

WOOD ADHESIVES MADE WITH PYROLYSIS OILS

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ABSTRACT

Phenol-formaldehyde resins represent an important type of adhesives employed in the production of wood-based panels of superior water resistance (exterior use products).

Phenol is a petrochemical product and the increased oil prices together with the need of reducing the demand on fossil fuels and promoting environmentally friendly products have encouraged developments in the use of alternative raw materials derived from renewable resources. Efforts in this field have accelerated in the latest two decades.

The research group of A.C.M. Wood Chemicals plc in this respect has studied the potential use of biomass derived pyrolysis oils (bio-oils), a portion of which comprises of phenolic compounds, for replacing part of the phenol needed in the formulation of a phenol-formaldehyde resin.

Phenol-formaldehyde resins were produced by substituting up to 50% of the phenol needed in the formulation with bio-oils and by modifying the synthesis procedure. The resins were successfully used in the production of oriented strand board and plywood. This difference in the field of application required an adaptation of the resin production sequence. The use of bio-oils provided in both cases phenolic adhesives with reactivity and performance equal to the non-modified resins.

Further increase in the substitution level is envisaged, with the aim to further reduce the resin cost. The lower toxicity of bio-oils as compared to pure phenol would facilitate resin manufacture. The conformity with the EU directive for sustainable development makes them attractive for further investigation.

INTRODUCTION

In view of the environmental strain caused by fossil fuels and chemicals, and their inherent vulnerable and limited supply, industry efforts were focused on identifying raw materials based on renewable resources. To this direction, the oil obtained by the pyrolysis of renewable biomass was seen as an attractive substitute for petroleum phenol in the production of phenolic type adhesives.

Phenol-Formaldehyde (PF) resins are extensively employed as bonding adhesives in the manufacture of composite wood panels or wood-based panels, imparting the water resistance required for exterior applications (e.g. external house walls, roofs). They are mainly the products of the reaction between phenol and formaldehyde, which is catalyzed by alkali to provide a thermosetting polymer called resole (Figure 1). Other phenolic compounds (e.g. resorcinol) can also react with formaldehyde to provide polymers of the same type with differences in adhesive cost and reactivity. Phenolic resins represent the second important type of wood adhesives following amino resins in terms of consumption volume. In North America, they account for approx. 32% of the total resin solids used compared to 59% for amino resins and the rest 9% for a variety of binders like isocyanates [1]. In Europe, due to board production and application habits, the percentage of PF resin solids applied is estimated to be lower with a higher use of amino resin types.

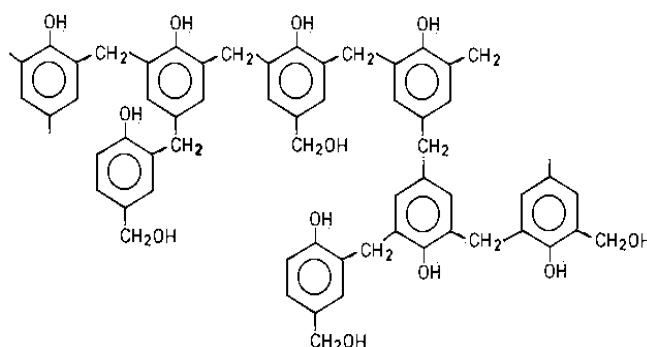


Figure 1: Resole structure.

Although much attention has been paid to biomass pyrolysis for the production of fuels, the research on its use for the production of valuable chemicals like phenol for wood adhesives is limited and relatively new. The oils obtained from fast pyrolysis processes consist of depolymerized biomass and contain compounds, which are derived from both the carbohydrates and the lignin [2, 3]. The chemical compounds in the pyrolysis oils include those of phenols, acids, alcohols, hydroxyls, esters, aldehydes, and unsaturated hydrocarbons. Waste resources, such as bark and sawdust from various kinds of wood, and kraft lignins (produced in papermills) represent main biomass feedstocks investigated and pyrolysis temperatures are in the range of 450-600°C. The phenolic compounds represent a fraction of about 12-17% w/w of the pyrolysis oils, hence it has been found that they may account for up to one-third of the pyrolytic oil [4, 5].

Analysis of the phenolic fraction of the bio-oil revealed the presence of a number of phenolic compounds apart from phenol: *o,m,p*-cresol, guaiacol, catechols, isomers of mono-, di- and tri-substituted phenol with methyl and ethyl groups, isomers of substituted guaiacol with methyl, ethyl, vinyl, allyl and propenyl groups [4-6]. In addition, a few carbohydrate-derived components are also present in this fraction such as furfuryl alcohol and other furfural derivatives. Although the phenolic fraction is a mixture, all compounds are derivatives of phenol and would have the same type of chemical properties. Therefore, efforts have been made to utilize the pyrolytic oil or its

phenolic fraction as a phenol source for thermosetting PF resins [2, 3, 6-14]. The potential for partial replacement of the formaldehyde resin component by the aldehyde fraction of the oil was also investigated.

