International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.06 pp 694-708, 2016

Analysis of Liquid Smoke Chemical Components with GC MS from Different Raw Materials Variation Production and Pyrolysis Temperaturelevel

I Ketut Budaraga[1]*, Arnim[2], Yetti Marlida[2], Usman Bulanin[3]

[1]Agricultural Technology Department, Faculty of Agricultural Ekasakti University, Veteran Dalamstreet 21th Padang, Indonesia
[2]Animal Production Department, Faculty of Animal Husbandry Andalas University Limau Manis street Padang City, Indonesia
[3]Fisheries Cultivation Department, Faculty of Fishires Bung Hatta University, Sumatra street Padang city, Indonesia

Abstract : This study aims to determine chemical components of liquid smoke obtained from pyrolysis from various raw materials (coconut fiber, coconut shells, cinnamon) with different pyrolysis levels on temperature of 100±10°C; 200±10°C; 300±10°C; and 400±10°C. This research is performed experimentally by measuring the chemical components using GC-MS. The measured parameterare the chemical components of liquid smoke. The results of research shows that the combination of raw materials with different pyrolysis temperature affects the content of chemical compounds in liquid smoke. Acetic acid and phenol are the most dominant compound of all liquid smoke samples, liquid smoke of coconut shell raw materials at pyrolysis temperature of 100°C has the highest chemical component of acetic acid and phenol at 62.20% and 22.26%. Furthermore, on cinnamon raw material at different pyrolysis temperature shows results that there are lots of chemical components and the measuringresult of liquid smoke using GC-MS also shows that chemical component of cinnamon liquid smoke at pyrolysis temperature of 100°C, 200°C, 300°C and 400°C has different chemical component area with liquid smoke of coconut fiberand coconut shell.
Key words: chemical components, *raw material, temperature, liquid smoke, chemical components, GC MS.*

Introduction

Liquid smoke is the condensation result of wood pyrolysis that contains many compounds formed by pyrolysis constituent process such as cellulose, hemicellulose and lignin that will produce organic acids, phenols, carbonyl compounds that have the role in food preservation. Those compounds have different proportions depending on the type, wood moisture content and temperature pyrolysis[1].

In this study, the writers use coconut fiber, coconut shell and cinnamon as liquid smoke raw material combined with pyrolysis temperature. Coconut shell and cinnamon are classified as hardwood type because there is enough lignin level, while coconut fiber is classified as soft wood type. Phenol is a disinfectant and antiseptic compound that is effective against positive gram and negative gram vegetative bacteria form, mycobakteria, fungi and viruses are not effective against spore form. In the form of liquid up to concentration of 1%, phenol has function as bacteriostatic whereas at higher concentrations it can act as bacterosidol, phenol at concentration of 0.5-1% can be used as local anesthetic and can be injected up to 10ml in the tissue as an analgesic[2].

Lignin is a complex polymer that has high molecular weight composed of phenyl propane units. The compounds derived from pyrolysis on lignin basic structure has important role in providing smoke scents on products. These compounds are phenol, phenol ethers such as guaiacol, siringol and homologues and its derivatives. Lignin begins to decompose at temperatures 300-350°C and at 400-450°C. The chemical components in the smoke have significant role in determining the quality of smoked products because apart from forming the flavor, texture and typical smoked color, it can also inhibit product damage[3].

All of wood distillate type contains compounds that can be extracted as phenol derivatives which can inhibit microbes' growth. Liquid smoke of the wood is used as preservative because there is similarity of chemical components contained in wood distillate on certain type of preservatives, where the compounds that act as preservatives are phenol and its derivatives. The efforts in providing added value from plantations waste crops in West Sumatra province still has not received optimal treatment such as coconut fiber, coconut shell and cinnamon, so it is necessary to study its chemical components. Liquid smoke produced in high temperature pyrolysis process in this study will analyze the chemical components by using GC-MS equipment. The purpose of this study is to determine the chemical components of liquid smoke from the treatment treatment combination of raw materials such as coconut fiber, coconut shell and cinnamon with different pyrolysis temperature.

Experimental

Tools and Materials

Tools and instruments that are used in this study among others are laboratory glassware, test tube rack, aluminum foil, evaporator paper filter, vortex, desiccator, hot plate, aerator, oven. analytical scales, label paper, rulers, pencils, aluminum foil, plastic, filter paper, cotton, erlenmeyer flask, becker glass, measuring cups, funnels, test tubes, stirrer, pipette, glass bottles, weighing bottle, measuring cups, oven, a set of rotary vacuum evaporator, centrifuge tools, volume pipettes, micro pipette, and perforator. The tools that are used in pyrolysis[4] consist a set of laboratory scale liquid smoke tools maker that consists of drum unit (kiln) stainless steel with capacity 3 kg, a condenser unit, glass pipes to release the smoke, distillate container (liquid smoke), gas stove with 1 furnace, water pumps, water containers, water hose, valve, PVC pipes, poles, clamps, thermometer, cable, jack, stop watch, measuring cups, microliter syringes 10 ml, luer lock syringe with diameter 25 mm-0.45 mm PVDF, lour lok syringes 10 ml, vials B x 40 mm and GC MS QP2010 and other tools such as electric stove, thermometer 500°C, erlenmeyer 125 ml and 500 ml, glass cup, centrifuge tube.

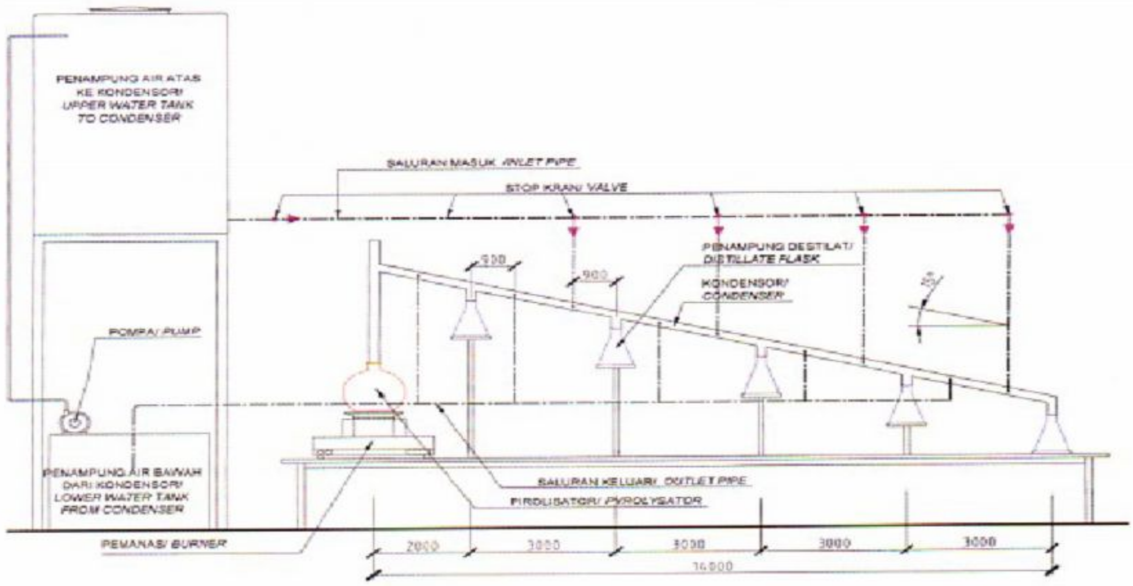
Materials and chemical reagents that are used in this study are coconut fibers and coconut shells wastes obtained from Pasar Raya Padang and cinnamon that has been cleaned from the outer skin is obtained from cinnamon farmers in Tanah Datar.

