Parametric Study of Biomass Oil (Palm Kernel Shell Oil) Based Bio adhesive Formulation

Nur ‘Aliah Arish , Azil Bahari Alias

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—Adhesives are used widely in the wood, metal, paper, leather, rubber and glass industries, the demand for these liquid natural adhesives gradually increased. Biomass is a lignocellulosic material which consists of components such as cellulose, hemi-cellulose and lignin. In commercial wood adhesive, phenol formaldehyde act as the raw material, but this substance is not environmentally friendly, cause pollutant and is harmful to human health. This study will compare the physical and chemical properties of the bio based phenolic resins derived from the palm kernel shell with the reference phenol formaldehyde. Formulating the produced palm kernel shell oil, bio based adhesive on a different set of parameters (temperature, time and catalyst loading) with comparison study to the reference phenol formaldehyde adhesive. The objective of the study is to characterize the physical and chemical properties of bio based phenolic resin from palm kernel shell oil and formulate a bio based adhesive on different set of conditions (temperature, time and catalyst loading. Method of formulation need to be improved in terms of increasing or keeping the amount of phenol required. As far as being studied in this paper, it is by manipulating the set of parameter through resinification reaction of bio based oil.**

Keywords— bio adhesive, biomass adhesive, characterization bio adhesive, palm kernel shell, phenolic resins.

I. INTRODUCTION

A study was done on to predict the time left before the fossil fuels run out and in occurrence for the depletion of oil in Malaysia, data shows the ratio of reserve oil, coal and gases to its usage (reserve-usage ratio). This shows that we are nearing to the run out of petroleum supply in another few years as seen in Fig 1, the Percent use of oil and gas domestically. There is a decrease in oil production in 2004 that is from 860,000 b/d to 640,000 b/d (barrel per day). Based on the energy policy in Malaysia, certain steps to aim for the reduction dependence on oil. Thus, the changes have been made to conserve the supply of petroleum by switching to biofuels made from biomass to replace the liquid fuels. Biofuels from biological sources or recycled oils aim to be used as transport fuel that can give promising result in longer term, therefore it is eligible for the study of palm kernel shell oil to be a placement for future adhesives in accordance to this depletion [1]

In Malaysia there is a high amount of oil palm kernel residue from oil palm industry, these shells disposals caused pollution to the environment. Palm kernel shell is a renewable source of biomass now its potential to be a bio adhesive material are being utilized. Bio based adhesive are being formulated as a substitute for commercial adhesive since it is pollutant free and less harmful to human health [2]. In this study it refers to the palm kernel shell oil as the phenolic resin, to reduce the dependence on fossil fuel sources. The oil palm industry is one of the most important agricultural products in Malaysia. Thus, this gives the potential to utilize these palm oil waste as biomass products [3].

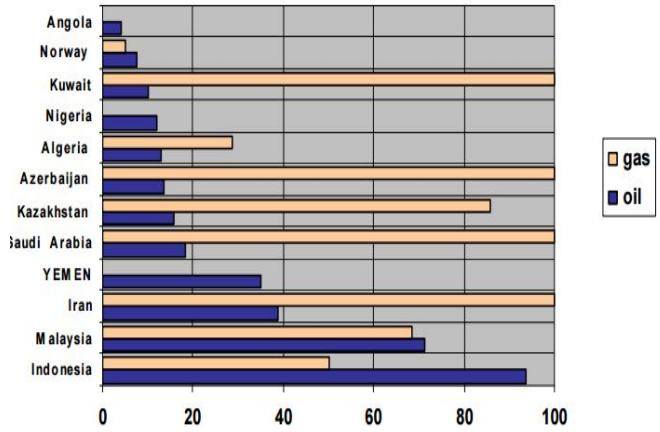

Fig 1 : Percent use of oil and gas domestically (Lahn, 2009).