In an attempt to better utilize pyrolysis oils for PF resin production, various pyrolysis routes were investigated. The aim was to appropriately modulate pyrolysis process to obtain bio-oil suitable for phenol replacement in the making of PF. Parameters such as source material, pyrolysis conditions, reactor configuration and biomass moisture content influence the yield and composition of pyrolysis oils [9]. Two trends are identified in recent pyrolysis procedures: a) increase of the phenolic fraction yield by modifying pyrolysis conditions and/or feedstock (e.g. bark as a raw material for pyrolysis, catalytic pyrolysis [10, 15, 16]) and b) production of phenol-rich but lower yield bio-oil by carefully selected pyrolysis reaction conditions. The latter can be used directly in the synthesis of PF resins without the need for fractionation [10-13].

The economics of producing PF resins with the use of bio-oils have been evaluated on a preliminary basis and found to be very competitive with the current cost of petroleum derived phenol [2, 3, 6, 12]. Complex fractionation methods, unutilised by-products, low phenolic fraction yields may affect process economics negatively.

In this framework, the A.C.M. Wood Chemicals research group has investigated the use of pyrolysis oils as a phenol and/or formaldehyde replacement in the synthesis of phenol-formaldehyde (PF) resins for the production of wood-based panels of superior water resistance with the aims to:

- identify resin raw materials that are less toxic than petroleum-derived phenol
- reduce the demand on fossil fuels and promote sustainable development by using alternative resin feedstocks derived from renewable resources
- reduce resin production cost by introducing raw materials of lower cost than phenol
- obtain resins with the same or enhanced quality than the ones conventionally synthesized.

The first three requirements are fulfilled by bio-oil. The scope of the present work was to evaluate, whether the remaining last requirement can also be fulfilled by pyrolysis oil. For this, various bio-oil samples were tested and a common problem encountered was bio-oil instability and heterogeneity as compared with petrochemical phenol. Preliminary trials have proven the feasibility of phenol replacement by bio-oil and the reality to achieve substitution levels above 15% by weight using fractionated bio-oil (due to the low phenolic content of total bio-oil) and modifying the resin synthetic route. These findings were considered promising and worthy of further investigation, of which results are presented herebelow.

METHODOLOGY AND RESULTS

Phenol-formaldehyde resins were successfully produced by substituting up to 50% of the phenol needed in the formulation with bio-oil and modifying the commercial synthesis Know How. The resins were intended for use in two main applications: production of either Oriented Strand Board (OSB) or plywood (PW) type panels. This difference in resin application requires a different approach in resin production sequence.

PF resin synthesis & testing

By the application of bio-oil samples in PF resin synthesis, to partially substitute the phenol required, modifications in the synthesis route were made necessary, e.g. increase of the sodium hydroxide level used to catalyse the condensation, change of the order of raw materials loading,

different number of polycondensation stages. PF resins were synthesised using various reaction routes and depending on their application (OSB or plywood). The final resin specifications were similarly different (Table 1).

Table 1: Specifications of PF resins according to their application.

	PW resins	OSB resins
Solids, %	42±1	50±1
Viscosity, cp	400-500	100-130
NaOH, %	6.0	2-3

Representative samples of the 40 and 50% substituted resins were subjected to GPC (Gel Permeation Chromatography) measurements, to determine their molecular weight distribution. The GPC graph of 40% substituted resin is very similar to the one of the control resin (Figure 1), while in 50% substituted resin a broad peak appears towards higher molecular weights, which could be due to the more complex composition of the bio-oils as compared to petroleum phenol, that produces higher molecular weight products.