Research Implementation

The stages on the implementation of this study consist of three phases:

1. Assembling liquid smoke pyrolysis tool

Liquid smoke extraction tool are made at laboratory scale that refers to the results of research and the characteristics of liquid smoke [4]. In this study, it uses liquid smoke tool maker which consists one unit of condenser with water container of drum capacity of 100 liters equipped with water pump to circulate cooling water for 14 meter with hose for water circulation, liquid smoke container of 5 Erlenmeyer tube with capacity of 500 ml, stainless stell kiln with capacity of 3 kg and LPG burner stove and at the end of pyrolysis pipe is equipped with vacuum pump to suck the smoke in order to obtain liquid smoke as in Figure 1 below.



Gambar 1. Alat penghasil asap cair skala laboratorium.

Figure 1. Laboratory Scale Liquid Smoke Tool Maker

2. Liquid smoke (production) pyrolysis process

Research on the production of liquid smoke by using pyrolysis refers to the above research activities as input in redesigning laboratory scale liquid smoke maker tool. After liquid smoke tool maker has been assembled then it is continued with liquid smoke production. This process is started from raw material preparation of dry coconut fiber, coconut shell and cinnamon with each material weights of 40 kg with water content ranges on 4-10%, then the materials are cleaned from dirt. Then, raw materials are cut in small and uniform size of ± 4- 9 cm^2. The next activities are to put the raw materials into pyrolysis reactor for five (5) hours with each sample weights around 3 kg at temperature of 100±10^{o}C; 200± 10^{o}C; 300±10^{o}C; 400±10^{o}C, by using LPG burner stove. Water pump is used to channel the water from water source into the condenser. Burner and water pump are switched on simultaneously. Distillate container (liquid smoke) is collected by using glass bottles. Temperature is measured by using thermometer and the measurements are performed every ½ hour at several places, which are in pyrolysator, distillates container, water resources, as well as condenser inlet and outlet. After 5 hours, it will produce three fractions, which are solid fraction in form of carbon, heavy fraction in form of tar, and light fraction in form of smoke and methane gas. Then light fraction is channeled into condensation pipe in order to produce liquid smoke while methane gas remains in gas form and is not condensed. Liquid smoke then are let to sit for one week, then the analysis is made. The purpose of deposition for 1 (one) week is to precipitate dirts in liquid smoke. After liquid smoke is sitted for 1 (one) week, then cytotoxic analysis is performed.

3. Chemical Component Analysis (gas)

Liquid smoke gas (aromatic compound) component analysis uses variety of methods[5, 6, 7, 10]. Measurement uses GC MS, which is Shimadzu type QP 2010, by using operational conditions as follows: Gas: Helium, Column: RTX-1MS, Stationary phase: Polymetilsiloxant, Temperature: Injector: 280°C, Oven: 80°C - 280°C, 20°C/min, Interface: 300^{o}C, Control modes: Split, Column flow: 1:14 ml/min, Split ratio: 200, Ionization mode: Electron Impact, Solvent delay: 3 minutes, M / Z: 45.00 - 350.00

The procedure of analysis with GC MS is performed on liquid smoke fractions of 12 samples that are derived from three liquid smoke ingredients combination such as coconut fiber, coconut shell and cinnamon is pyrolyzedat temperature 100+10^{o}C, 200+10^{o}C, 300+10^{o}C dan 400+10^{o}C.Sample preparation is previously performed: liquid smoke that will be analyzed is deposited for one week then it is filtered by using Whatmanno.42 filter paper. Filtering is repeated by using microliter syringes and syringe filters. The filter result is diluted with methanol up to 1000 times, then the time to check operating conditions GC MS QP2010 such as: Operating conditions GC MS QP2010 when it is used for analysis as follows: oven temperature 75°C is maintained for 5 minutes, then it is increased up to 130°C with temperature increase rate of 8°C/minutes and is maintained for 3 minutes, then it is increased again to 290°C with temperature increase speed of 10°C/minutesthat is maintained for 3 minutes and then it is increased again to temperature of 300°C for 24 minutes. Ion source temperature is 200°C. Helium is used in this analysis had 99.999% purity. Regulated gas pressure is 75.0 kPa and gas flow rate is 0.57 ml/min, while injector temperature is 250°C. When the condition of GC MS is ready to be operationalized then it is inserted into sample tube and is injected into GC MS QP2010 with the procedure of liquid smoke sample 0.2 µlis injected in GC MS (tool conditions has already been programmed) with specification: the used column is GL capillary column science TC 17 (0.25 mm x 30 m, helium carrier gas, initial temperature of 50°C (hold for 5 minutes), final temperature of 250°C at a temperature increase rate of 4°C per minute, 40-45 Kpa pressure, interface temperature of 230°C with ionization energy 120 kv (mass range 33-400). Mass spectrum interpretation of analysis results is done by comparing mass spectrum in NIST 62 data base.

Results and Discussion

GC-MS analysis is performed in order to determine the compounds types that are contained in liquid smoke. The mixture of compounds that are passed to gas chromatography will be separated into individual components. Compounds from each liquid smoke sample can be seen in table 1, 2 and 3, below. Full peak graph in liquid smoke components on different raw materials treatment combination with different pyrolysis temperature can be seen in the pictures 2,3,4,5,6,7,8,9,10,11,12, and 13.

Table 1. Ten dominant compounds in coconut fiberliquid smoke as the result of GC MS detection with four different pyrolysis temperatures

No	Liquid smoke type	Pyrolysis temperature	Chemical components	RT (retention)	(%)area
1	Coconut fiber	Temperature 100 ±10°C	**1.Acetic acid**	**13.77**	**41.56**
			2.Phenol	**33.74**	**31.54**
			3.Phenol,4-Methyl- 2-Furancarboxaldehyde 3-Furaldehyde-	14.7	5.56
			4. Phenol,2-Methoxy-	28.32	4.75
			5. Phenol,4-Methyl-	36.37	3.18
			6. Propionic Acid	17.16	2.73
			7. 2(3H)-Furanone,dihydro- Gamma.Butirolactone Butan-4-Olide	19.92	1.83
			8. Phenol,4-Methyl- Phenol,3-Methyl	36.58	1.29
			9.2-Cyclopenten-1-one	10.30	1.13
			10. 2-Methoxy-4-Methylphenol	31.55	1.11
		Temperature 200 ± 10°C	**1.Phenol**	**33.74**	**39.00**
			2.Acetic Acid	**13.81**	**33.94**
			3.Phenol,4-Methyl- Phenol,3-Methyl	36.37	5.20
			4. 2-Furancarboxaldehyde Pyrazole,1,4-Dimethyl 1H-pyrazole,3,5-Dimethyl	14.07	5.08

