PARAMETRIC STUDY OF LEUCAENA OIL BIOADHESIVE FORMULATION

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***Abstract*-A gradually increase in the value of crude oil and a serious worry about the production of non-renewable energy have encouraged the finding of another renewable sources for fuel, energy and new material production. The aim of this study is to produce and characterize the physical and chemical properties of bio based phenolic resin compound derived from the *Leucaena sp. wood* by gasification method. This study also carried out to formulate Bio-based phenol formaldehyde adhesive at different condition (temperature, time and catalyst loading) and comparison study with the commercialized petroleum based phenol formaldehyde resole resin adhesive. In order to produce the bio based phenol resin, we use gasification method by using upgraft gasifier reactor while to formulate the phenol formaldehyde which are reaction in the basic condition. The phenol resin and bioadhesive were further analyzed by GC-MS to know the component and composition by percentage in phenolic resin and phenol formaldehyde. The results indicated that the reaction temperature had more effect on the products distribution than the retention time.**

***Keywords— Leucaena sp. Wood*, phenol resin, phenol formaldehyde, gasification, bioadhesive**.

1. INTRODUCTION

Nowadays there is a growing the use of composite material such as strand board, flake board and composite lumber, the wood industry is growing rapidly. One material have been used widely as the wood adhesive due to their excellent bonding, water resistance and durability. The material is phenol formaldehyde. However, phenol is the primary component of the resin used in the wood adhesive derived from fossil fuel resources (petroleum and coal).[1] However, there is a main issue of using this type of resin that is high cost. This is because it follows the fluctuation of the petroleum price. In addition, this type of resin has the material that is considered as the major indoor pollutant and thus very harmful for our health. Thus finding renewable material as other option for the raw material has become the main thing in interest for the resin production.[2]

In current years, increasing in the value of crude oil and a serious concern about the production of non-renewable energy have encouraged the finding of another renewable sources for fuel, energy and new material production.[3] Among these new renewable sources of fuel, energy and material is the use of biomass to produce phenol resin. Thus, there is a solid interest in exploring renewable material as an alternative of feedstock foe phenol formaldehyde resin manufacture. [4] *Leucaena sp.* wood is the one of the biomass that can be used in the production phenol resin. *Leucaena leucocephala* has been studied for biomass production because its reported yield of undergrowth corresponds to a dried mass of 2,000–20,000 kg/ha/year, and that of wood 30–40 m^3/ha/year, with up to twice those amounts in favorable climates. It is also efficient in nitrogen fixation, at more than 500 kg/ha/year. Young trees reach a height of more than 20 ft in two to three years so it has very fast growth rate. In the other hand, *Leucaena sp* wood has been a focus on the environmental concern. There is a enormous potential for *Leucaena sp* to be improved in the production of high-value added products. Thus, the capability of *Leucaena sp* to substitude phenolic compounds in phenol formaldehyde resin is studied.[5]

The method use in order to produce the bio oil is gasification. The gasification of biomass is a procedure used to convert solid biomass into gasified state and then condense the gas. Then it will change the phase from the gas form in liquid form. In the gasification process will conducted at higher temperature.[6] Gasification of biomass can produce phenol resin and make the adhesive mixture due to its free hydroxyl (-OH) group that can polymerize with various functional groups to produce different polymers.[7] Gasified biomass therefore can be used as a part of adhesive mixture by combined it with synthetic adhesive like formaldehyde. overall, gasification of biomass by using the upgraft gasifier reactor that produce product in the form of gas then the gas will condense by using condenser can be used in the production bio-adhesive. It will produce bio-oil. Then, the bio-oil will further the GCMS analysis behavior of the biomass residues. [8] In this study, *Leucaena sp.* wood is the raw material in production of bioadhesive. *Leucaena sp.* will undergo thermochemical conversion to produce the bio-oil in the middle of the process. The product of gasified *Leucaena sp.* which is known as bio- based phenolic resin and then, it will transform into adhesive by adding formaldehyde. The gasification *Leucaena sp.* by using upgraft gasifier reactor that consist four processes which are pyrolysis, drying, combustion and reduction. In this reactor, high temperature will introduce. The research is carried to compare the chemical and physical properties of bio-based phenolic compound derived from the *Leucaena sp. wood.* This study also carried out to formulate Bio-based phenol formaldehyde adhesive at different condition (temperature, time and catalyst loading) and comparison study with the commercialized petroleum based phenol formaldehyde resole resin adhesive.[9]