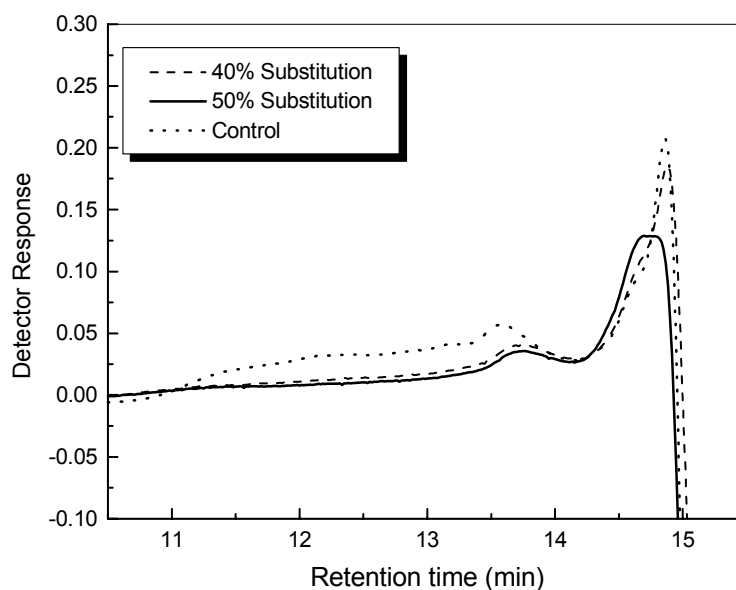


Figure 1: GPC graphs of control, 40 and 50% modified resins.

Furthermore, the DSC (Differential Scanning Calorimetry) scans of bio-oil modified versus control phenolic resins are shown in Figure 2. Both of the modified- and the control-PF scans show a large positive (exothermic) peak, which is due to the polymerisation reaction of the resins. The results of the DSC analysis are given in Table 2.

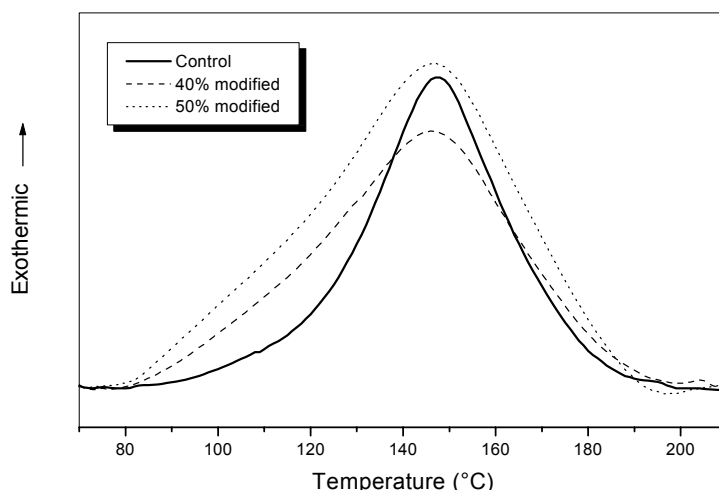


Figure 2: DSC scans of control and bio-oil modified PF resins.

Table 2: Results of DSC analysis of control and bio-oil modified PF resins.

Resin	Onset, °C	Peak max, °C	Endset, °C	Reaction heat, J/g
Control	85	147	195	95.2
40% modified	79	146	206	110.0
50% modified	75	146	196	151.0

The DSC thermograms show that the modified PF resins cure faster than the control one, since all peak characteristics (onset, maximum, endset) are shifted to lower temperatures. The higher heat of reaction of the modified PF resins suggests that the polymer crosslinking density is higher compared to the control PF resin.

OSB, plywood preparation & testing

Pilot scale production of OSB was carried out, by employing 50% bio-oil modified resin. Standard aspen wood strands (*populus tremuloides*) with a nominal thickness of 0.7mm and a length of 142mm were mixed with the gluing mixture, including the resin and additives, and formed to mats, which were subsequently hot-pressed to final panels at a temperature of 210°C and for 220s total pressing time. The target panel density and dimensions were 640kg/m³ and 76 x 76 x 1.1cm respectively. For comparison, panels were produced under equal conditions and using a conventional phenolic resin.

The board properties were determined and main values are presented in Figure 3 in comparison with the corresponding values of conventional phenolic resin and the standard requirements (Canadian standard CSA 0437): the board tensile strength (IB, N/mm²), bending strength (MOR, N/mm²), thickness swelling after immersion in water for 24h (TS, %) and bonding durability (BD, MOR after 2h boiling of the board samples). In each case replicate boards were produced and the results shown represent average values. It is obvious that the resin performance was not negatively affected by the incorporation of bio-oil, since the modified resin has equivalent or even better performance than the control resin.