			5. Phenol,2-Methoxy	28.32	4.97
			6. Propionic Acid	17.16	2.22
			7. Phenol,4-Methyl Phenol,3-Methyl	36.58	1.68
			8. Gamma.Butirolactone Butan-4-Olide 2(3H)-Furanone,dihydro	19.89	1.43
			9. Phenol,4-Ethyl Phenol,3-Ethyl	38.55	1.23
			10. 2-Methoxy-4-Methylphenol	31.56	1.22
		Temperature 300 ± 10°C	**1. Acetic acid**	**13.73**	**50.18**
			2. Phenol	**33.73**	**32.65**
			3. Phenol, 4-methyl-	36.36	3.88
			4. Phenol, 2-methoxy-	28.31	3.06
			5. Propionic acid	17.14	2.81
			6. GAMMA. BUTYROLACTONE. 2(3H)-Furanone,dihydro Butan-4-Olide	19.90	1.57
			7. Phenol, 4-methyl- Phenol, 3-methyl	36.57	1.40
			8. Phenol, 4-ethyl- Phenol, 3-ethyl- Phenol, 2-ethyl-	38.54	0.89
			9. BUTANOIC ACID	20.43	0.86
			10. 2-methoxy-4-methylphenol	31.55	0.72
		Temperature 400 ± 10°C	**1. Acetic acid**	**13.77**	**39.36**
			2. Phenol	**33.73**	**35.91**
			3. 2-furancarboxaldehyde 1H-pyrazole,3,5-Dimethyl- 2-Furancarboxaldehyde	14.06	4.94
			4. Phenol,2-Methoxy	28.31	4.93
			5. Phenol, 4-methyl Phenol, 3-methyl	36.36	4.82
			6. Propionic acid	17.15	2.38
			7. Phenol, 3-methyl- Phenol, 4-methyl-	36.57	1.48
			8. 2-methoxy-4-methylphenol	31.55	1.39
			9. Phenol, 4-ethyl- Phenol, 3-ethyl- Phenol, 2-ethyl-	38.55	1.39
			10.Gamma.Butirolactone 2(3H)-puranone,dyhidro-	19.89	1.28

From the results of gas chromatography spectra at coconut fiber liquid smoke, the dominant compounds of each peak in the sample are acetic acid and phenol with various area volume. The biggest chemical components in pyrolysis temperature of 100°C, 300°C dan 400°C are acetic acid respectively at 41.56%, 50.18% and 39.36%, while the second component is phenol compounds respectively at 31.54%, 32, 65% and

39.36%. This result is somewhat different from the results of study[8], which uses the raw materials from various types of wood and coconut shell at combustion temperatures of 350-400°C, where the dominant compound of liquid smoke in this research is phenol with total area volume of 44.13%. The chemical components of coconut fibers liquid smoke on pyrolysis of 200°C shows that the biggest component is phenol at 39.00% and asetic acid at 34.94%. This result is nearly similar with the results of study[8]

According to results of study[11], it shows that 2 kg of rice fiber can produce 154 ml liquid smoke, meanwhile for liquid smoke characterization grade 3 is produced at value pH 2, liquid smoke grade 2 with value pH 2 and grade 1 liquid smoke with value pH 4. Analysis GC- to identify the presence of 17 compounds in grade 1 liquid smoke. Research[12] aims to determine phenol content in liquid smoke from palm kernel shells (ACCKS) that is produced at temperature 600°C, 700°C, 800°C. Pyrolysis process is performed by using furnace tool that is covered with inflammable white cement in the surrounding so that the smoke does not escape into the air and produced liquid smoke will be maximal. Temperatures that are used 600°C, 700°C, 800°C by using spiral type condenser with 30 windings. The produced liquid smoke is deposited for 7 days and then it is put in the centrifuge with rotation speed of 3800 rpm for 60 minutes, filtered and distilled at 125°C temperature for 60 minutes. Liquid smoke are analyzed (characterization) by using GC-MS and phenol are identified for each temperature, at temperature 600°C is 35.09%, temperature 700°C is 37.962% and the temperature 800°C is 37.494%.

Table 2. Ten dominant compounds in coconut shell liquid smoke as the reault of GC MS detection with four different pyrolysis temperatures

No	Liquid smoke type	Pyrolysis temperature	Chemical components	RT (Retention)	(%) area
2	Coconut shell	Temperature 100 ±10°C	**1. Acetic acid**	**13.53**	**63.60**
			2. Phenol	**33.79**	**22.26**
			3. Furancarboxaldehyde	14.06	3.64
			4.Phenol, 2-methoxy-	28.34	2.70
			5. Propionic acid	17.14	1.99
			6. Phenol, 2,6-dimethoxy	40.13	0.88
			7.2-propanone, 1-hydroxy Acetic acid, methyl ester 2-propanone, 1-hydroxy	8.57	0.66
			8. 1,2-BUTAN 2(3H)-Furanone,dihydro- 2(3H)-Furanone,dihydro-	19.83	0.54
			9. 1-Hydroxy-2-Butanone Propanoic Acid,2,2-Dimethyl	10.87	0.51
			10. 2-Cyclopenten-1-one	10.13	0.40
		Temperature 200 ±10°C	**1.Acetic Acid**	**13.27**	**34.04**
			2. Acetic Acid	**13.00**	**23.83**
			3. Phenol	**33.65**	**18.97**
			4Phenol,2-Methoxy	28.33	3.20
			5. Acetic Acid	12.98	2.78
			6. 2-Furancarboxaldehyde	14.09	2.19
			7. Propionic Acid Propanoic Acid	17.03	2.17
			8. 2-Propanone,1-Hydroxy	8.86	1.48

			Acetic Acid,Methyl Ester		
			9. 1-Hydroxy-2-Butanone 3-Furanol,Tetrahydro	11.07	1,01
			10. 2-Methoxy-4- Methylphenol	31.56	0.87
		Temperature 300 ±10^{o}C	**1. Phenol (E)-Hex-2-en-4ynal**	**33.46**	**35.35**
			2. Phenol,2-Methoxy	**28.33**	**7.78**
			3. Propionic Acid Propanoic Acid	**16.91**	**6.17**
			4.Phenol,3,4-Dimethoxy Phenol,2,6-Dimethoxy Phenol,3,6-Dimethoxy	**40.13**	**3.94**
			5. Acetic Acid	**12.36**	**3.79**
			6. Acetic Acid,Methyl Ester	9.78	3.15
			7. Furfural 2-Furancarboxaldeyde	14.17	3.14
			8. 2-Methoxy-4- Methylphenol Benzen,1,4-Dimethoxy	31.56	2.82
			9. 1-Hydroxy-2-Butanone Propanoic Acid, 2,2- Dimethyl	11.77	2.58
			10. Acetic Acid	12.40	2.41
		Temperature 400 ±10^{o}C	**1. Acetic Acid**	**13.28**	**40.20**
			2. Phenol	**33.63**	**23.45**
			3. Acetic Acid	13.21	7.63
			4.Acetic Acid	13.12	4.80
			5. Phenol,2-Methoxy	28.32	3.70
			6. Phenol,3,4-Dimethoxy Phenol,2,6-Dimethoxy	40.11	2.83
			7.2-Furancarboxcaldehyde	14.08	2.09
			8. Acetic Acid,Methyl ester 3-Propanone,1-Hydroxy 1-Propanol,2-Methyl	8.65	1.82
			9. Propionic Acid Propanoic Acid	16.99	1.74
			10. 2-Methoxy-4- Methyphenol Benzene,1,4-Dimethoxy	31.56	1.23

From the results of gas chromatography spectra at coconut shell liquid smoke, the dominant compounds of each peak in the sample are acetic acid and phenol with various area volume. The biggest chemical components in pyrolysis temperature of 100^{o}C, 200^{o}C dan 400^{o}C are acetic acid respectively at 63,60%, 34,04%, dan 40,20% while the second component is phenol compounds respectively at 22,26%, 18,97% dan 23,45%. This result is somewhat different from the results of study[8], which uses the raw materials from various types of wood and coconut shell at combustion temperatures of 350-400°C, where the dominant compound of liquid smoke in this research is phenol with total area volume of 44.13%. The chemical components of coconut shell liquid smoke on pyrolysis of 300^{o}C shows that the biggest component is phenol at 35,35% and propionic acid at 6,17%. This result is nearly similar with the results of study[8].