The production palm kernel oil alone consists of 12% of the production palm oil. The residue of this palm kernel shell was being a concern to the environment as in the 90s it was still seen as a partial waste, but more than 350,000 tons of PKS in the early 2000 were sold [4]. Lignin a complex macromolecule was discovered to be one of the main component in palm kernel shell. Having major functional group such as phenolic, methoxyl and carbonyl influence the reactivity of lignin thus phenol derived from lignin allows for reduced of cost for adhesive production and lower toxicity for adhesive industry[5].

Gasification process can occur in fixed bed gasifier, entrained flow gasifier and in bio oil it occurs in a fluidized bed reactor for lignocellulosic biomass to avoid decomposition and formation of the carbon layer inside the reactor. These complex liquids are steam gasified effectively inside a reactor with the aid of a catalyst such as nickel at a temperature of 800 °C to yield high conversion of hydrogen gas [6].Therefore, with controlled amount of oxygen is advantageous instead of combustion due to the formation on syngas instead of exhaust gas composed of carbon dioxide, sulphur oxide and nitrogen oxide. Through this method it is more economical as palm kernel shell can be processed into marketable bio oil and support a cleaner environment. Palm kernel shell as bio oil can be converted into chemical and high quality fuel when applied to steam and a controlled amount of oxygen[7]

Phenol formaldehyde, a common adhesive component is an important adhesive in the water resistance wood based panel production, however, being a petrochemical product, the major problem is that its price increases along with the fluctuation of petroleum prices. Therefore, the concern is to produce a lower cost phenolic resin, being a bio based substance which is less toxic. Thus the potential and ability of palm kernel shell(Figure 2) oil as a bio based adhesive are being investigated in this study as many available research conducted are focusing on empty palm oil branch as bio adhesive instead of palm kernel shell.

Fig 2: Raw palm kernel shell

II. METHODOLOGY

A. Materials and Method

Material. The palm kernel shell (PKS) oil which are being synthesized through the gasification, 95% ethanol, sodium hydroxide(alkaline), 37%-40% formaldehyde, silicon oil bath (for heating purpose) for a resinification process to produce the bio adhesive.

Preparation of Phenol

The bio oil was produce thorugh the process of upraft gasification of 50 kg/h feed raw palm kernel shell at 800°C[8]

Resinification process of bio adhesive. The phenolic oil was first evaporated from moisture to increase its viscosity using a rotary evaporator equipment. The phenolic oil was then mixed in a flask with ethanol, sodium hydroxide as the alkaline catalyst and formaldehyde. The alkaline catalyst is to provide for the composition of pH. Next it was heated in a silicone oil bath under constant stirring. The ethanol in flask was removed by air circulated oven at 60°C to produce a viscous liquid. The procedure for producing the adhesive below after the evaporation process is summarized as in Figure 3 below.

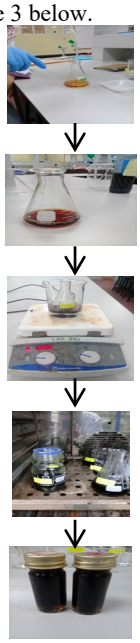

Fig 3:Summarized procedure of the resinification of bio adhesive

The resinification product was studied for its viscosity, pH value and solid content through the effect of resinification time, resinification temperature and catalyst loading have on resinification process. The apparatus used is as in Figure 4.

Formulation of material used for this was done by ratio of formaldehyde/phenol of 2.5 and NaOH/phenol of 0.3 value that is adopted from previous study [9].

Fig 4 : The apparatus used for resenification process.

III. RESULTS AND DISCUSSION

A. Characterization of Liquefied PKS.

Physical characteristics analysis of the liquefied PKS based on the appearance, odour and pH value were measured and was tabulated as in Table 1 below. The result shows that pH value for bio based phenolic resin is 2.9 which is acidic and suitable for adhesive preparation compared to alkaline. The liquid PKS having an appearance of light brown in colour with pungent smell.

Table 1: Physical properties of PKS.