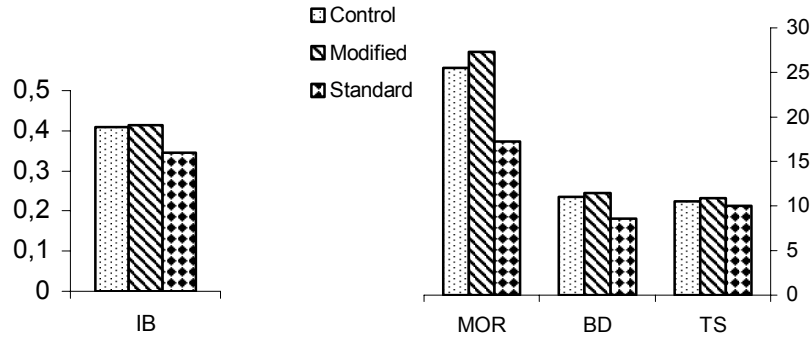


Figure 3: Tensile (IB) and bending (MOR) strength, 24h thickness swelling (TS) and bonding durability (BD) of pilot scale OSB produced with bio-oil modified PF resin.

Industrial scale production of plywood was realized by employing phenolic resin modified with bio-oil at 40% substitution level. Two different types of wood veneers were employed: poplar (hardwood) and okoume (tropical) veneers. The gluing mixture was spread on the veneers and 9-layer panels were formed with 18 or 20mm thickness. After 10-15 min assembling time, panels were pressed at 120°C and press time corresponding to their thickness.

Representative results from testing of the board properties are given in Figure 4. The board samples were tested according to the requirements of bond type WBP (Weather and Boil Proof) of British Standard 6566, using the knife test for assessing the bond quality. The bond quality of the modified resin was compared with that of the conventional resin (control) and the value of plant control. The panel bond performance, however, is highly dependent not only on the resin type but also on the type of wood veneers. The results show that the bond quality of the bio-oil modified resin is equal or even better than that of the conventional resin and higher than the plant control value.

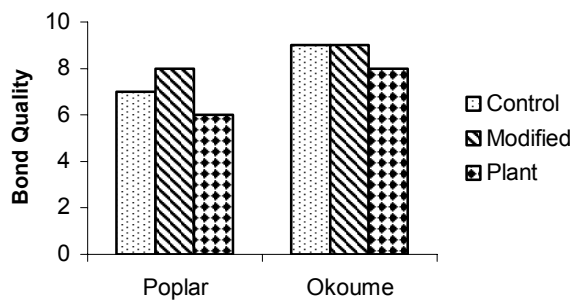


Figure 4: Bond quality of industrial plywood produced with bio-oil modified PF resin.

CONCLUDING REMARKS

The pyrolysis oil can be used in the manufacture of phenolic resins for various panel types with positive results. The reactivity and performance of the modified resins are equal to the ones of the conventional resins. An up to 50% phenol substitution was realized already and further increase in the substitution level is envisaged. To provide significant savings for the resin manufacturer the

phenol substitution level should be above 40% and the price of the pyrolysis oil should be maximum 50% of the phenol price. Its lower toxicity as compared to phenol and its conformity with the EU directive for sustainable development (it is produced from renewable resources) make it attractive for further investigation.

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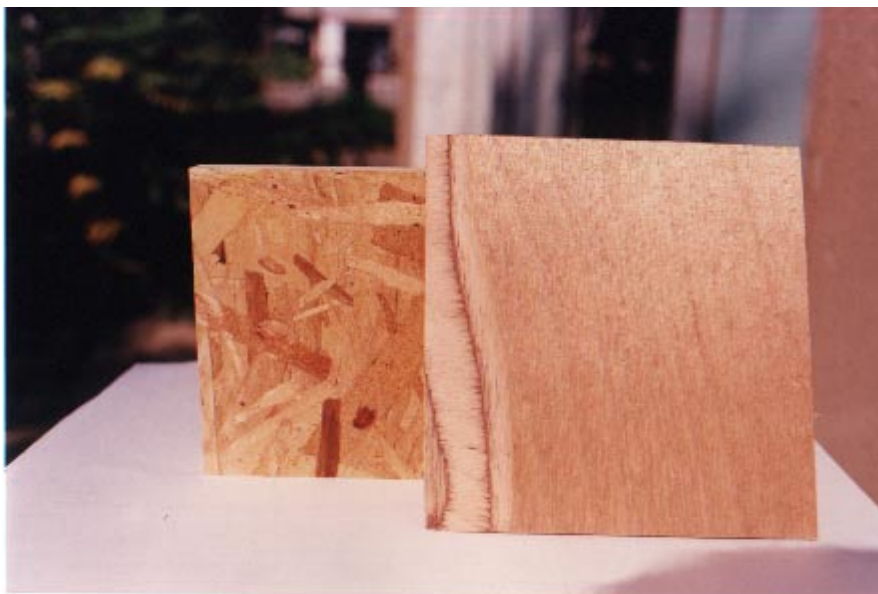
The A.C.M. Wood Chemicals plc group is involved in the development and manufacturing of formaldehyde-based resins and resin additives for the production of wood-based panels. The Adhesives Research Institute (A.R.I.) Ltd., based in Thessaloniki, Hellas, is the research and development centre of the group, specialised in the wood and adhesives chemistry and its aim is to

- develop new products and processes for the wood panel industry following trends and meeting the most stringent international regulations
- test and verify the performance and effectiveness of products and technologies already in use
- reduce formaldehyde emissions from the whole production chain of wood panels
- identify and successfully incorporate environmentally friendly materials and production processes (renewable raw materials, natural resins, panel recycling)
- offer training in a continually updated Know How.

