

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 950°C with temperature intervals at 50°C. 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

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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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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 to 150°C, followed by the second stage of the hemicellulose pyrolysis process at 150 to 200°C, then the third stage of the cellulose pyrolysis process at 250 to 300°C, and the fourth stage is the lignin pyrolysis process at 400°C. 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 500°C (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.

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 900°C 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, $T = 1000^{\circ}\text{C}$), 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 50°C , 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 900°C , where the liquid smoke results were collected with a temperature interval variation of 50°C which is indicated in Table 1

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

No	Temperature (°C)	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 650°C , ± 750 to 800°C , ± 900 to 950°C , which are presented in figures 1 to 3, and in Table 2 to 4.

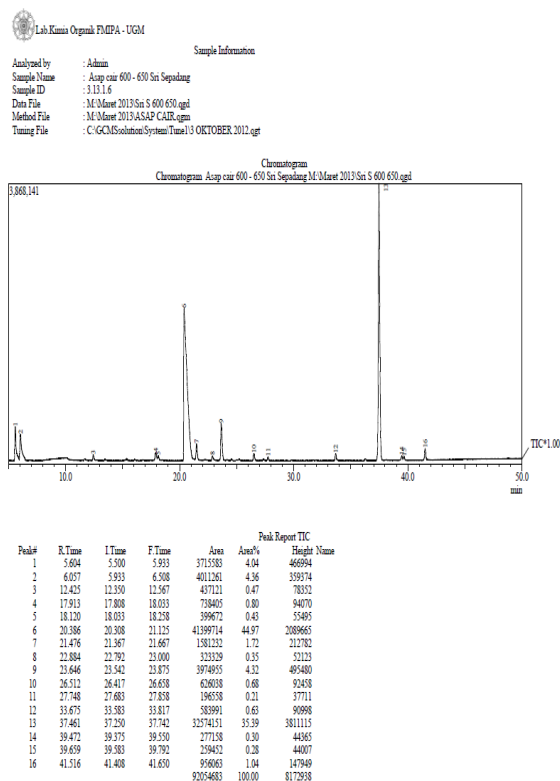


Figure 1. Chromatogram of the liquid smoke palm shell analysis at 600 to 650°C

A.

Table 2. The compound analysis results of liquid smoke palm shells at 600 to 650°C using GC-MS

No	Molecular Formula	Area (%)	Fragmentation	Suspected Compound
1	CH ₃ H ₆ O	4.04	58,43,39	Dimethyl ketone
2	CH ₃ OH	4.36	33,32,31	Methanol
3	C ₅ H ₅ N	0.47	79,52,39	pyridine
4	C ₅ H ₆ O	0.80	82,56,54,39	5-Methylfuran
5	C ₆ H ₈ O	0.43	96,81,67,53,39	2-Methyl-2-Cyclopentanone
6	C ₂ H ₄ O ₂	44.97	60,43,41	Acetic acid
7	C ₅ H ₄ O ₂	1.72	96,73,67,43,39	2-Furaldehyde
8	C ₆ H ₆ O ₂	0.35	110,95,71,67,39	Acetylfuran
9	C ₃ H ₆ O ₂	4.32	74,57,45	Propionic Acid
10	C ₄ H ₈ O ₂	0.68	88,73,60,41	Butanoic Acid
11	C ₅ H ₆ O ₂	0.21	98,81,60,42,41	Furfuryl Alcohol
12	C ₇ H ₈ O ₂	0.63	124,109,95,81,65,53,39	p-Methoxyphenol
13	C ₆ H ₆ O	35.39	94,74,66,55,39	Phenol
14	C ₇ H ₈ O	0.30	108,91,79,51,39	p-Methylphenol
15	C ₇ H ₈ O	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

