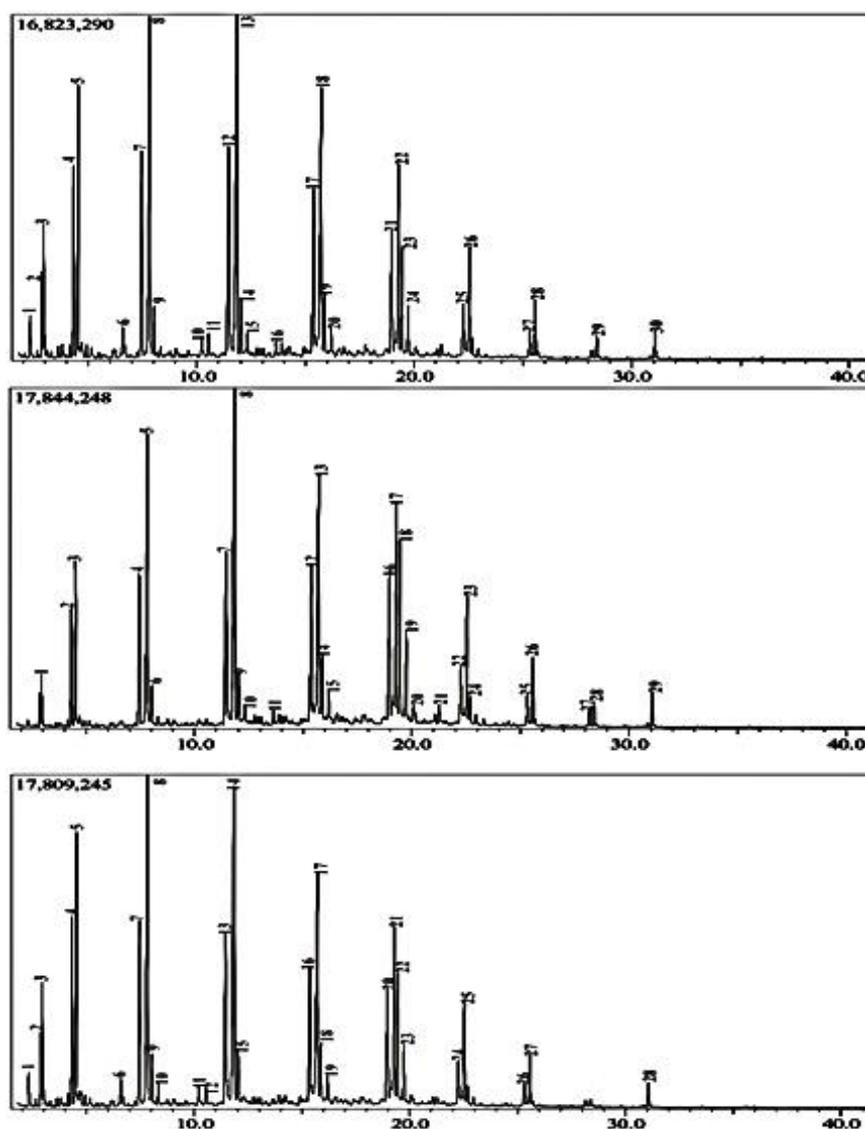
Figure 2. The GC chromatograms of the distillate of BCO produced from the cassava root sample subjected to torrefaction for 30 minutes (a), 60 minutes (b), and 90 minutes (c).

By comparing the chromatogram of the distillate derived from non-terrified root (Figure 1) to those of the distillates produced from torrefied roots (Figure 2) it can be seen that in Figure 2, the components are more concentrated in the shorter retention time. This feature implies that the more components with lower molecular weights were found in the sample derived from the torrefied roots. Very identical feature of the chromatograms in Figure 2 suggest that the three distillates are composed of mostly the same compounds, although some differences should also be acknowledged as seen in Table 2.

The compositional data of the samples presented in Table 2, showing that to the limit of analytical method used, the distillates are pure hydrocarbons and most of them are in the range of biogasoline, in which butane (C_4) is the only component outside the biogasoline range found.

Table 2. Chemical composition of distillate of the BCO resulted from pyrolysis of the cassava roots subjected to torrefaction for 30, 60, and 90 minutes.