REFERENCES

1. Sellers T. Jr. (2001) "Wood Adhesive Innovations and Applications in North America", *Forest Prod. J.*, 51(6): 12-22.
2. Diebold J., Power A. (1988) "Engineering Aspects of the Vortex Pyrolysis Reactor to Produce Primary Pyrolysis Oil Vapors for Use in Resins and Adhesives", *Research in Thermochemical Biomass Conversion*, Bridgwater, A.V., Kuester, J.L., Elsevier Applied Science, London, pp.609-628.
3. Chum H.L. et al. (1991) "Inexpensive Phenol Replacements from Biomass", *Energy from Biomass and Wastes XV*, Eds. Klass, D.L., pp.531-540.
4. Elder T.J., Soltis E.J. (1980) "Pyrolysis of Lignocellulosic Materials. Phenolic Constituents of a Wood Pyrolytic Oil", *Wood and Fiber*, 12(4): 217-226.
5. Achladas G.E. (1991) "Analysis of biomass pyrolysis liquids: separation and characterization of phenols", *J. of Chromatography*, 542: 263-275.
6. Chum H.L., Diebold J.P., Scahill J.W., Johnson D.K., Black S., Schroeder H.A., Kreibich R.E. (1989) "Biomass Pyrolysis Oil Feedstocks for Phenolic Adhesives", *Adhesives from Renewable Resources*, R. Hemingway and A. Conner, Eds., ACS Symp. Series, No 385, pp.135-151.
7. Gallivan R.M., Matschei P.K. (1980) "Fractionation of Oil obtained by Pyrolysis of Lignocellulosic Materials to recover a Phenolic Fraction for use in making Phenol-Formaldehyde Resins", US Pat. No. 4 209 647.
8. Chum H.L., Black S.K. (1990) "Process for Fractionating Fast-Pyrolysis Oils, and Products derived therefrom", US Pat. No. 4 942 269.
9. Pakdel H., Roy C. and Lu X. (1997) "Effect of Various Pyrolysis Parameters on the Production of Phenols from Biomass", *Developments in Thermochemical Biomass Conversion*, Bridgwater, A.V., Boocock, D.G.B., Blackie Academic & Professional, London, Vol. 1.

10. Roy C., Calve L., Lu X., Pakdel H. and Amen-Chen C. (2000) “Wood Composite Adhesives from Softwood Bark-Derived Vacuum Pyrolysis Oils”, Proceedings of Wood Adhesives 2000, USA, in press.
11. Lu X., Roy C. and Pakdel H. (2000) “Process for the Production of Phenolic-rich Pyrolysis Oils for Use in Making Phenol-Formaldehyde Resole Resins”, US Pat. No. 6 143 856.
12. Himmelblau D.A. (1995) “Phenol-Formaldehyde Resin Substitutes from Biomass Tars”, Proceedings of Wood Adhesives 1995, Forest Products Society, Madison, WI, pp.155-162.
13. Himmelblau D.A., Grozdits G.A. and Gibson M.D. (2000) “Performance of Wood Composite Adhesives Made With Biomass Pyrolysis Oil”, Proceedings of Wood Adhesives 2000, Forest Products Society, Madison, WI, in press.
14. Kelley S.S., Wang X-M., Myers M.D., Johnson D.K. and Scahill J.W. (1997) “Use of Biomass Pyrolysis Oils for Preparation of Modified Phenol Formaldehyde Resins”, Developments in Thermochemical Biomass Conversion, Bridgwater, A.V., Boocock, D.G.B., Blackie Academic & Professional, London, Vol. 1.
15. Sharma R.K., Bakhshi N.N. (1993) “Catalytic Upgrading of Pyrolysis Oil”, Energy & Fuels, 7: 306-314.
16. Samolada M.C., Papafotica A. and Vasalos I.A. (2000) “Catalyst Evaluation for Catalytic Biomass Pyrolysis”, Energy & Fuels, 14: 1161-1167.



Picture 1: OSB and plywood panels