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JCNaR
Journal of Chemical Natural Resources

Effect of Pyrolysis Temperature on Polycyclic Aromatic Hydrocarbon (PAH) and Organic Acid Compounds From Oil Palm Shell Liquid Smoke

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Abstract. The effect of pyrolysis temperature on polycyclic aromatic hydrocarbon and organic acid compounds from oil palm shell liquid smoke has been successfully conducted. In this study, variations of temperature were used at 600 to 950ºC with temperature intervals at 50ºC. Liquid smokes obtained were characterized using GC-MS and FTIR. The GC-MS and FT-IR analysis results showed the presence of organic acid compounds such as acetic acid and propanoic acid. In contrast, no found polycyclic aromatic hydrocarbons (PAH) compounds. The higher the pyrolysis temperature involved the higher the organic acid contents.

Keywords: Liquid Smoke, Organic Acid, PAH, Pyrolysis

Received [9 May 2020] | Revised [16 June 2020] | Accepted [27 July 2020]

1 Introduction

Food quality is determined by taste, texture, color, and nutritional value. The quality of food value can be improved by preserving food. The purpose of adding food preservatives is to extend shelf life by preventing the growth of spoilage microorganisms. There are many ways to obtain food preservatives that are taken by various food industry players, but based on economic interests, the food preservatives produced are made from cheap materials, so that they can reduce the operational costs of the food industry. In addition, it is not uncommon for certain food preservatives to be harmful to human health. Some natural food preservatives can be obtained from organic materials and are safe for the health of consumers. Liquid smoke is natural food preservative.

Palm shells contain fiber components such as cellulose, hemicellulose, and lignin. These three components when condensed from their pyrolysis will produce liquid smoke containing

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Journal Homepage: http://jcnar.usu.ac.id

phenolic, carbonyl, and acid compounds. According to Girard (1992), the three compounds have functional properties as antibacterial, and antioxidant, and have a role in providing a specific taste. Therefore, palm shells can be utilized as liquid smoke. Palm oil shells are a type of solid waste by-product of the palm oil processing industry, which currently still poses problems for the environment. Due to the waste is produced in large quantities and is hard to degrade or decompose naturally in the environment. Oil palm shells contain lignin (29.4%), hemicellulose (27. 7%), cellulose (26.6%), water (8.0%), extractive components (4.2%), ash (0.6%). Hence, the waste has great potential to be developed into products that are useful and provide added value from the economic aspect, and are environmentally friendly (Prananta, 2009).

Liquid smoke is a condensation product from steam or combustion of materials that contain lots of lignin, cellulose, and hemicellulose, such as wood, bark, shell, palm shell, coir, bamboo, leaves, and so on. There are three stages in the pyrolysis process. The first stage is to remove biomass water at 120 to150ºC, followed by the second stage of the hemicellulose pyrolysis process at 150 to 200ºC, then the third stage of the cellulose pyrolysis process at 250 to 300ºC, and the fourth stage is the lignin pyrolysis process at 400ºC. At a further stage, the pyrolysis process will produce new compounds resulting from the pyrolysis of condensation products such as phenol, tar, and PAH compounds that occur is more than 500ºC (Girard, 1992 in Halim, 2005).

Next, the pyrolysis process is to manufacture the liquid smoke that can use various types of raw materials such as wood, oil palm heads, coconut shells, husks, pulp or wood sawdust, etc. During the combustion process, components of wood will experience incomplete combustion and produce various kinds of compounds including phenols, carbonyls, acids, furans, alcohols, lactones, hydrocarbons, polycyclic aromatics, and so on. Smoke is a complex system consisting of the dispersed liquid phase and the gaseous medium as the dispersion. The reaction that occurs in the pyrolysis process is a decomposition of polymer constituents into organic compounds with a weight of low molecular weight due to the influence of heat which includes oxidation, polymerization, and condensation reactions (Tranggono et al in Mansur, 2009).

One of the biomass wastes that is the focus of this research is to develop palm oil shells as raw material for making liquid smokes. Several recent researchers have reported the utilization of liquid smoke for various purposes. One of the interesting uses of liquid smoke is fish preservation, called fish smoking.

Polycyclic Aromatic Hydrocarbons (PAH) compounds is firstly found in *Eucalyptus grandis* by AS Pimentaa, BR Vitala, JM Bayonabr, and R. Alzagab in 1998. In addition, F. Chinnici, N. Natali, U. Spinabelli, and C. Riponion in 2006 had researched the same compound from liquid smoke using wood as raw materials.