2. METHODOLOGY

2.1 Materials

Leucaena sp. wood, Leucaena oil (bio-oil) from SARAFIAH NATURAL RESOURCES SDN BHD (Port Klang Selangor Darul Ehsan). Other chemical used for this bioadhesive preparation include ethanol with concentration of 95%, formaldehyde with concentration of 37%- 40% and sodium hydroxide solution (alkaline catalyst).

2.2 Preparation of phenol resin (leucaena oil).

The pieces of *Leucaena sp.* wood is weighed by using the weighing scale. In the upgraft gasifier reactor, the flowrate is 50 kg/h at 800°C. After an hour, the product gas came out from the upgraft gasifier reactor will enter the condenser. The product is bio oil. Then, the organic compound of the bio-oil that had been produced determine by using the Gas Chromatography Mass Spectrometry (GCMS). [10]

2.3 Preparation of phenol formaldehyde (bioadhesive)

The bio-oil produced from the condenser will evaporate to separate oil and water by rotary evaporator. The oil that had been collected will mix with ethanol, alkaline catalyst (NaOH) and formaldehyde. Then, the mixture is charge into the flask and heat up at 90°C in silicon oil bath under constant stirring from 5 to 15 minutes. Then, the system is cool down at room temperature at

25°C. The ethanol is removing at 60°C and low pressure by using air circulated oven. The product is dark red brown color viscous liquid.[11] Figure 2.2 provided the picture of GCMS. The product obtained will characterized by using Gas Chromatography Mass Spectrometry (GCMS). The physical properties of adhesive is inspect such as viscosity, solid content and pH value. [12]