Type of resole resin	Appearance	Odour	pH value
Bio based phenolic resin	Light brown liquid	Pungent smell	2.9

Chemical characteristics analysis of the liquefied PKS was conducted using the GCMS instrument analyzer under the condition of 375°C ,holding time of 30 min and heating rate 30°C min-1 The result is displayed in Figure 5 below, whereas the major compound existed was analyzed with their respective relative area % and findings was tabulated as in Table 2. The value of area% presented in here represent the relative concentration of specific compound in the degraded lignin that was able to pass through the GC column.

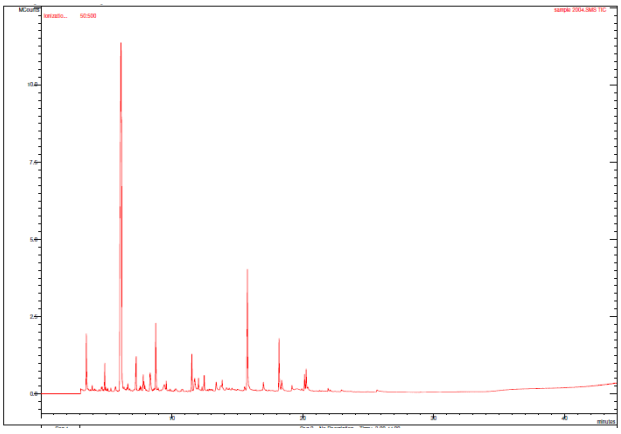

Fig 5: Chromatogram of bio based phenolic resin of PKS

From Figure 5 analysis, it shows that the bio based phenolic oil consists of mainly phenolic derivatives and alcohol. The presence of alcohol can be predicted from the interaction between lignin side chain and the compound present are derivatives of phenolic group with alkane substituents such as –methyl, -ethyl and -pentyl . It is shown that phenolic compound shows the highest percentage of phenol area is 32.98% compared to other chemical compound presents, thus this allows the phenolic oil to substitute as the component for adhesive production [10]. From the analysis the

amount of phenol was abundantly found after 6 minutes of cracking of these volatile substances that result in percent area of 32% phenol.

Table 2: GCMS Analysis of bio based phenolic resin.

Retention time (min)	Compound	Area (%)
4.644	2-Cyclopenten-1-one, 3-methyl	0.72
4.855	2-Propenamide, N-methyl	1.39
5.088	2,4-Dimethyl-2-oxazoline-4-methanol	0.53
6.094	Thiophene, 2-pentyl	0.206
6.617	Phenol	32.98
7.241	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	1.912
8.33	Phenol, 4-methyl	1.708
8.754	Phenol, 2-methoxy	2.87
9.184	2-Chloroethanol	0.468
9.551	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy	0.731
11.506	2-Methoxy-5-methylphenol	1.642
13.372	1,2-Benzenediol, 3-methoxy	1.164
13.827	Phenol, 4-ethyl-2-methoxy	1.834
15.75	Phenol, 2,6-dimethoxy	7.77
18.173	Benzaldehyde, 3-hydroxy-4-methoxy	2.286
20.245	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	1.209

B. Characterization of bio based Phenolic Formaldehyde Resin

After the resinification process was done the chemical characteristics analysis was conducted using the GCMS instrument analyzer for reaction parameter such as the temperature, time, and catalyst loading as seen in Table 3. This is conducted under different operating condition using a total of 9 samples of prepared adhesives. With this the amount of phenol obtained after the resinification was observed. GCMS analysis was performed to analyzed the highest amount of phenol existed in the adhesive that was prepared operating condition.

Table 3 : Resinification reaction parameter

Experiment	Temperature(°C)	Time (min)	Catalyst loading,NaOH(g)
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

The amount of phenol based on temperature as in experiment 1 as plotted in Figure 6, the highest amount of phenol was obtained at temperature of 85°C that is 35%. Increase in temperature allows for the increased in resinification was probably due to the reactivity of phenolic compound with formaldehyde increased[11] It is known that formaldehyde could react at ortho- or para- position of the phenol to produce ortho-methylolphenols, paramethylolphenols, dimethylolphenols and other higher methylolphenols once reacted with phenol during resinification. However the slight decreased of phenol amount at 90°C could be the result of overheating the compound that result in the decrease of lignin component. The controlled amount of time and catalyst loading was set at 60 in and 0.5 g of NaOH. When the temperature is too high the lignin content decreased thus resulting in decrease of phenol content inside adhesive[12]