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Several relevant studies on previous liquid smoke still found harmful compounds such as the presence of tar and PAH (Sri Sunarsih, et al., 2012)

Based on the description above, it is necessary to conduct research on liquid smoke from oil palm shells with pyrolysis temperature variations from 600 to 900ºC which is expected to produce liquid smoke which has antibacterial, antioxidant, and good flavor retaining properties and can also prevent the formation of harmful compounds.

2 Materials and Methods

2.1 Equipments

In this study, a pyrolysis reactor (cooking furnace made of refractory stone, T = 1000ºC), spiral cooling column (6m), smoke pipe, and a set of distillation apparatus were used.

2.2 Materials

The main material used in this study was palm oil shells.

2.3 Sample Preparation

The palm shells used are from PT. Indah Pontjan, Perbaungan District, which was still wet and dried before use in the sun for 1 day to reduce the water content in the shells.

2.4 Fabrication of Liquid Smoke from Palm Shell Process

Firstly, 10 kg of palm shells were put into a cooking furnace equipped with a thermometer. Then the writing furnace was turned on while the water was circulated as coolant is circulated through the circulation hose into the spiral pipe cooling barrel.

The smoke resulting from the combustion flowed through a spiral pipe and then cooled through a spiral pipe cooling barrel. The liquid smoke produced is accommodated in a plastic bottle when it first drips, and the temperature is recorded. Every increase at 50ºC, liquid smoke resulted was accommodated in another plastic bottle. Then the heating process was stopped until no more liquid smoke drips. The liquid smokes obtained were mixed with tar, so the separation was carried out by distilling the liquid smokes. After the liquid smokes have been produced, the compounds were determined using Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared (FT-IR).

3 RESULT AND DISCUSSION

Based on the research that has been carried out, the liquid smoke palm shell was obtained at a heating temperature of 600 to 900ºC, where the liquid smoke results were collected with a temperature interval variation of 50ºC which is indicated in Table 1

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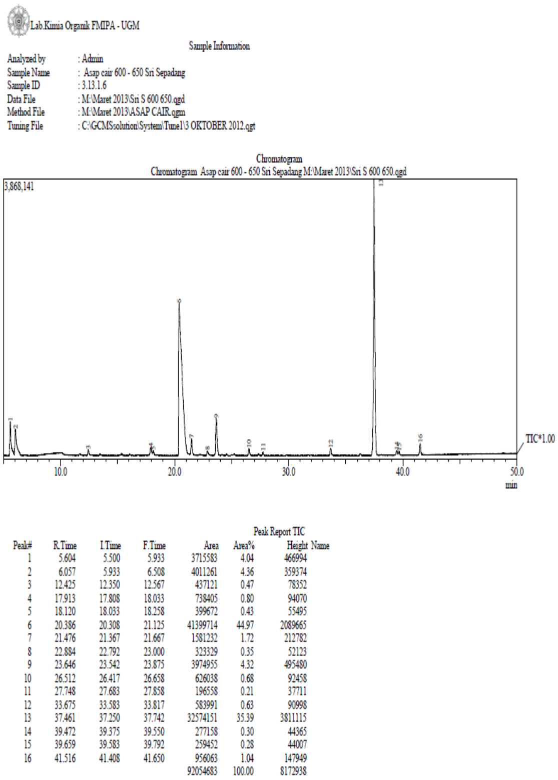
Table 1. Liquid smoke volume at various pyrolysis temperatures of palm oil shell

No	Temperature (ºC)	Liquid Smoke Volume (mL)
1	600-650	42.0
2	650-700	39.0
3	700-750	35.1
4	750-800	31.5
5	800-850	29.0
6	850-900	24.0
7	900-950	20.0
	Total	**221.0**

3.1 Identification of Liquid Smoke Compounds Using GC-MS

Based on the identification results of the liquid smoke content using GC-MS were obtained the peak chromatogram and the suspected compound to be contained in liquid smoke were obtained at ±600 to 650ºC, ±750 to 800ºC, ±900 to 950ºC, which are presented in figures 1 to 3, and in Table 2 to 4.



Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Name
1	5.604	5.500	5.933	3715583	4.04	466994	
2	6.057	5.933	6.508	4011261	4.36	359374	
3	12.425	12.350	12.567	437121	0.47	78352	
4	17.913	17.808	18.033	738405	0.80	94070	
5	18.120	18.033	18.258	399672	0.43	55495	
6	20.386	20.308	21.125	41399714	44.97	2089665	
7	21.476	21.367	21.667	1581232	1.72	212782	
8	22.884	22.792	23.000	323329	0.35	52123	
9	23.646	23.542	23.875	3974955	4.32	495480	
10	26.512	26.417	26.658	626038	0.68	92458	
11	27.748	27.683	27.858	196558	0.21	37711	
12	33.675	33.583	33.817	583991	0.63	90998	
13	37.461	37.250	37.742	32574151	35.39	3811115	
14	39.472	39.375	39.550	277158	0.30	44365	
15	39.659	39.583	39.792	259452	0.28	44007	
16	41.516	41.408	41.650	956063	1.04	147949	
				92054683	100.00	8172938	

Figure 1. Chromatogram of the liquid smoke palm shell analysis at 600 to 650ºC

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A.

Tabel 2. The compound analysis results of liquid smoke palm shells at 600 to 650ºc using GC-MS

No	Molecular Formula	Area (%)	Fragmentation	Suspected Compound
1	CH_3H_6O	4.04	58,43,39	Dimethyl ketone
2	CH_3OH	4.36	33,32,31	Methanol
3	C_5H_5N	0.47	79,52,39	pyridine
4	C_5H_6O	0.80	82,56,54,39	5-Methylfuran
5	C_6H_8O	0.43	96,81,67,53,39	2-Methyl-2-Cyclopentanone
6	$C_2H_4O_2$	44.97	60,43,41	Acetic acid
7	$C_5H_4O_2$	1.72	96,73,67,43,39	2-Furaldehyde
8	$C_6H_6O_2$	0.35	110,95,71,67,39	Acetylfuran
9	$C_3H_6O_2$	4.32	74,57,45	Propionic Acid
10	$C_4H_8O_2$	0.68	88,73,60,41	Butanoic Acid
11	$C_5H_6O_2$	0.21	98,81,60,42,41	Furfuryl Alcohol
12	$C_7H_8O_2$	0.63	124,109,95,81,65,53,39	p-Methoxyphenol
13	C_6H_6O	35.39	94,74,66,55,39	Phenol
14	C_7H_8O	0.30	108,91,79,51,39	p-Methylphenol
15	C_7H_8O	0.28	108,91,79,51,39	o-Methylphenol
16	$C_{10}H_{12}O_2$	1.04	164,149,131,121,103,91,77,65,55,39	Eugenol

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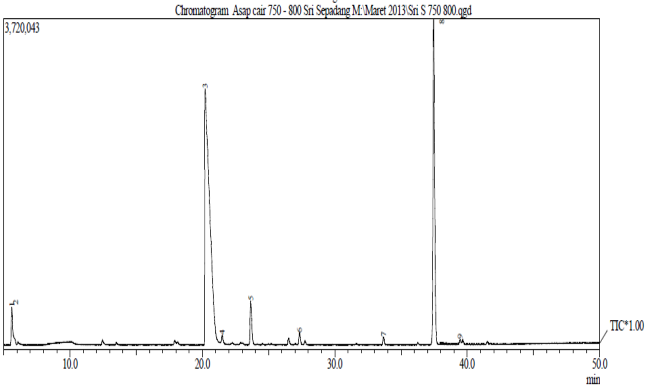
Lab.Kimia Organik FMIPA - UGM

Sample Information

Analyzed by	: Admin
Sample Name	: Asap cair 750 - 800 Sri Sepadang
Sample ID	: 3.13.1.6
Data File	: M:\Maret 2013\Sri S 750 800.qgd
Method File	: M:\Maret 2013\ASAP CAIR.qgm
Tuning File	: C:\GCMSsolution\System\Tune1\3 OKTOBER 2012.qgt

Chromatogram

Chromatogram Asap cair 750 - 800 Sri Sepadang M:\Maret 2013\Sri S 750 800.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Name
1	5.604	5.508	5.767	3039005	2.75	418506	
2	5.892	5.767	5.933	472394	0.43	31264	
3	20.202	20.133	21.100	70258742	63.51	2872473	
4	21.487	21.417	21.608	417008	0.38	69555	
5	23.643	23.533	23.858	3893408	3.52	485113	
6	27.331	27.233	27.483	892848	0.81	124929	
7	33.681	33.592	33.775	431231	0.39	71841	
8	37.462	37.283	37.733	30890846	27.92	3649074	
9	39.462	39.400	39.725	337152	0.30	38085	
				110632634	100.00	7760840	

Figure 2. Chromatogram of the liquid smoke palm shell analysis at 750 to 800ºC

Tabel 3. The compound analysis results of liquid smoke palm shells at 750 to 800ºC using GC-MS

