SYNTHESIS OF PHENOLIC FORMALDEHYDE RESOLE RESIN AS WOOD ADHESIVE USING BIO OIL

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ABSTRAK

Resin jenis resol fenol/formaldehid memiliki aplikasi yang sangat luas dalam bidang teknik kimia, mulai dari insulasi termal hingga sebagai bahan adhesif dalam industri kayu. Resin ini memiliki keunggulan sifat fisis yaitu tingginya ketahanan terhadap kelembapan dan cuaca, yang selanjutnya berguna dalam penggunaan konstruksi luar dan lembap. Sekarang, telah dikembangkan teknologi-teknologi baru untuk memproduksi bahan adhesif kayu dari bio oil. Resole resin dibuat dengan mereaksikan antara fenol dengan formaldehid, di mana 50% dari fenol yang bereaksi disubstitusi oleh fraksi fenol/netral yang diekstraksi dari bio oil. Dalam penelitian ini, lima macam komposisi reaktan digunakan untuk membandingkan kualitas dan sifat fisis masing-masing resin. Setiap resin memperoleh perlakuan yang sama selama sintesis. Hasil dari penelitian ini kurang memuaskan, semua sampel gagal merekatkan kedua permukaan kayu. Akan tetapi, resin yang memiliki kualitas rendah ini dapat diatasi dengan beberapa modifikasi menggunakan bahan aditif.

***Kata Kunci**: Resole resin, Bio oil, Adesif kayu, Ffenol, Formaldehid*

INTRODUCTION

Phenol/formaldehyde resins as an adhesive resin are utilized in a wide range of applications especially in wood working industries as an adhesive to bond wood layers in such as particle board (PB), plywood, fiber boards (FB), and glued wood construction products[1]. The high moisture and weathering resistance of the phenolic adhesive bond and its specific strength makes it useful for the wood materials to be used for outdoor construction and in high humidity regions[2].

With the increasing use of composite wood materials, such as strand board, flake board, and composite lumber, the industries have a great demand of adhesives. The adhesives for these wood products are currently made from petroleum and natural gas. However, the production of petroleum-based phenol, as the raw material of the adhesives, is quite expensive and efforts in recent years is to develop a new technology to partially substitute the phenol in such resins with inexpensive phenols derived from wood-based or other biomass products or extracts[3]. The substitution is about 50% of the phenol in the resin which means that the production of the phenolics extract is expected to be 50% of the cost of the phenol derived from petroleum, so net savings for the cost of the resins will be about 25% [4].

The pyrolysis of biomass is known to produce a complex mixture of phenolic compounds[3]. Biomass conversion by means of high heating rate or fast pyrolysis produces high yields of liquid fuels which is more common known as "bio oil". Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. As a result, it decomposes into mostly and aerosols and some charcoals. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil[5]. Biomass contains particular lignocellulosic materials which in nature this lignin acts as an adhesive to bind the cellulose fibers together[3]. Therefore, lignin and lignin-derived material from wood would be a natural starting point for the development of biomass-based adhesive resins.

Table 1. Chemical Compound Composition of Bio Oil by Biomass Technology Group (BTG - 2003)

Chemicals	Concentration (wt%)
Hydroxy-acetaldehyde	Up to 17 (from cellulose)
Levoglucosan	Up to 47 (from cellusose)
Levoglucosene	Up to 24 (from cellulose)
Phenolic compounds	30-100
Wood preservatives	
Methylarylether	
Calsium carboxylate salts	
Furfural, furfuryl alcohol	up to 30 (from cellulose)
Steroids	detected in vacuum pyrolysis oil
Nicotine/taxol precurors	