In the research[13]of slow pyrolysis on firwood (AbiesbornmüllerianaMattf.) sawdust by using fixed-bed reactor,the effect of temperature ranges between 350 and 600°C on gas, liquid and solid products was examined. The maximum bio-oil yield of 45.9% is obtained at the final pyrolysis temperature of 500°C. The elemental analysis and heating value of the bio-oil and bio-charcoalare determined, and then the chemical composition of bio-oil is investigated by using chromatographic and spectroscopic techniques such as Gas Chromatography-Mass Spectrometry (GC/MS) and Proton Nuclear Magnetic Resonance (1H-NMR). The liquid product is mainly composed of phenolics, Including 2-methoxy-phenol, 2-methyl-phenol, phenol, as well as aldeyhdes, acids, esters, alcohols and ketones. The chemical characterization has shown that the bio-oil obtained from the residues of forestry production, such as firwood sawdust, can be used as environmental foodstock, which is an ideal candidate for alternative fuels. Moreover, bio-charcoal can be used as energy source and active carbon.

Table 3. Ten dominant compounds in cinnamon liquid smoke as the results of GC MS detection with four different pyrolysis temperature

No	Liquid smoke type	Pyrolysis temperature	Chemical component	RT (retention)	(%) area
3	Cinnamon	Temperature 100 ±10°C	**1. Acetic Acid**	**2.60**	**54.76**
			2. Phenol,2,6-Dimethoxy	**39.55**	**6.18**
			3. Phenol	32.58	5.54
			4. 2-Furancarboxaldehyde	13.75	2.78
			5. Propionic Acid Propanoic Acid	16.44	2.67
			6. Benzoic Acid, 4-Hydroxy-3-Methoxy 2H-pyran-2,4(3H)-dione,3,Acetil-6	40.91	2.20
			7. Gamma.Butyrolactone 2(3H)-Furanone,dihydro	19.30	1.62
			8. Corylone 2-Cyclopenten-1-one,2-Hydroxy-3-m 1,2-Cyclopentanedione,3-Methyl	26.35	1,62
			9.Acetic Acid,Methyl Ester	9.73	1.47
			10. 2,3,5-Trimethoxytouluene 2,4-Dimethyl-3-(Methoxycarbonyl)-5 Hydroquinone,Mono-TMS	41.7	1.30
		Temperature 200 ±10°C	**1. Phenol,2,6-Dimethoxy Phenol,3,4-dimethoxy**	**40.16**	**8.95**
			2. Propionic Acid Propanoic Acid	**17..02**	**7,22**
			3. Phenol,2-Methoxy	28.31	5.56
			4. Acetic Acid	12.78	5.24
			5. 2-cyclopenten-1-one,2-Hydroxy-3-m Corylone 1,2-Cyclopentanedione,3-Methyl	27.25	5.08
			6. Methanamine,N-Methyl-N-Nitroso	10.93	4.91

			7. Acetic Acid	12.91	4.31
			8. Gamma.Butyrolaxtone Butan-4-Olide 2(3H)-Furanone, dihydro	20.16	4.16
			9.1,2-Benzenediol	45.89	9.14
			10.Furfural 2-Furancarboxaldehyde	14.26	3.10
		Temperature 300 ±10^{o}C	**1. Phenol,3,6-Dimethoxy**	**40.16**	**10.36**
			2. Propionic Acid Propanoic Acid	**16.98**	**9.79**
			3.2-Cyclopenten-1-one,3-Hydoxy- 3-m Corylone 1,2-Cyclopentanedione,3-Methyl	27.24	6.29
			4.Phenol,3-Methoxy Phenol,2-Methoxy	28.22	5.43
			5.2-Propanone,1-Hydroxy Ethanol,2,2-Iminobis Acetic Acid,Methyl Ester	10.48	5.09
			6.1,2-Benzenediol	45.88	4.94
			7. Furfural 2-Furancarboxaldehyde	14.24	4.58
			8. Phenol	33.21	4.16
			9. GAMMA. Butirolactone 2(3H)-Furanone,Dihydro	20.07	3.65
			10Acetic Acid	15.90	2,98
		Temperature 400 ±10^{o}C	**1. Furfural 2-furancarboxaldehyde**	**14.32**	**9.26**
			2. Phenol, 2,6-dimethoxy	**40.16**	**9.15**
			3. Acetic acid	**13.34**	**7.34**
			4. Propionic acid Propanoid acid	17.20	6.26
			5. Phenol, 2-methoxy	28.29	6.08
			6. 2-cyclopenten-1-one, 2-hydroxy- 3-m Corylone 1,2-cyclopentanedione, 3-Methyl	27.28	4.96
			7.GAMMA.Butyrolactone 2(3H)-Furanone, dihydro	30.26	3.55
			8. Phenol Phosphonic acid	33.68	3.09
			9. Methanamine, N-methyl-N- Nitroso	12.03	3.09
			10. 1,2-Benzenediol	45.88	2.88

From the results of gas chromatography spectra, the dominant compounds of each peak in the sample are cinnamon at pyrolysis temperature of 200^{o}C, 300^{o}C dan 400^{o}C are phenol respectively at 8,95%, 10,36% dan 9,26% and acetid acid with area volume respectively at 7.22%, 9.79% and 7.34%. These results are far too different from the results of study[8]that uses raw materials from various types of wood and coconut shell at combustion temperatures of 350-400°C, which the dominant compound of liquid smoke in the research is phenol with total area volume of 44.13%.

From the results of measurements by using GC-MS above, coconut fiber and coconut shell liquid smoke generally have basic components of phenol and acetic acid compounds that are greater than cinnamon. Highpyrolysis temperature does not show more phenol and acetic acid chemical components obtained, it does not significantly affect the amount of obtained peak area volume. Based on the components that are contained in the liquid smoke above, it means that coconut fiber, coconut shell and cinnamon have greater potential as a food preservative. However, it needs to be noticed that there iis toxic element content in liquid smoke.

In addition, from the measurement of liquid smoke by using GC-MS, it also shows that chemical component of cinnamon liquid smoke that is burned at combustion temperatures of 100°C, 200°C, 300°C and 400°C have the chemical component area that is far too different (smaller) with liquid smoke from coconut fiber and coconut shell. This is because cinnamon basic compounds is different with coconut fiber and coconut shell. Phenol content in liquid smoke from the decomposition of lignin on the combustion temperature of 400°C means that at combustion temperature of 300°C, it should not contain phenol[9]. However, in this study shows that at combustion temperature of 300°C, the amount of phenol is not too much different from phenol contained in liquid smoke with combustion temperature of 400°C. In other words, phenol is not only produced from lignin decomposition, but also can be produced from the decomposition of hemicellulose or cellulose at combustion temperatures below 300°C.

Phenol and its derivatives become the most dominant compounds of all liquid smoke samples. This is because the components that are most dominant in wood smoked material, especially hardwood,is lignin. Lignin, when burned and pyrolyzed, will produce phenol compounds. From table 1-3 above that liquid smoke data that is analyzed by GC MS,the combination of cinnamon raw materials with pyrolysis temperature of 400°C has lots of chemical components, namely RT to 53. This means that cinnamon has lots of liquid smoke gas component, Cinnamon gas component exceeds gas components of coconut shell and coconut fiber. The combination of GC with MSwill result a good analysis methods. Researchers can analyze organic solution, put it in the instrument, separate it into component and directly identify that solution. Then, researchers can calculate the quantitative analysis of each component. To calculate each method, it can be visualized in a two-dimensional graph. In GC-MS (Gas Cromatografy Mass Spektroscopy) analysis method,it readsthe spectra contained in that combined two methods. In GC spectra, if the samples contain many compounds, which can be seen from the peak in that GC spectra,based on retention time data that is already known from the literature, it can be identified the compounds from the sample.