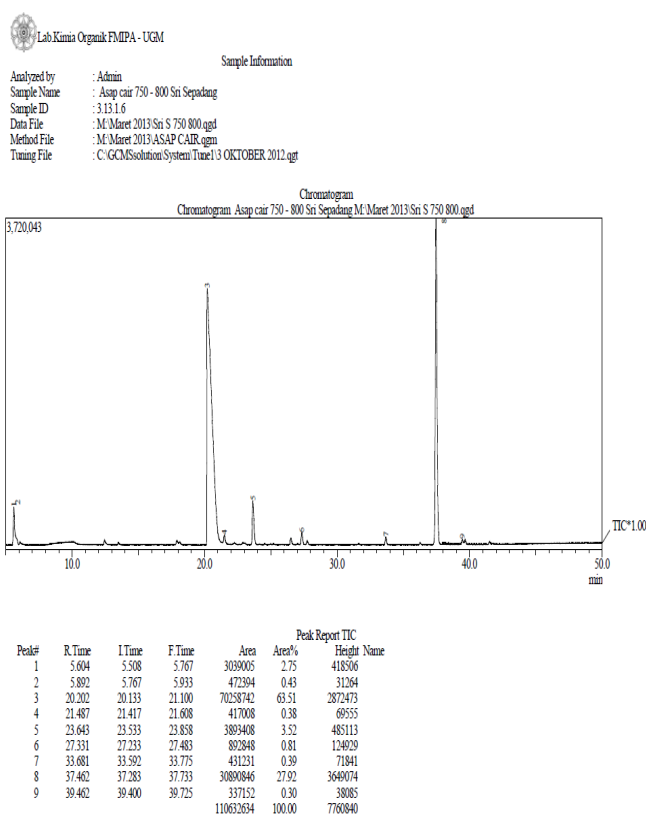


Figure 2. Chromatogram of the liquid smoke palm shell analysis at 750 to 800°C

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

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

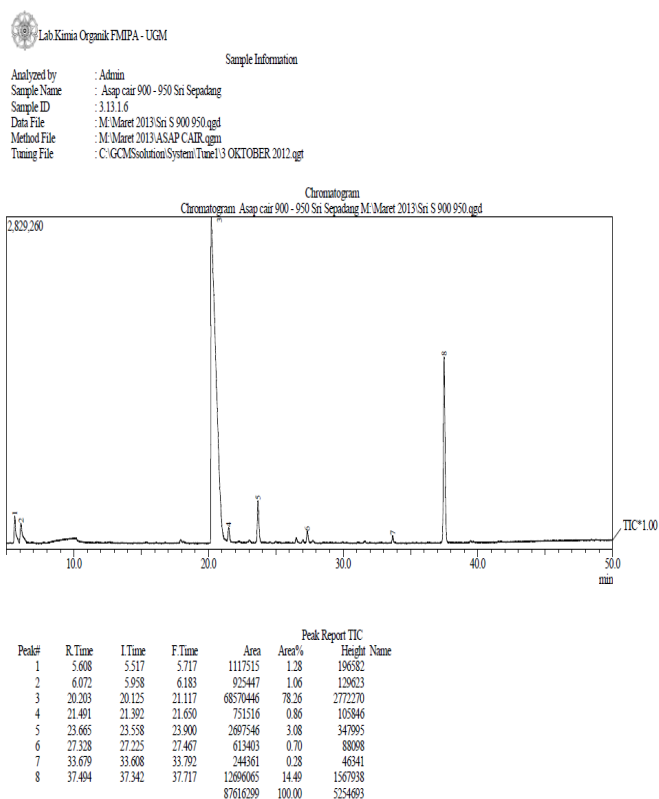


Figure 3. Chromatogram of Palm Shell Liquid Smoke Analysis at 900 to 950°C

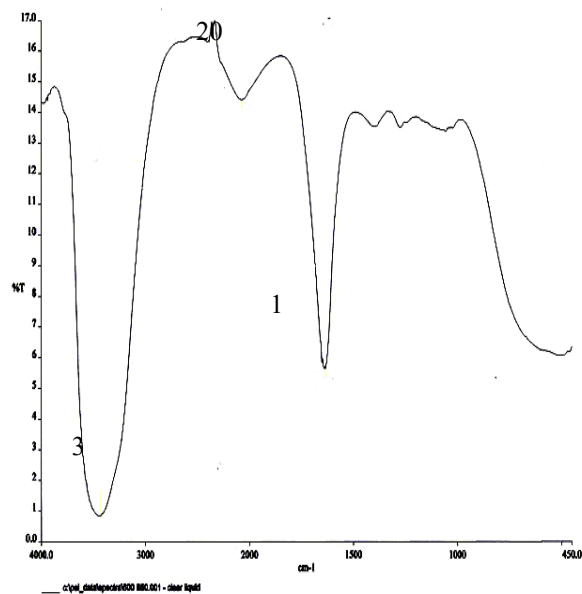
Tabel 4 The compound analysis results of liquid smoke palm shells at 900 to 950°C using GC-MS

No	Molecular Formula	Area (%)	Fragmentation	Suspected Compound
1	C ₃ H ₆ O	1.28	58,43,39	Dimethyl ketone
2	CH ₃ OH	1.06	33,32,31	Methanol
3	C ₂ H ₄ O ₂	78.26	60,43,41	Acetic acid
4	C ₅ H ₄ O ₂	0.86	96,73,67,43,39	2-Furaldehyde
5	C ₃ H ₆ O ₂	3.08	74,57,45	Propanoic Acid