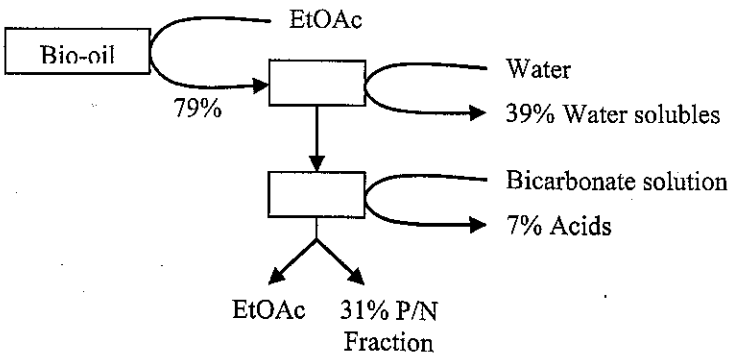

Fig.1. Process for the separation of P/N fraction from bio oil [5]

The bio oil compound composition along with its phenolic fraction content is shown in Table 1.

Phenolic Resins

Phenol/formaldehyde resins are produced industrially by the reaction of phenol with excess of formaldehyde in the presence of an alkaline catalyst (pH 8-13). The resins commonly known as resoles, will resemble the phenol alcohols and have methylol side or end groups[6]. The solvent used is water and the ratios of phenol to formaldehyde is in the range of 1 : 1 – 3. For this reaction the common industrial catalyst is sodium hydroxide, however, ammonia, HMTA, or a variety of metallic hydroxides can be used[7]. Formaldehyde is usually in 37% solution (formalin) or can be used in its polymeric form, paraformaldehyde. Formaldehyde is preferred because of its high reactivity and freedom from side reactions[6].

The general approach of producing phenolic fraction from bio oil is by extracting it with a suitable solvent, e.g. ethyl acetate, followed by sequential back-extraction with water and bicarbonate solutions. This is because the initial separation with ethyl acetate is obviously not very selective. Typically ~ 30% of the bio oil was recovered as the Phenolic/Neutral fraction, whereas this yield is rather higher than the normal pyrolytic lignin content of bio oil (~ 20-25%) [5].

This work focuses on how to synthesize the phenol/formaldehyde resin by partially substituting the phenols with phenolic compound extracted from bio oil. The experiment is conducted into three processing steps. First, extraction separates out the phenolic fraction from the bio oil. Next, resin synthesis mixes these phenolics along with traditional phenol and formaldehyde. Finally, the resin adhesives are tested on a wood specimen surface by soaking it in tap water after hot pressing it under high temperature and pressure.

Experimental

Materials

Bio oil, ethyl acetate (99.5%), natrium bicarbonate, phenol (99+%), formaldehyde (37% as formalin), NaOH pellets, HCl (95%), MilliQ water were available from the Chemical Engineering Department at the Rijksuniversiteit Groningen, Netherlands. Natrium bicarbonate was prepared as a 5% by weight aqueous solution of natrium bicarbonate. Sodium hydroxide was prepared in the concentration of 3 – 4 N and also HCl was in the concentration of 10% by volume aqueous solution.

Bio-oil extraction

The extraction method referred to the one conducted by Bridgwater[5]. 25 ml of bio oil was dissolved in 50 ml of ethyl acetate and the pH reaches 2-4. The mixture was stirred for 30 minutes and then filtered using a vacuum filter. The residue containing the phenol/neutral fractions, was then separated and washed with water to remove the water soluble materials, preferably the water to oil solution ratio will be 1:6 to 1:1. The remaining ethyl acetate soluble fraction (organic- light fraction) was then further extracted with 5 %w/w aqueous solution of natrium bicarbonate. The pH of the bicarbonate extraction was maintained at approximately 8-9.5 and the ratio of bicarbonate solution to oil is 6:1 to 0.5:1. The solution formed two layers which were the strong organic acids and highly polar compounds, and the ethyl acetate-soluble layer containing the phenols and neutral fractions remained on the bottom. This ethyl acetate layer was then separated, and the ethyl acetate was evaporated using a rotavapor at vacuum pressure.