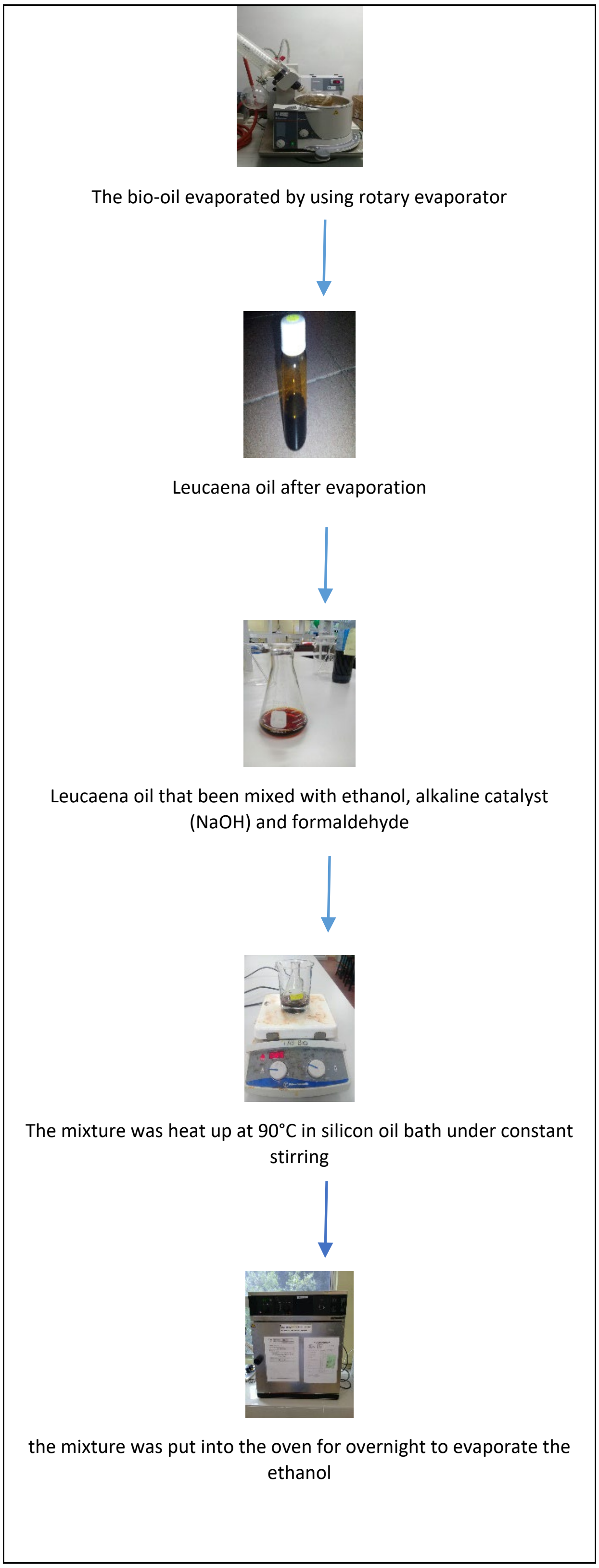


Figure 2.1 The methodology of production bioadhesive

Figure 2.2 HP-5890 gas chromatograph that had been used.

Experiment/operating condition	Temperature, °C	Time, min	Catalyst loading(NaOH)
1	80	60	0.5
	85	60	0.5
	90	60	0.5
2	85	30	0.5
	85	60	0.5
	85	90	0.5
3	85	60	0.4
	85	60	0.5
	85	60	0.6

Table 2.1 Showed the control variable in the formulating the bioadhesive

3. RESULTS AND DISCUSSION

3.1 Characterization of Leucaena Oil

In the previous, the biomass is one of renewable source uses in the industry that been practiced. Biomass can produce phenol resin through gasification process by upgraft gasifier. There are category that had been we tested through physical and chemical characterization. Physical characterization, we observed by using organoleptic properties while the chemical characterization we tested on the component and composition in the leucaena oil by using GCMS analytic. In this test, we want to know the percentage area of phenol in the leucaena oil.

3.2 Physical Characteristic

After the gasification of Leucaena oil, bio based phenolic resin is obtained from Figure 3.2. The appearance, odor, viscosity, pH value, solid content and free formaldehyde content of the bio based phenolic oil were measured and presented. I observed the appearance and odor of bio based phenolic obtained from gasification of Leucaena. The result show that the appearance of bio based phenolic resin is dark brown liquid and has pungent smell. The result obtained is the same when compared with the pure phenolic resin. The viscosity and pH values of bio-based phenolic resin are 0.82 and 3.76 respectively which is closed compared to the pure phenolic resin.[13] The bio-oil have a pH in the range of 2-4 due to the presence of organic acids. Solid content is the proportional of non - volatile material contained in the phenolic oil.[14] Most typical solid content in pure phenolic is around 50%. The result obtained shows only 39.88% of solid content. This may due to the unreacted phenol evaporated during the heating period, led to a lower non-volatile content for the bio phenol resin.

Formaldehyde is a toxic component that is present in phenolic resin. Its quantification is important to the characterization of the phenolic resin. The method developed for the identification and quantification of free formaldehyde content in phenolic resin is bio based on the determination of free carbonyl compound by derivatization with 2,4- dinitrophenylhydrazine (DNPH), using gas chromatography (GCMS).[14] The standard of free formaldehyde content in phenolic resin must be less than 0.2%. Result obtained from GCMS shown that the free formaldehyde content in the bio based phenolic resin is 0.1% which is safe.

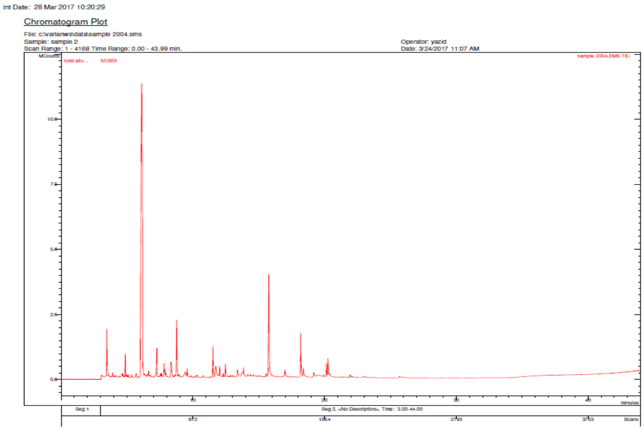
Figure 3.2 Phenolic resin that had been produce by gasification