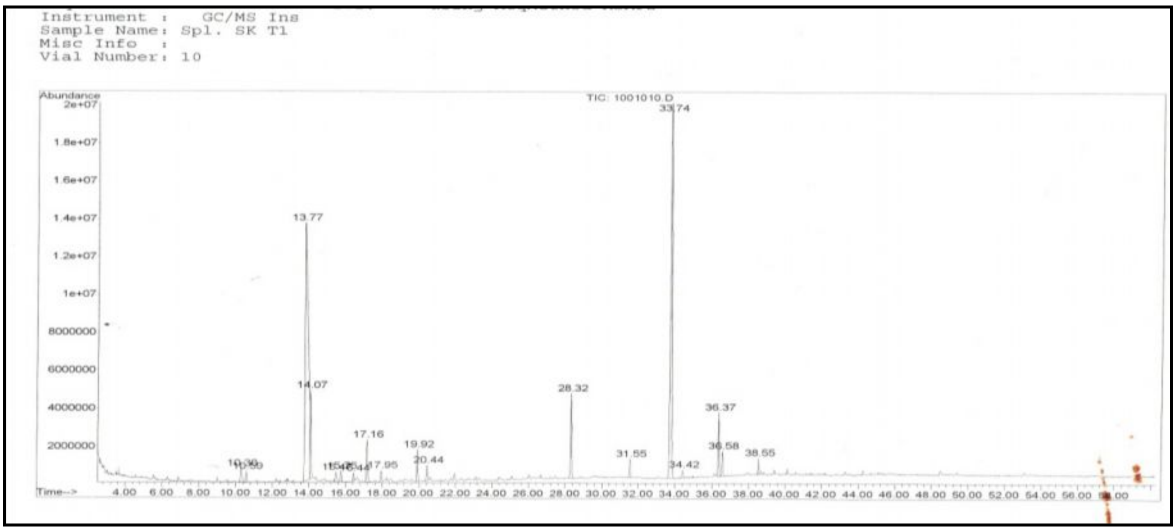


Figure 2. Graphic of compounds that are contained in coconut fibers liquid smoke at pyrolysis temperature of 100 ± 10°C detected by GC MS

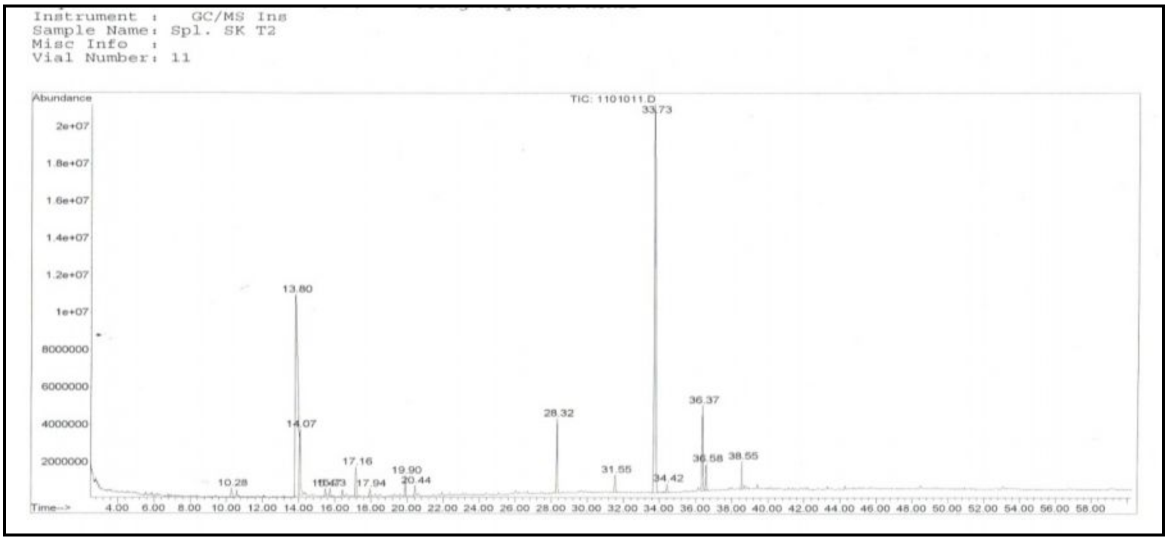


Figure 3. Graphic of compounds that are contained in coconut fibers liquid smoke at pyrolysis temperature of 200 ± 10°C detected by GC MS

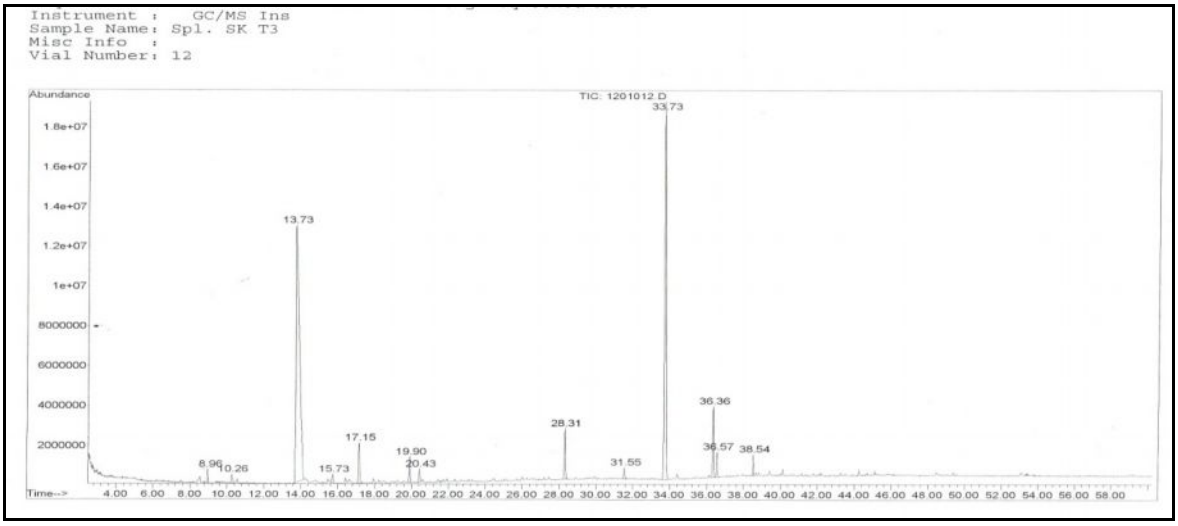


Figure 4. Graphic of compounds that are contained in coconut fibers liquid smoke at pyrolysis temperature of 300 ± 10°C detected by GC MS