The yield of the phenol/neutral fraction was calculated based on the initial volume of bio oil, 25 ml. The determination of the percentage of phenol fraction extracted used the following formula:

$$\%\ \text{extract phenol} = \frac{\text{mass of phenol extract obtained, g}}{\text{mass of phenol in initial bio oil, g}} \text{x} 100\% \quad (1)$$

Feed composition was varied according to the table 2.

Resole synthesis

Feed composition was varied according to the following table.

For sample B the resin synthesis used the bio oil as such, without any previous extraction applied. The bio oil was simply mixed with the other reagents and then further tested. Sample C uses phenol extract obtained from the extraction of bio oil with ethyl acetate as solvent with catalyst 0.85 ml gradually increased until pH 8-10.

The reaction took place in a 250 ml three necked vessel equipped with a reflux condenser, stirrer, and thermometer and placed on an oil bath. The reagents were added to the vessel, and the mixture was stirred and heated in the oil bath at 70°C for 2 h. After 2 hours, sufficient 10% sulfuric acid was added to reduce the pH to 6-7 and stop the reaction. By using a rotavapor, the solution was then vacuumed with pressure regulated at about 30 - 50 mmHg and water was removed through the condenser. The temperature of the water bath should not exceed 70°C. The vacuum evaporation is applied until all the water is evaporated and the solution formed a viscous gel.

Resole curing

Plywood was cut into small pieces (5 cm wide by 10 cm long) and used to place the resin while it was cured. A pair of wood pieces where bonded together with the resole resin sample whereas only one of the plywood surface was coated.

The adhesive coated area was varied for each resin sample of 120, 170, 200, 280 and 360 grams of adhesive per square meters. These bonded wood pieces were then hot-pressed at 14 bar for 30 minutes. The hot-press temperature was incremented at 140, 150 and 180°C for each sample resin and each varied adhesive coated area. Twenty seven pairs of wood samples were used for the resole curing process.

Water-resistance test

The wood samples bonded by the resole resin adhesives were soaked in boiling tap water at 100°C. The samples were tested for 72 hours and observed whether the adhesive still could

Table 2. Feed Composition Variation

Compound	Resole Sample				
	B_1	B_2	B_3	C_1	C_2
Crude bio oil, ml	20	20	20	-	-
Phenol 99+ %, g	-	17.76	-	-	6.8
Phenolic fraction, g	-	-	-	13.6	6.8
Formaldehyde 37 % $_{(aq)}$, ml	-	-	46.4	25.5	25.5
NaOH $_{(aq)}$ 3- 4 N as catalyst, ml	2	2	2	0.85 (increased)	0.85 (increased)

bond the pair of wood or not. All of the twenty seven pairs of samples that had been cured were used for the water-resistance test.

RESULT AND DISCUSSIONS

Bio oil extraction

The phenolic fraction was initially assumed to be 83% from the total bio oil. In table 3 it is listed the percentage of phenol/neutral fraction extracted from the four experiments.

The yield from the fourth experiment showed that 92% of phenol was extracted which was out of range from the first three. This happened because during evaporation not all the solvents were evaporated, so the remaining solution after evaporation still contained ethyl acetate and the volume calculated was more than it should be. Another explanation for this phenomenon was that some of the low molecular weight compounds already evaporated during the sequential extraction process, resulting high content of phenols in the bio oil. From the first experiment, the phenol/neutral fraction was analyzed using Gas Chromatography – Mass Spectroscopy (GCMS) HP5890 type II series GC with MS detector to find out the compound contained in the final fraction.

Table 4 shows that the methoxyl functional group phenols are monomer products that could be associated with pyrolytic lignin contained in the bio oil. The fraction also contained hydroxyl compound which is very suitable for adhesive formulation replacing phenol at greater than a 50% level. Besides the phenol compounds, this fraction also contains acetaldehyde of about 4.04% mol. These two compounds are basically the raw material of resole resin having acetaldehyde replacing formaldehyde as the aldehyde. The extract was then stored and used in the sample C resole synthesis process. About 43.5 % components were also identified containing several different kinds of compounds.