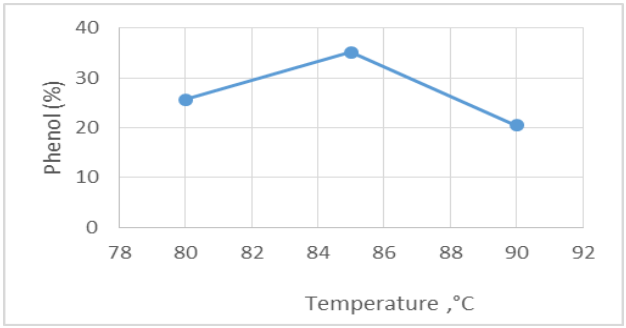

Fig 6 : Percentage of phenol at different temperature.

The second experiment conducted was based on the effect it has on the different time condition, Figure 7. The optimum time for producing the adhesive is at 60 minutes where the amount of phenol is the highest. The probable reason for this is that increasing reaction time leads a much complete reaction[13]. When using long time, the viscosity of resinification product increases. However, when comparing the percent of phenol area available between the parameter of time and temperature there is a significant difference in the value. This may probably due to the effect from evaporating the liquefied PKS using the rotary equipment. The evaporation was conducted at 90°C with no specific time taken due to purifying the liquefied PKS from other moisture such as water.

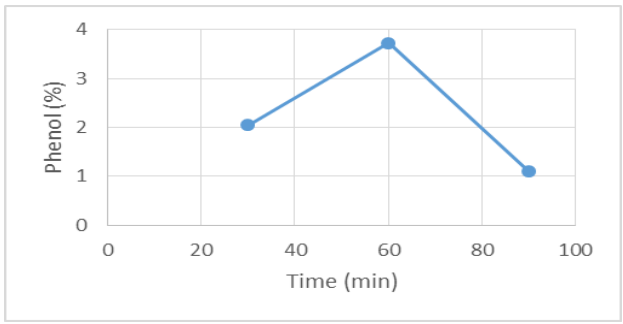

Fig 7 : Percentage of phenol at different time of resinification.

The evaporation was however being done based on eye-basis referring to the flow of droplets coming out from the evaporator at that time, it is considered purify when no more droplets of liquid seen.

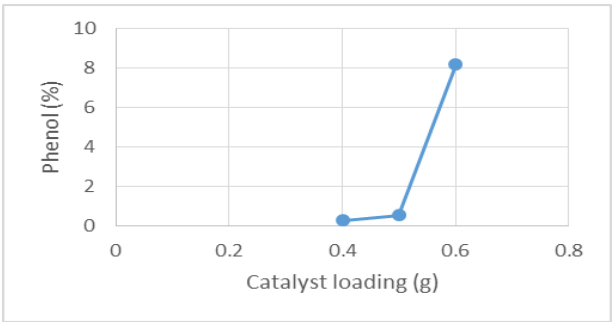

Fig 8 : Percentage of phenol at different catalyst loading.

The third experiment was conducted based on the effect of resinification has on amount of phenol, at different catalyst loading. Figure 8. The amount of phenol has as a slight increase from 0.4g NaOH to 0.5g NaOH.The highest of phenol percent value obtained is at 0.6 g catalyst loading of NaOH, compared to 0.4 and 0.5g of catalyst loading due to the amount was so small that it cannot be passed through the GC column. It is discovered

that the amount of phenol to formaldehyde ratio was considered among the importance factor for formulization of the adhesive, the 2.0-3.0. Higher F/P ratios were found to enhance hydroxymethylation and increase the degree of polymerization, thus in this experiment the amount of ratio is 2.5[14]. The ratio of NaOH/liquefied PKS is also an important factor due to the role of catalyst loading in lignin structure, the higher amount of catalyst loading will result in more degradation of lignin thus lowers the resinification reaction. As chosen for this formulation is 0.3, that as referring to range of suitable ratio of catalyst loading/liquefied PKS which is 0.3 to 0.7. Other than that, another possibility could be due to the temperature used to crack the adhesive, boiling point of phenol is at 182°C, however cracking was done at 352°C, which is higher and may have cause the phenol to be vaporize [15].