No	Molecular Formula	Area (%)	Fragmentation	Suspected Compound
1	C_3H_6O	2.75	58,43,39	Dimethyl ketone
2	C_3H_6O	0.43	58,43,39	Dimethyl ketone
3	$C_2H_4O_2$	63.51	60,43,41	Acetic acid
4	$C_5H_4O_2$	0.38	96,73,67,39	2-Furaldehyde
5	$C_3H_6O_2$	3.52	74,57,45	Sour Propanoate
6	$C_4H_6O_2$	0.81	86,56,42	Butyrolactone
7	$C_7H_8O_2$	0.39	124,109,81,53	o-Methoxyphenol
8	C_6H_6O	27.92	94,74,66,55,39	Phenol
9	$C_7H_8O_2$	0.30	107,90,77,63,51	p-Methyl Phenol

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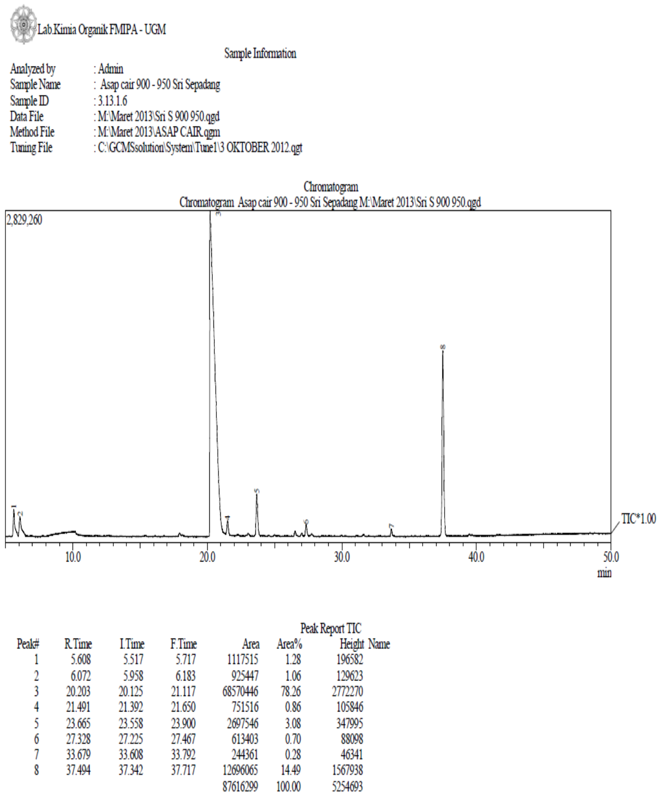

Figure 3. Chromatogram of Palm Shell Liquid Smoke Analysis at 900 to 950ºC

Tabel 4 The compound analysis results of liquid smoke palm shells at 900 to 950ºC using GC-MS

No	Molecular Formula	Area (%)	Fragmentation	Suspected Compound
1	C_3H_6O	1.28	58,43,39	Dimethyl ketone
2	CH_3OH	1.06	33,32,31	Methanol
3	$C_2H_4O_2$	78.26	60,43,41	Acetic acid
4	$C_5H_4O_2$	0.86	96,73,67,43,39	2-Furaldehyde
5	$C_3H_6O_2$	3.08	74,57,45	Propanoic Acid
6	$C_4H_6O_2$	0.70	86,56,42	Butyrolactone
7	$C_7H_8O_2$	0.28	124,109,95,81,53	o-Methoxyphenol
8	C_6H_6O	14.49	94,74,66,55,39	Phenol

3.2 Identification of Liquid Smoke Compounds Using FT-IR

FT-IR test results indicated in figure 4 show that the three typical bands found in liquid smoke at 600 to 650ºC were the band at 3435.0 cm^{-1}, which indicated the presence of OH groups, the band at 2067.14 cm^{-1}, which showed aromatic benzene, and the band at 1633.5 cm^{-1}, which