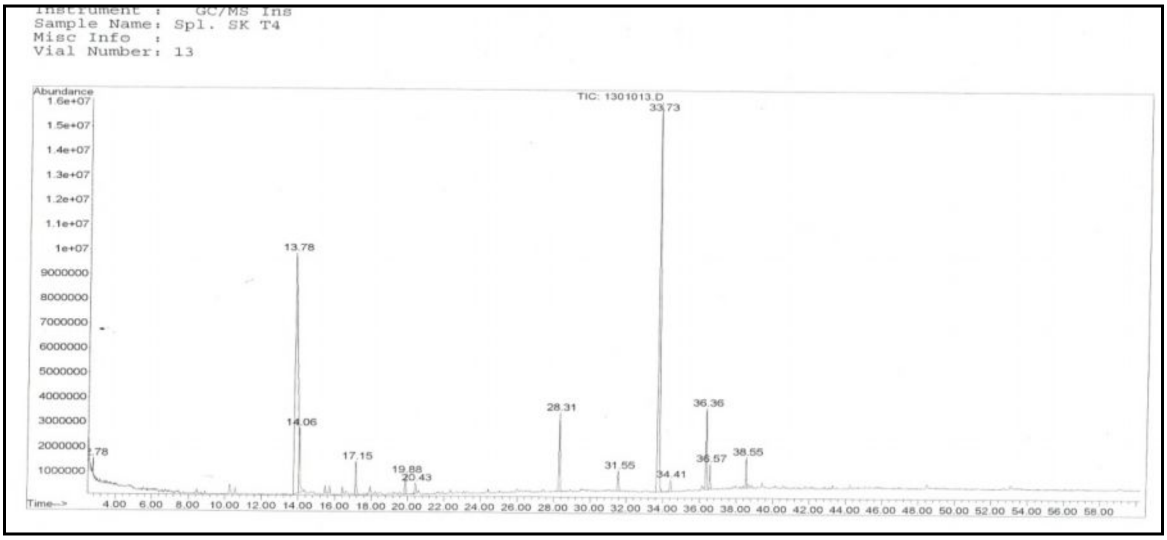


Figure 5. Graphic of compounds that are contained in coconut fibers liquid smoke at pyrolysis temperature of 400 ± 10°C detected by GC MS

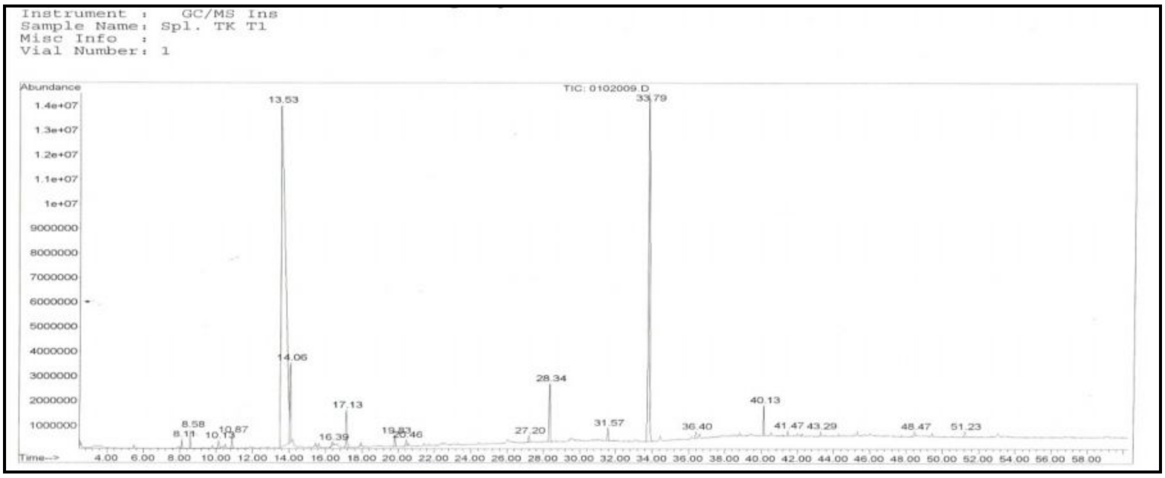


Figure 6. Graphic of compounds that are contained in coconut shell liquid smoke at pyrolysis temperature of 100 ± 10°C detected by GC MS

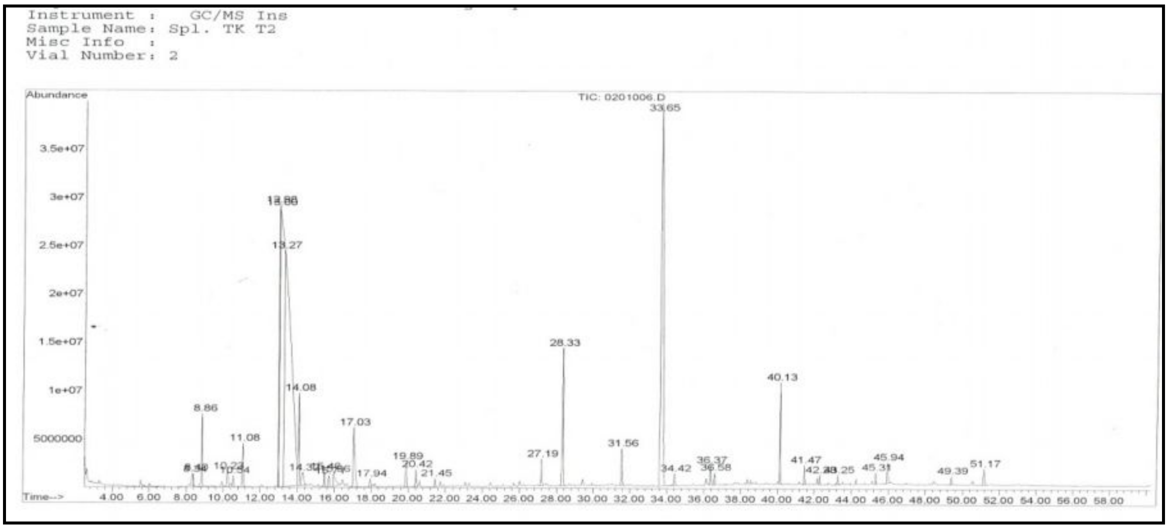


Figure 7. Graphic of compounds that are contained in coconut shell liquid smoke at pyrolysis temperature of 200 ± 10°C detected by GC MS

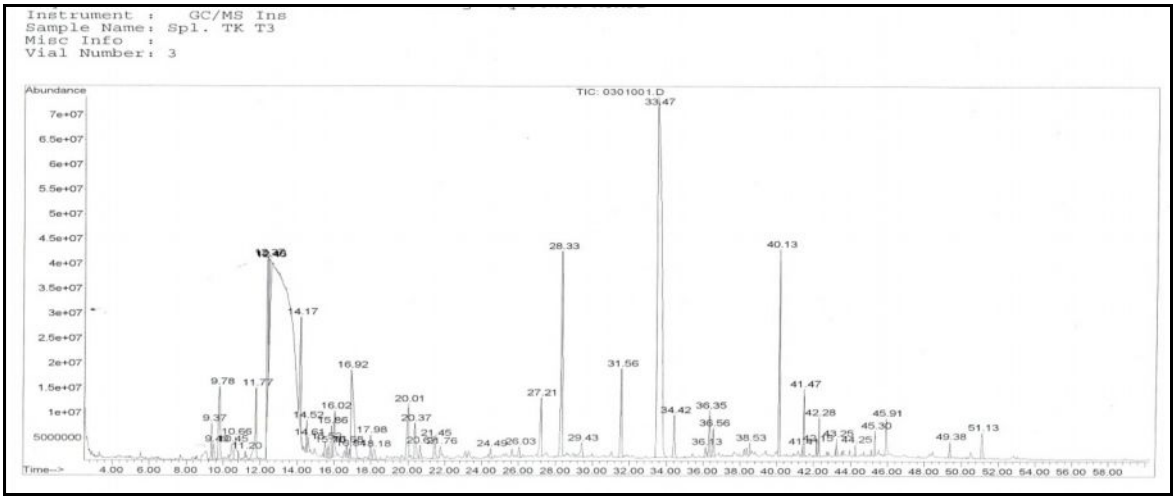


Figure 8. Graphic of compounds that are contained in coconut shell liquid smoke at pyrolysis temperature of 300 ± 10°C detected by GC MS