Compound	Torrefaction time (min)		
	30	60	90
Isobutane	+	-	+
1-Hexene	+	-	+
Hexane	+	+	+
1-Heptene	+	+	+
Heptena	+	+	+
Toluena	+	-	+
Octene isomer	+	+	+
Octene isomer	+	+	+
Octene isomer	-	-	+
Octane	+	+	+
Ethylbenzene	+	-	+
1,8-Nonadiene	+	-	+
Nonene isomer	+	+	+
Nonene isomer	+	+	+
Nonene isomer	+	+	-
Nonane	+	+	+
Cyclopropene, 1-butyl-2-ethyl	+	-	-
Cyclopropene	-	+	-
Decene isomer	+	+	+
Decene isomer	+	+	+
Decane	+	+	+
1H-Indene	-	+	-
Cyclopropane, 1-methyl-2-(1-methylpentyl)	-	+	-
Nonane, 2-methyl	-	+	-
Undecene isomer	+	+	+
Undecene isomer	+	+	-
Undecene isomer	+	+	-
Undecene isomer	+	+	+
1,4-Undecadiene	+	+	-
Decadiene isomer	-	+	+
Decadiene isomer	-	-	+
Undecane	+	+	+
1-Dodecene isomer	+	+	+
4-Dodecene isomer	+	+	+
2-Dodecene isomer	+	+	+
Dodecane	+	+	+
Tridecane	+	+	+

The GC chromatogram of the distillate of the BCO produced from the roots subjected to 120 minute torrefaction is shown in Figure 3, and the components of the sample are listed in Table 3.
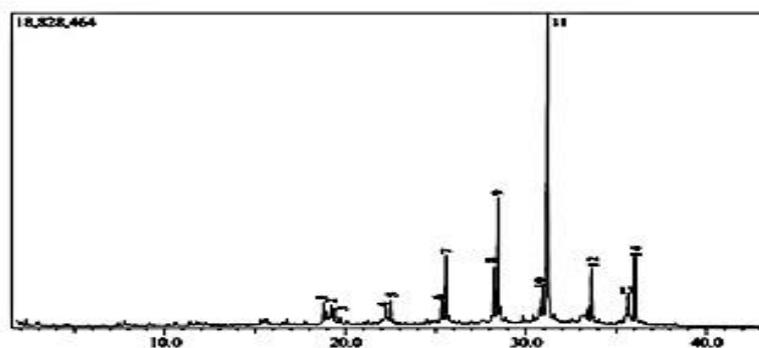
Figure 3. The GC chromatogram of the distillate of BCO produced from the cassava root sample subjected to torrefaction for 120 minutes.

Table 3. Chemical composition of distillate of the BCO resulted from pyrolysis of the cassava roots subjected to torrefaction for 120 minutes

Peak No	Retention Time (min)	Compounds	Molecular Formula	% Relative
1	18.798	Decane	$C_{10}H_{22}$	2.49
2	19.212	1-Undecene	$C_{11}H_{22}$	3.74
3	19.405	2-Undecene	$C_{11}H_{22}$	1.90
4	22.244	Pentylbenzene	$C_{11}H_{16}$	2.87
5	22.503	Undecane	$C_{11}H_{24}$	2.43
6	25.330	1-Dodecene	$C_{12}H_{24}$	3.30
7	25.586	Dodecane	$C_{12}H_{26}$	6.17
8	28.227	3-Dodecene	$C_{12}H_{24}$	6.18
9	28.471	1-Dodecyne	$C_{12}H_{22}$	12.28
10	30.923	4-Dodecene	$C_{12}H_{24}$	4.51
11	31.220	Tridecane	$C_{13}H_{28}$	37.29
12	33.646	1-Tetradecene	$C_{14}H_{28}$	5.45
13	35.669	3-Tetradecene	$C_{14}H_{28}$	4.22
14	36.044	Pentadecane	$C_{15}H_{32}$	7.16

As can be seen, the chromatogram of the distillate obtained from the root torrefied for 120 minutes (Figure 3) is significantly different to those of the distillates presented in Figure 2.   It is also obvious that the chromatogram of the sample in Figure 3 is characterized by the existence of fewer compounds and the shift of the components toward higher molecular weights, compared to the features of the chromatograms of the samples in Figure 2.   These differences suggest that torrefaction up to 120 minutes caused the cassava root becomes more difficult to pyrolyzed, which is probably due to carbonation of the root components during the torrefaction.

4. Conclusion

The results of this study demonstrated that biogasoline can be produced from co-pyrolysis of cassava root and palm oil using zeolite-A prepared from rice husk silica and aluminium foil. It is also observed

that torrefaction of cassava root affects the pyrolysis feature, in which torrefactions for 30, 60, and 90 minutes were found to result in enhanced production of biogasoline, while prolonged torrefaction to 120 minutes was found to impart deteriorate effect. In this respect, torrefaction for 30 minutes is sufficient to optimize the formation of biogasoline.

Acknowledgement

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