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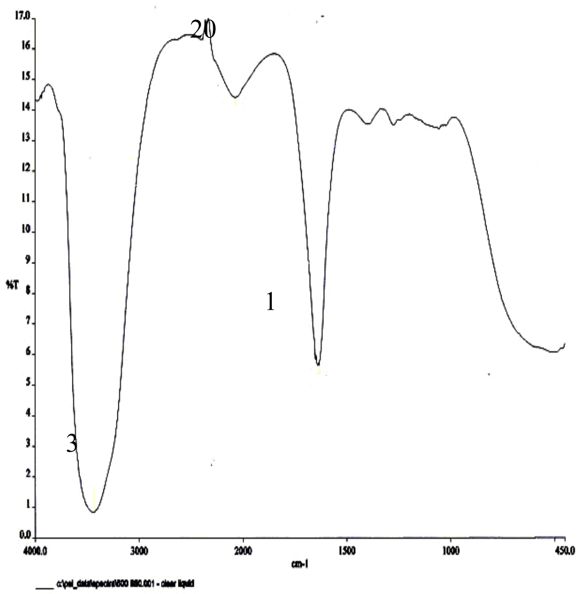
assigned C=C bond or N-H groups. In addition, the band found in liquid smoke at 750 to 800ºC were the band at 3400 cm^{-1}, which showed the presence of OH groups, the band at 2077.96 cm^{-1}, which assigned aromatic benzene, the band at 1633.89 cm^{-1}, which indicated C=C bond or N-H groups, and the band at 1272.96 cm^{-1}, which showed C-O bonds as presented in figure 5. Furthermore, the bands were also observed in liquid smoke at 900 to 950ºC spectra as shown in figure 6 which shows that the band at 3435 cm^{-1}, which indicated the presence of OH groups, and the band at 2075.8 cm^{-1}, which showed aromatic benzene, the band at 1637.2 cm^{-1}, which



assigned C=C bonds or N-H groups, and the band at 1273.7 cm^{-1}, which indicated C-O bonds.

Figure 4. Spectra data of liquid smoke palm oil shell at 600 to 650ºC

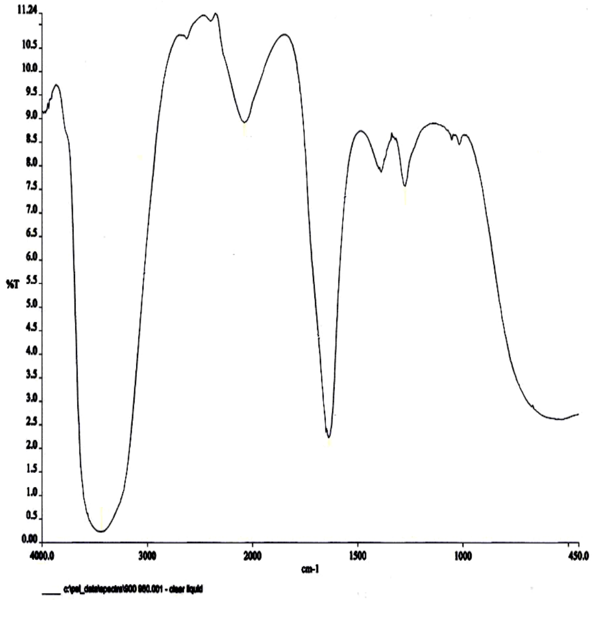


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Figure 5. Spectra data of liquid smoke palm oil shell at 750 to 800ºC

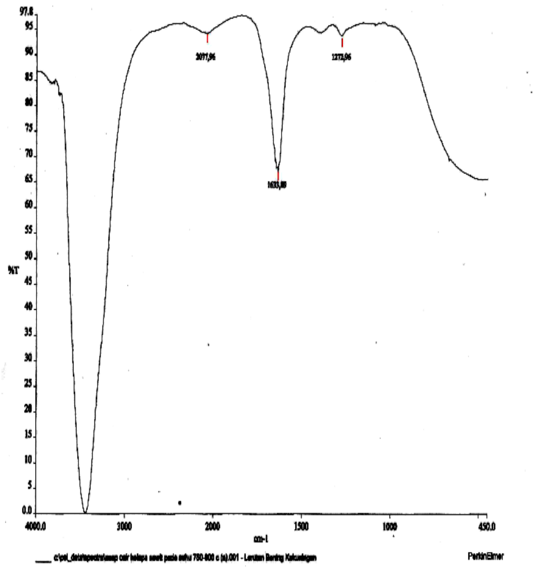

Figure 6. Spectra data of liquid smoke palm oil shell at 900 to 950ºC

4 Conclusion

In conclusion, liquid smoke palm oil shells were successfully fabricated via a pyrolysis reactor. This is supported by the characterization result obtained from GC-MS and FT-IR. Liquid smokes were also found to be potential materials for food preservatives. In this study, GC-MS analysis showed that no found carcinogenic PAH compounds were in the liquid smoke and the largest content contained in the liquid smoke were acetic acids, phenol, and propanoic acid compounds. This is because the higher the pyrolysis temperature used so the higher the organic acid concentration obtained from liquid smoke.

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