Type of resole	Appearance	Odour	viscosity	pH	Solid content	Free formaldehyde content
Pure phenolic resin	Dark brown liquid	Pungent smell	0.96	3.78	48%	≤ 0.2%
Bio based phenolic resin	Dark brown liquid	Pungent smell	0.82	3.76	39.88	0.1%

Table 3.2 Physical properties of the Leucaena oil PF resins.

3.3 Chemical characteristic

Gas chromatography analysis of phenolic resin were carried out in a variant GCMS instruments analyzer under 375 °C, heating rate of 30 °C min-1 and cracking time 30 min. The result was shown in Figure 3.1. The detected compounds and their relative area % for the major component are summarized in Table 3.2. The relative area % for each compound was defined by the percentage of chromatographic area of the specific compound out of the total area of 50 largest identified peaks. The area % value presented here shows only the relative concentration of the specific compound among the volatile fraction of the degraded lignin that could pass through the GS column. [15]



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Chromatogram Plot

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Sample: sample 2

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Figure 3.2 chromatogram of the bio based phenolic resin produced from gasification.

Retention time (min)	Compound	Area%
3.401	Propane, 2-methyl-1-nitro-	1.282
4.8911	2-Propenamide, N-methyl-	2.279
5.8717	2-Cyclopenten-1-one, 3-methyl-	1.757
6.1254	Phenol	2.945
6.6996	2,4-Dimethyl-2-oxazoline-4-methanol	5.128
7.3069	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	3.943
8.4102	Phenol, 4-methyl	2.271
8.8129	Phenol, 2-methoxy	4.687
9.5951	2-Methoxy-5-methylphenol	1.542
11.8369	2,3-Pyridinediamine	0.979
11.9663	1,4:3,6-Dianhydro-à-d-glucopyranose	2.371
12.4481	2-Chloroethanol	2.035
13.392	1,2-Benzenediol, 3-methoxy-	0.934
13.8594	Phenol, 4-ethyl-2-methoxy-	2.821
15.7523	Phenol, 2,6-dimethoxy	7.16
18.1729	1,2,4-Trimethoxybenzene	2.815
19.1647	Benzaldehyde, 3-hydroxy-4-methoxy	1.042
19.6818	Thiophene, 2-pentyl	0.471
20.1167	5-tert-Butylpyrogallol	0.951
20.2461	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.595

Table 3.2 GSMC analysis result bio based phenolic resin

From the result of GCMS analysis it shows that the bio based phenolic oil contains ester, phenolic derivatives, alcohol and carboxylic acids compound. The detected esters mainly consist of ethyl esters with carboxylic acid. The ester might be generated by esterification between ethanol and some lignin-derived intermediates. The presence of alcohol compound could be generated by both of the cleavage of ether linkages and lignin side chains.[16] The major group is monomeric phenolic compounds and derivative including phenolic groups with short-chain alkane substitutes such as –methyl, -ethyl, -methylethyl, and propyl groups. The table 4.2 shows that the percentage of phenol and phenolic derivative are the largest compared to the other chemical component. As a result that had been obtained to make bio based phenolic oil as a good alternative to be use an adhesive. [17]

3.4 Characterization of bioadhesive

Bioadhesive or phenol formaldehyde is produce when the chemical substances which are ethanol, formaldehyde and sodium hydroxide as catalyst are mixed with phenol resin.

3.5 Chemical characterization

Gas chromatography analysis of phenolic resin were carried out in a variant GCMS instruments analyzer under 375 °C, heating rate of 30 °C min-1 and cracking time 30 min. The result was shown in Figure 3.4 and 3.5. After obtaining the phenolic oil from the gasification of *Leucaena sp*. resinification process was carried out to produce adhesive at different operating condition which is temperature, time and catalyst loading. For each operating condition, we had three sample. So, total sample is 9 and every sample are tested for GSMS.