Resole synthesis

Resole B_1 formed a black viscous gel after 10-15 minutes of evaporation. This indicates that water, as the solvent, was well evaporated resulting an increased viscosity of the B_1 sample. The sample was then cooled until it reached room temperature.

The second variation sample B_2, however, after a long period of evaporating time, it did not form a gel. This was caused by the lack of aldehyde in the reactant composition. The amount of phenols was twice as much as sample B1, causing the pH of the solution to be much lower (acidic condition). This explains why the solution remained in its original form as a liquid and evaporation did not have any effect on it.

The synthesis of resole B_3 showed the best result being more viscous and sticky. This appearance was caused by the certain amount of pyrolytic lignin contained in the crude bio oil. Lignin is a polymeric substance with a phenolic structure which makes it one of the foremost candidates as a substitute for phenol. It is a highly-branched, three dimensional polymer with a great

Table 3. Yield of phenolic fraction based on the initial volume of bio oil

Experiment	Initial volume of bio oil, ml	Yield of phenol fraction, %
1	25	46.51
2	25	64.34
3	32	60.56
4	32	92.05

Table 4. Semi-quantitative results from GCMS analysis of phenolic/neutral fraction

Compounds	% mol	Compounds	% mol
Acetaldehyde	4.04	Phenol, 3-fluoro-	0.10
Acetic acid	5.96	Mequinol	1.18
Hexadecanoic acid	2.27	Phenol, 2-methoxy-4-methyl-	0.64
2-Furancarboxaldehyde	2.81	Phenol, 2,6-dimethoxy -	4.73
Ethanone, 1-(2,4-dihydroxyphenyl)	0.44	Phenol, 2,6-dimethoxy-4-(2-propenyl)	15.17
Ethanone, 1-(2,5-dihydroxyphenyl)	1.72	Isoeuganol (cis+trans)	5.96
Benzenemethanol, 4-hydroxy-	1.72	Pyridine, 2,6-dimethoxy-	5.76
Benzenemethanol, 3-methoxy-4-nitro	6.26	Others	43.50

variety of functional groups providing active centers for chemical interactions[8]. This is the reason for its activity with formaldehyde. Evaporation time took for at least 15 minutes, longer than the evaporation time for resole B_1 caused by the excess amount of water as a solvent due to the excess amount of formaldehyde. After it was placed in a sample bottle, the B_3 resole resin was left to cool off by natural convection until room temperature is attained. At room temperature, resole B_3 became much more viscous.

For resole C_1, phenol will be under alkaline condition and form a phenoxide ion while releasing water. The stable resonance of this ion will then undergo nucleophilic substitution at either the *ortho* or *para* positions of the ring. Then formaldehyde was added by drops to the alkaline phenol solution while it was being stirred and heated. The addition was done when the oil bath temperature reached 50°C before the reaction temperature was attained. In the solution, formaldehyde was attacked with water forming methylene glycol which substituted the ring at either the ortho or para positions forming a mono-substituted hydroxymethyl phenol (HMP). Because the formaldehyde was in excess, the substitution of methylene glycol continues to form di- and tri-substituted hydroxymethyl phenols. This formation of prepolymer resole resin was held for around 2 hours. Fig. 2 simplifies the whole mechanism starting from the reaction between phenol and formaldehyde until mono-, di-, and tri-substituted HMPs formation.