6	C ₄ H ₆ O ₂	0.70	86,56,42	Butyrolactone
7	C ₇ H ₈ O ₂	0.28	124,109,95,81,53	o-Methoxyphenol
8	C ₆ H ₆ O	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 650°C 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

assigned C=C bond or N-H groups. In addition, the band found in liquid smoke at 750 to 800°C 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 950°C 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 650°C

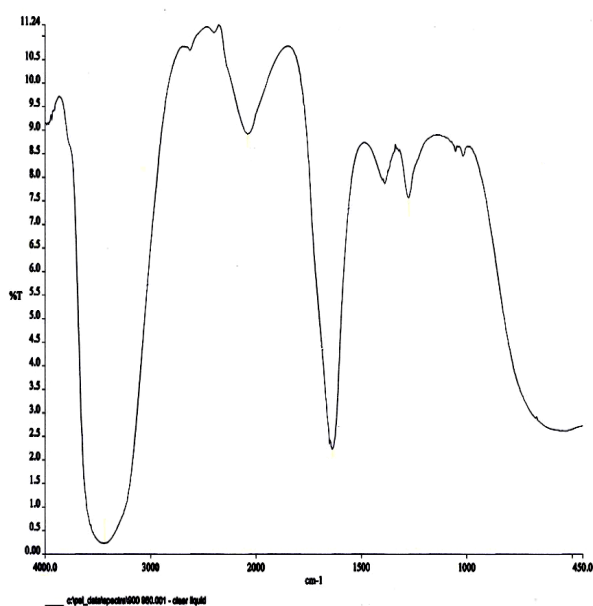


Figure 5. Spectra data of liquid smoke palm oil shell at 750 to 800°C

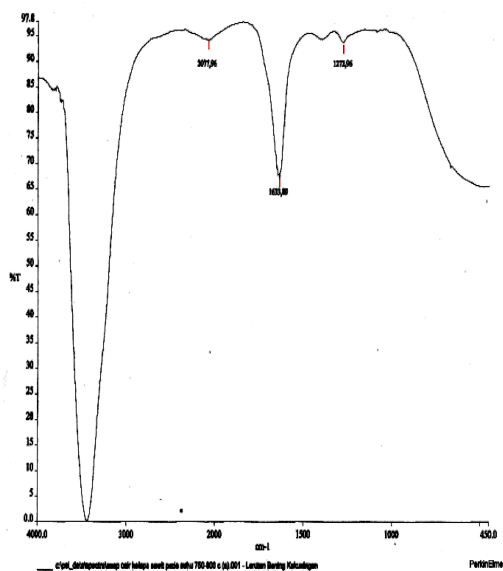


Figure 6. Spectra data of liquid smoke palm oil shell at 900 to 950°C

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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