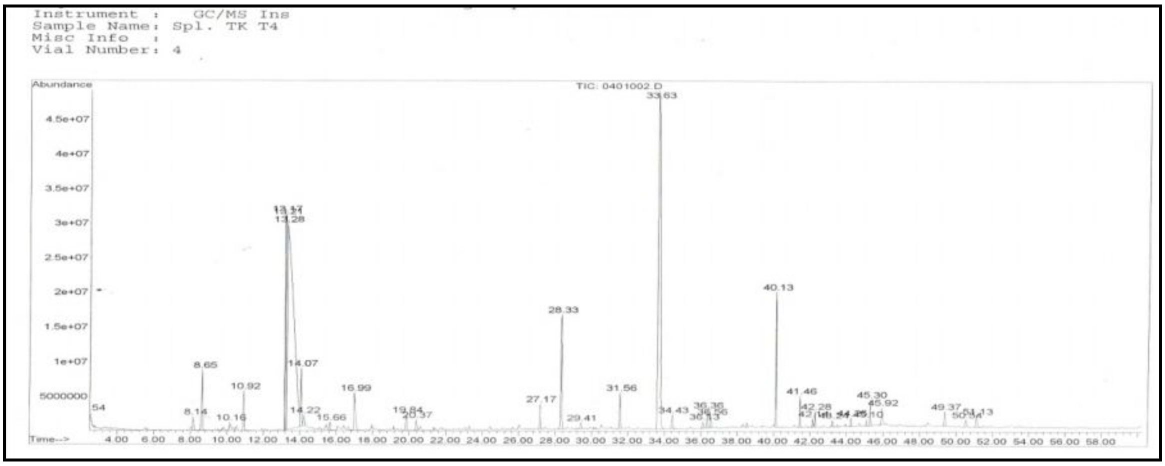


Figure 9. Graphic of compounds that are contained in coconut shell liquid smoke at pyrolysis temperature of 400 ± 10°C detected by GC MS

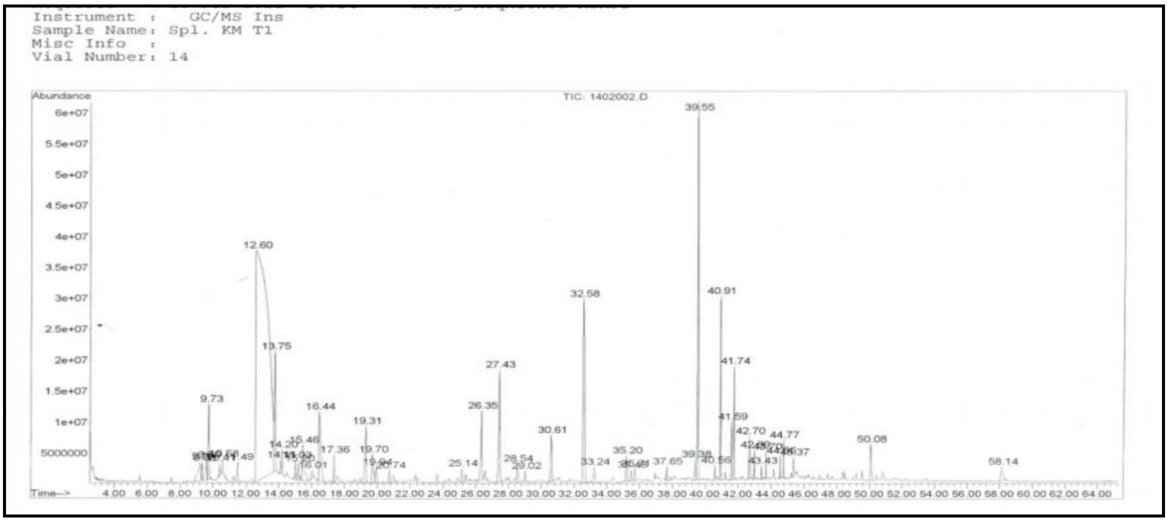


Figure 10. Graphic of compounds that are contained in cinnamon liquid smoke at pyrolysis temperature of 100 ± 10°C detected by GC MS

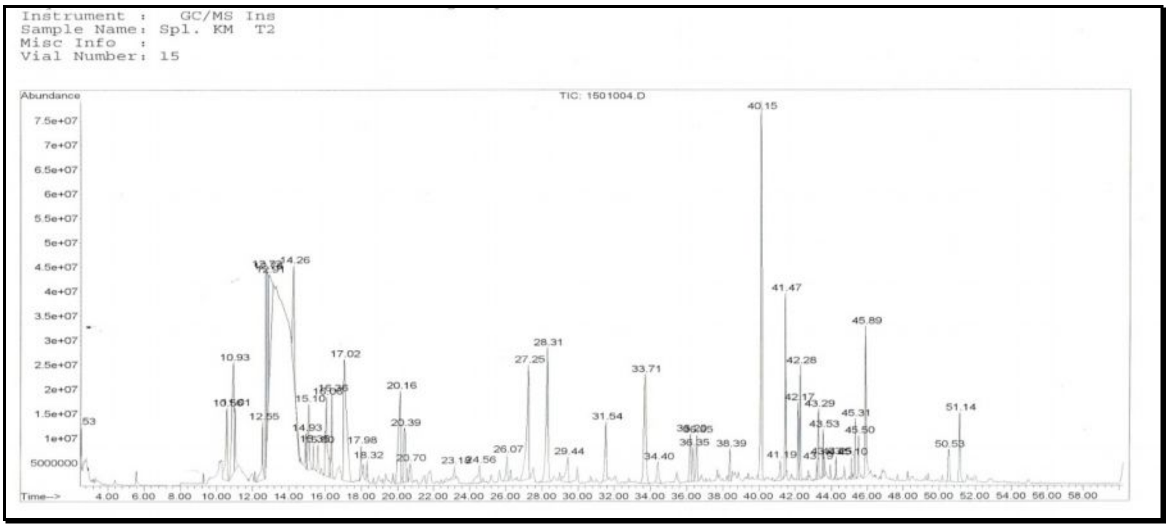


Figure 11. Graphic of compounds that are contained in cinnamon liquid smoke at pyrolysis temperature of 200 ± 10°C detected by GC MS

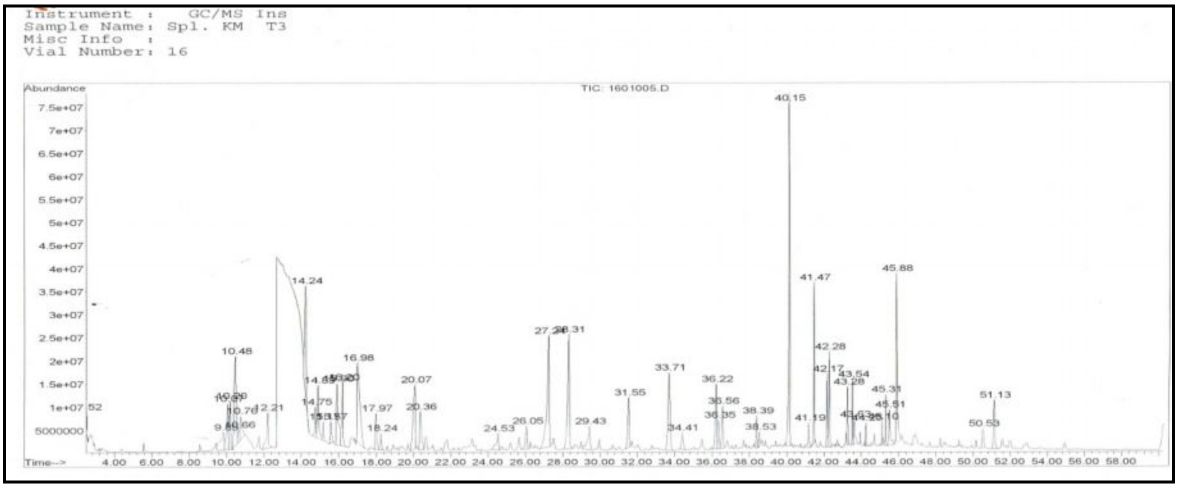


Figure 12. Graphic of compounds that are contained in cinnamon liquid smoke at pyrolysis temperature of 300 ± 10°C detected by GC MS