The mono-, di- and tri-substituted HMPs then formed quinone methide under alkaline conditions and released water. At this stage the formation of intermediate quinone methide was solvent assisted (Fig. 3A). Evaporation was then applied at 70°C, 50 mmHg to evaporate the solvent. Although the amount of water decreases, the forming of intermediate quinone methide was still expected to happen by the support of hydrogen bonding between the hydroxymethyl group and the phenolic hydroxyl (Ffig. 3B). However, during the long period time of evaporation (2 – 3 hours) the solution did not show any sign of solvent evaporation. The solution was

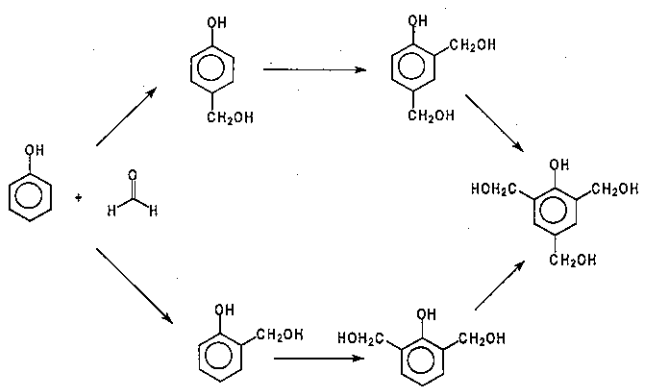

Fig. 2. The formation of mono-, di- and tri-substituted hydroxymethyl phenol (HMP)

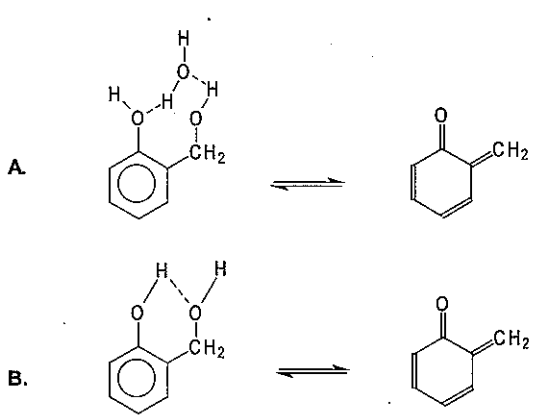

Fig. 3. Quinone methide formation

still in liquid form and no increased viscosity occurred. This shows some possible explanations.

First, there was no reaction at all between phenolic compounds and formaldehyde. As previously mentioned, the phenols used in resole C_1 was the phenolic compound extracted from bio oil. According to table 4, this phenolic fraction contained more than just various types of phenols but also other compounds such as acids and aldehydes. Between the phenols itself, there could be a competition between the different types of phenols in reacting with formaldehyde. Because there were so many phenols, in the end none of them reacted with formaldehyde and no alkaline catalytic reaction happened. The phenols might have formed phenoxide ion, however they then compete with one another in attacking the methylene glycol. This competition was a result of the different affinities of each of the phenols towards methylene glycol. If reaction did happen, then the resole only consists of almost entirely of mono- substituted hydroxymethyl phenol (HMPs) which in result would be infinitely soluble in water. Another explanation for this case was that the solution was too alkalis. In an alkaline condition, formaldehyde tends to undergo what is called the Cannizaro reaction. The reaction takes place by nucleophilic addition of hydroxide ion to the aldehyde. The net result is that one molecule of aldehyde has undergone oxidation and at the same time reduction to produce alcohol[9]. Therefore formaldehyde would produce formic acid and methanol. The higher the alkalis concentration, more formic acid will be released. By time, instead of being alkalis, the solution will be in an acidic condition which in result did not perform the condensation reaction that was expected to happen. Condensation occurs in an alkaline condition whereas the ring electrons of the adjacent HMP attack the electrophilic methide carbon resulting in the formation of methylene bridge units. The reaction is accomplished through the application of pressure and heat and forms phenol formaldehyde prepolymer.

The same condition also happened for resole C_2. The result showed the same appearance as resole C_1. It remained in a dilute liquid form, with no sign of solvent evaporation. The viscosity of the resin was such in the low range that application on wood samples wood be impossible.

By way of summary, it may be stated that not only the reactant composition that effected the resole performance, but also the reaction conditions. The later must be properly handled in order to obtain an excellent quality resole.