Effect the temperature on the percentage area phenol %

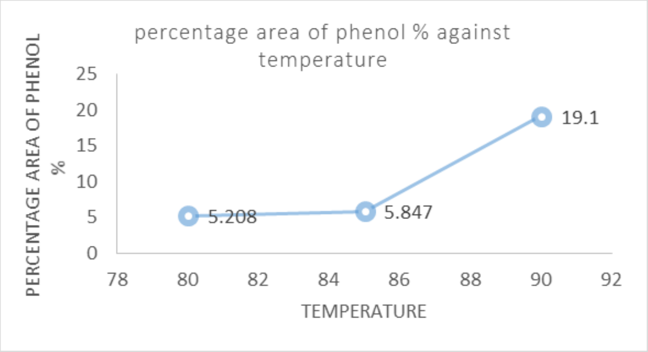

Figure 3.4 Effect the temperature on the percentage area phenol %

Figure 3.4 showed the effect of resinification temperature on the percentage area of phenol. The the percentage area of phenol % increased slightly when resinification temperature was increased from 80°C to 85°C, and then Increasing temperature from 85°C to 90°C make the percentage area of phenol % increased drastically. When temperature was higher than 85°C, increasing temperature obviously improved the percentage area of phenol %. The probable reason for the results is that the reactivity of phenolic compounds with formaldehyde increased with resinification temperature, which increased the percentage area of phenol % of resinification liquid. Therefore the optimized temperature is 90 °C. The probable reason for this is that increasing reaction time leads a much complete reaction. [18]

Effect Time on the Percentage Area Phenol %

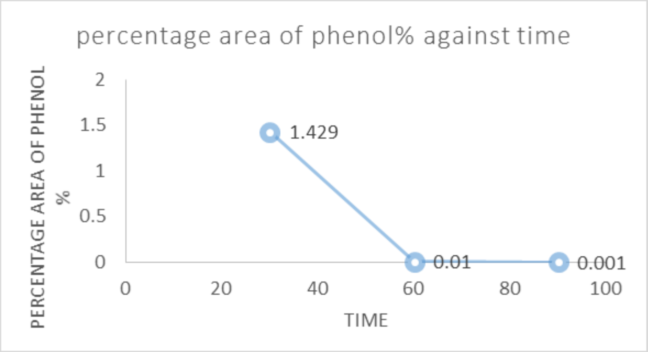

Figure 3.5 Effect time on the percentage area phenol %

Figure 3.5 showed the effect of resinification time on the percentage area of phenol. The percentage area of phenol % decrease significantly when resinification time was increased from 30 mins to 60 mins, and as time rises from 60 mins to 90 mins it made the percentage area of phenol % declining. When times rises 90 mins, increasing temperature obviously improved the percentage area of phenol %. The probable reason for the results is that the reactivity of phenolic compounds with formaldehyde decreasing with resinification time, which increased the percentage area of phenol % of resinification liquid.[19] Therefore the optimized time is 30 mins.

Effect catalyst loading (NaOH) on the Percentage Area Phenol %.

The effect of resinification catalyst loading (NaOH) on the percentage area of phenol. The percentage area of phenol % constant when resinification catalyst loading was increased from 0.4 g to 0.6 g. This is because the catalyst loading (NaOH) increase the rate of reaction by lowering activation energy. [20] In this experiment, probably that at 0.4 g it reached optimum amount catalyst loading. So, the percentage area of phenol % remain constant when the amount of catalyst loading increase.

4.0 CONCLUSION

From gasification process produce high amount of phenol by upgraft gasifier reactor. The physical properties of bio oil that produce almost same with the commercialized oil which cruel oil from petroleum. Then, the chemical properties of the bio oil show it significantly to futher the resinification process. The L*eucaena sp.* is acceptable to replace the the commercialized oil. In the production of bioadhesive, reaction temperature had more effect on percentage area of phenol % than time and catalyst loading (NaOH). At 90°C is the optimum temperature in the production of phenol formaldehyde.

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