IV. CONCLUSION

In conclusion, from the result obtained the optimum condition for formulation in producing bio based phenolic resin is at 85°c temperature, with time of 60 min and catalyst loading of 0.6g. at this point the highest value of phenol can be obtained. However, recommendation can be made towards this study in order to gain more suitable formulations that is the amount of chemical to produce the adhesive. As proven in this study, the ratio value was obtained from previous study. This can ensure the exact effect resinification has on the chosen parameter during experiment and in producing the bio based phenolic resin that have the same strength for substituting the use commercial adhesive.

ACKNOWLEDGMENT

Thank you to my supervisor Dr Azil Bahari Alias for his guidance and patience, Dr Wan Azlina(UPM) and all of the staff in Faculty of Chemical Engineering,Universiti Teknologi MARA.

References

[1] Sorrell, S. (2009). *An assessment of the evidence for a.* United Kingdom: UK Energy Research.

[2] Elham, P. B. (2001). *The Production Of Palm Kernel Shell Charcoal.* Degree Of Master Of Science, Faculty Of Forestry, Selangor.

[3]. *National Biomass Strategy(2013.* Agensi Inovasi Malaysia (Aim).

[4]Dit, M. (2005). *Palm Kernel Shell (Pks) Is More Than Biomass For.* Lafarge Malayan Cement Bhd, Malaysia.

[5]C. Guozhang Et Al., (2016) The Lignin Pyrolysis Composition And Pyrolysis Products Of Palm Kernel Shell, Wheat Straw, And Pine Sawdust, Guangzhou Institute Of Energy Conversion, Chinese Academy Of Sciences, Guangzhou, China

[6] Sakaguchi, M. (2010). *Gasification Of Bio-Oil And Bio-Oil/Char Slurry.* The University Of British Columbia, Chemical And Biological Engineering, Vancouver.

[7] Christopher Higman, M. V. (2003). *Gasification.* Gulf Professional Publishing.

[8] R Ahmad Et Al., (2014) Characterization Of Bio-Oil From Palm Kernel Shell Pyrolysis . School Of Environmental Engineering, University Malaysia Perlis , Malaysia.

[9]Siddiqui, H. (2013). *Production Of Lignin-Based Phenolic Resins Using.* The University Of Western Ontario, Chemical And Biochemical Engineering, Ontario

[10] Doering (1992) "Lignin modified phenol-formaldehyde resins " US 5202403 A

[11]Ding F et al., (2011) Optimization of Resinification of Liquefied Products from Trash Antiseptic Wood. Advances in Natural Science .Vol. 4, No. 2, pp. 143-146. Canadian Research & Development Center of Sciences and Cultures

[12]Hale K.(2013)The Potential Of Canola Protein For Bio-Based Wood Adhesives Department Of Biological And Agricultural Engineering, College Of Engineering Kansas State University Manhattan, Kansas.

[13] Yong Z. (2013) Development of Bio-based Phenol Formaldehyde Resol Resins Using Mountain Pine Beetle Infested Lodgepole Pine Barks .Faculty of Forestry University of Toronto, Canada.

[14] Alfonso T et al.,(2017) Preparation, Characterization and Mechanical Properties of Bio-Based Polyurethane Adhesives from Isocyanate-Functionalized Cellulose Acetate and Castor Oil for Bonding Wood

[15] Klaigaew, K et al.,(2015). Liquid Phase Pyrolysis of Giant Leucaena Wood to Bio-Oil over NiMo/Al2O3 Catalyst. International Conference on Alternative Energy in Developing Countries and Emerging Economies.