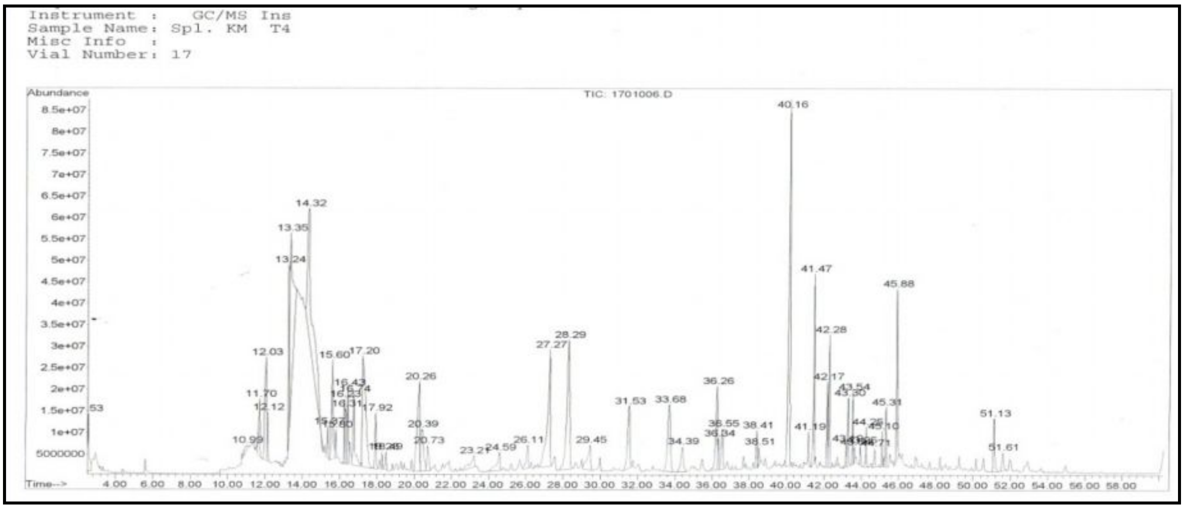


Figure 13. Graphic of compounds that are contained in cinnamon liquid smoke at pyrolysis temperature of 400 ± 10°C detected by GC MS

Conclusions

1. The results of study on raw material combinations with different pyrolysis temperature affects the content of chemical compounds in liquid smoke. Phenol and its derivatives becomes the most dominant compounds of all liquid smoke samples, and cinnamon raw materials combination that is combined with pyrolysis temperature of 400^{o}C has enough chemical components.
2. The results of liquid smoke measurements by using GC-MS also shows that chemical component of cinnamon liquid smoke at pyrolysis temperature of 100^{o}C, 200^{o}C, 300°C dan 400^{o}C have chemical component area volume that is far too different (smaller) with liquid smoke from coconut fiber and coconut shell.
3. Phenol compounds are compounds that are antimicrobial and antioxidant because phenol has the ability to kill food spoilage microbial.

Acknowledgment

We would like to thank Directorate General of High Education, Ministry of Education, in correspond to Implementation Agreement of Competitive Research Grant, National Priority, Rector of Ekasakti University, The Head of LPPM Ekasakti University, The Dean of Agriculture Faculty Ekasakti University, Supervisors of

Andalas University and Bung Hatta University Laboratory team and staff that have provided help in this activity.

References

1. Pszczola, D.E.Tour Highlights Production and Users of Smoke Based flavours. Food Technology (1)70-74. 1995.
2. Pastor-Villegas, J., Pastor-Valle, J.F., Meneses Roddriguez, J.M., & Garcia Garcia, M. Study of Commercial Wood Charcoals for the Preparation of Carbon Adsorbents Journal of Analytical and Applied Pyrolysis. 2006, 76. 103-108.
3. Branen, A.L., P.M. Davidson and B.Katz. Antimicrobial Properties of phenolic Antioxidants and Lipids. Food Tech. 1980, 34: 42-53.
4. Rodiah N.S., Bagus Setiadi, Bandol Utomodan tri Nugroho Widianto. Rekayasa Alatpenghasil Asap Cair Untuk ProdukiIkan Asap Uji Coba Alat Penghasi lAsap Cair SkalaLaboratorium. Journal of Post Harvest and Maritime Affairs and Fisheries BiotechnologyVol. 1 No.1. Juni 2006.
5. Guillén M.D., and M. L. Ibargoitia. "GC/MS analysis of lignin monomers, dimmers and trimers in liquid smoke flavourings", Journal of the Science Food Agriculture, 1999, 79: 1889-1903.
6. IUPAC. Recommended Method for a thin-layer-chromatographic screening method for the determination of benzo(a)pyrene in smoke food. Pure &Appl Chem., 1987, vol 59 No. 12 pp. 1735-1738.
7. Fatimah I. Pengaruh Laju Pemanasan Terhadap Komposisi Biofuel dari Serbuk Kayu Menggunakan Virolisis Cara Vakum, UII Research Report, UII Research Institute, Yogyakarta, 2003.
8. Tranggono, Suhardi, B. Setiadji, P. Darmadji, Supranto dan Sudarmanto. Identifikasi Asap Cair dari Berbagai Jenis kayu dan Tempurung Kelapa. J. Food Science and Technology 1996, 1(2): 15 - 24.
9. Maga, J. Smoke in Food Processing.Florida:CRC Press-Inc Boca Rotan.1988.
10. Z wang and J.R. J.Pare. Gas Choromatography (GC) Principles and Aplications Chapter 3 in text book Instrument methods in food analysis Edited JRJ.Pare and JMR Blanger Enviromental Canada, Enviromental Technology Centre Otttawa Ontario Canada K1AOH3Elsivier. 1997.
11. Ariani D. Dwi Rasy Mujiyanti, Dewi Umaningrum, Yuda Arimba Harlianto. Studi Kajian Kandungan Pada Asap Cairdari Sekam Padi. Proceeding in Chemistry National Seminar, Department of Chemistry ISBN 978-602-0951-05-8 Surabaya National University 3-4 October 2015.
12. Desi Ardilla, Tamrin, Basuki Wirjosentono, Eddiyanto.Identifikasisenyawafenolasapcairpadapiro lisissu hutinggi. 2015, Agrium ISSN 0852-1077 (Print) ISSN 2442-7306 (Online) October 2015 Volume 19 No. 3
13. PirolizaJelove. Pyrolysis of Firwood (*Abiesbornmülleriana*Mattf.)Sawdust: Characterization of Bio-Oil and Bio-Char.2015, DrvnaIndustrija66 (2) 105-114 (2015)

*****