Resole B_1 and B_3 both showed the best result than the others. This could be caused by the lignin contained in the bio oil. So when the reaction occurred, although there was not any reaction between the phenols, or other component, with formaldehyde, the lignin itself already has a viscous property. Only by a short time of evaporation the resin's viscosity increased. However, lignin generally has lower reactivity than phenol. This means that less phenol could be replaced by lignin. For this reason a potentially interesting variation on the use of lignin in resole resins is to use the pyrolytic lignin as active filler instead of as a phenol replacement. Study on lignin-phenol-formaldehyde (LPF) resins has been conducted over the years[8] mainly because it has two advantages. First, lignin is readily available as a by product of wood pulping and second, lignin is a stable solid. Resole C_1 and C_2, on the other hand, did not show a good result. The viscosities remained low even with the addition of pure phenol. These resins could be modified by the use of thickeners and additives such as wheat flour, ground Alder bark or METHOCEL (cellulose methyl ether). These compounds could be added at the end of the reaction[3].

Curing process and water-resistant test

The phenolic formaldehyde prepolymers continue to crosslink as water evaporates. The whole reaction of additional crosslinking reaction is illustrated in Fig. 4 (A-C).

Eighteen out of twenty seven samples showed a good result in the hot press. The pair of wood was joined together as a product of the cured resin having stronger bonded properties. The resin exhibited a strong increase in viscosity due to the water evaporation. However, the samples with 120 grams of resole resin per square area did not tend to show the expected performance at any temperature applied. So the 120 g/m^2 samples were not further tested in the boiling water. On the other hand, the rest of the samples were water resistant tested but unfortunately none of them showed a satisfying result. After 1 hour the samples began to break up because the resin dissolved in the tap water. This phenomena show that the resole's viscosity

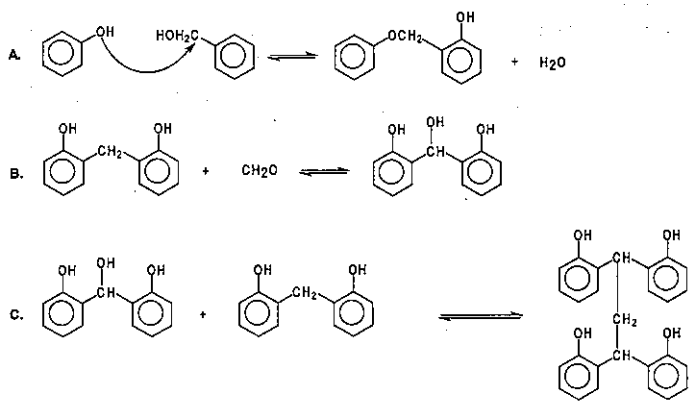

Fig. 4. Additional crosslinking reactions in the cure of the resols

was still too low which means that crosslinking density of the polymer was also low. High crosslinking density is a consequence of high total methylene bridge concentration. The highest methylene bridge concentration was found for resols having formaldehyde/phenol ratio between 1.3 and 1.4[10]. As a result the resole resin penetrated too deep inside the wood pores that there was no resin left on the surface to bond together the wood surfaces. The resin's low viscosity was also affected by sodium hydroxide content inside the resole. Apart from its catalytic action, the base has same other important features such as providing low viscosity for a high average molecular weight resin and an excellent water solubility. A high caustic content in the resin causes the high water absorption because of its high hygroscopic behavior. As a further result, the resole resin has a poor quality. Since the chemistry of these adhesive systems is complex, further research is expected to attain a better understanding of the properties of these adhesive systems.

Conclusion

The resins having phenolic fraction as their component showed a much unsatisfactory result. This was due to, first, various kinds of phenols contained in the phenolic fraction resulting a reactive competition between the phenols during the reaction. Second, the solution condition was too alkalis, so formaldehyde underwent the Cannizzaro reaction.

In order to improve the quality of the resin, further research and modification is expected to attain a better result of the properties of these adhesive systems. However, before applying 50% substitution of the phenol, it is of use to have a better understanding of pure phenol/ formaldehyde synthesis mechanism with frequent analysis of the samples.

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