Asian Journal of Chemistry Vol. 14, Nos. 3–4 (2002), 1387–1392

Formation of Industrially Important Chemicals from Thermal and Microwave Assisted Oxidative Degradation of Industrial Waste Lignin

L.P. NAGPURKAR† A.R. CHAUDHARI‡ and J.D. EKHE*
Department of Applied Chemistyr, Visvesvaraya Regional College of Engineering, Nagpur-440 001, India

The lignin recovered from the industrial waste black liquor which was obtained from Simplex Paper Mills, Gondia, Maharashtra State, was subjected to purification using 1,4-dioxane. The purified lignin was oxidized using alkaline nitrobenzene as an oxidizing agent by the thermal degradation method and under the microwave irradiation. The low molecular weight compounds formed during the degradation were extracted and analyzed through HPLC. *p*-Hydroxybenzaldehyde and vanillin were the main compounds identified. Formation of some other compounds was also noticed. These studies have established the merits of microwave technique over conventional thermal degradation of lignin oxidation at normal pressure. It also provides the simpler method for the determination of above two important chemicals for systematic study and also explores the possibilities of utilization of industrial waste–alkali lignin.

Key Words: Oxidative Degradation, Chemicals, Industrial waste lignin, Thermal, Microwave.

INTRODUCTION

Very large quantities of wood are consumed annually in the form of lumber, fuel, wood, paper, cellulose and its products. Lignin is one of the major waste products in the pulp and paper industries. For the delignification of wood materials, Soda process and sulphite process are commonly practised and it is of commercial importance in India. Now-a-days the raw material bamboo is increasingly being supplemented by several agricultural residues like bagasse and other grasses. Increasing recurring production and almost no utilization of lignin possess a disposal problem and has become a matter of environmental concern has mostly, it is burnt to destroy it.

†Department of Chemistry, M.B. Patel College of ACS, Sakoli, Distt. Bhandara-441 802, India
‡Department of Chemistry, Priyadarshini College of Engineering and Architecture, Nagpur-440 022, India

Lignin is a polymeric natural product arising out from enzyme initiated dehydrogenative polymerization of primary precursors[1], *e.g.*, coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol. Considerable amount of research work has been reported on the sulphonated lignin, but alkali lignin is also of commercial importance and under utilized. In order to explore its potential to produce low molecular weight aromatic carbonyl compounds of industrial importnace, it was decided to undertake the oxidative degradation of industrial waste lignin by thermal method and particularly using microwave irradiation.

Several other methods such as hydrogenation[2], alkali fusion[3], pyrolysis[4], etc. have been reported which can be used commonly for lignin degradation. Microwave energy is increasingly utilized by the chemists since last decades[5–7]. It has established its merits over the conventional methods[8–10] such as energy saving, less reaction time, higher yields, easy sampling, etc. Besides synthetic organic chemists, microwave is also used for application to waste treatment[11], polymer technology[12], ceramics[13], alkane decomposition[14], other decomposition processes including hydrolysis of peptide and proteins[15] etc. However, mild oxidation has a potential to produce low molecular weight compounds of industrial importance. This method is useful to characterize the nature of lignin. Interestingly, the aromatic aldehydes formed do not undergo the classical Cannizzaro's reaction[16] as the hydroxy group at *para* position stabilizes the carboxyl group due to resonance stabilized phenolate ions.

Although some work to produce vanillin from lignin degradation has been reported but the lignin source and method of commercial delignification etc. influences the type of low molecualr weight compounds formed and their relative proportion. The lignin undergoes several internal structural changes and hence may produce different other compounds which are structurally very close and difficult to analyze through the TLC; hence, the newer rapid, reproducible and reliable method to analyze such products is also a need of lignin chemists to study lignin degradation systematically. Hence in this research work lignin is oxidized to produce industrially important low molecular weight compounds[17, 18]. In order to enhance the yields in shorter time, thermal degradation method is not found to be advantageous; hence, microwave irradiation technique has been used. Similarly, the HPLC method to characterize a few components in the mixture has been developed.

EXPERIMENTAL

The weights of the compounds were taken on the electronic balance, type AX 200, Shimadzu Corporation, Japan. The microwave oven used for oxidative degradation of alkali lignin was Kenstar model no. OM 9918C, 900 watts, which was modified for the use of reflux condenser so as to perform the reactions at normal pressure (Fig. 1). The chemicals used for the experiment were of AR grade, and used without purification. All standards and solvents used for HPLC analysis were of HPLC grade (Supelco). HPLC analysis was carried out with the equipment. Spectra Physics, C18 column, 5 micron, nucleosil, column length 250 mm, diameter 4 mm, UV detector. The quantitative estimations are based on the injection of the standards under identical conditions.

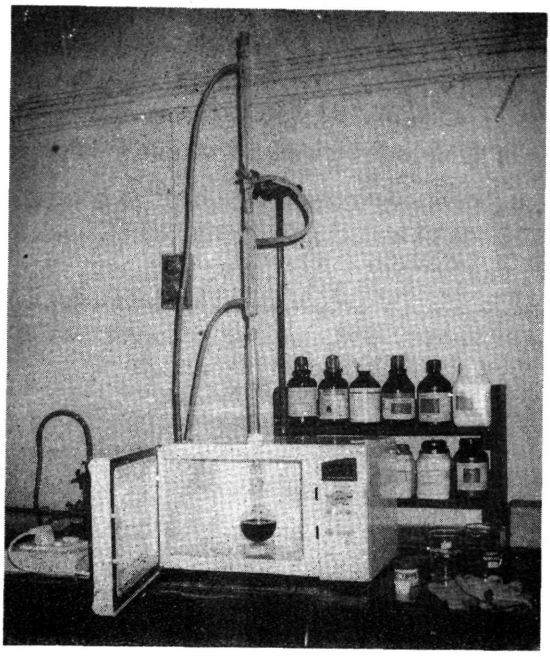

Fig. 1. Modified Microwave Oven

(i) Isolation and purification of lignin from black liquor

Black liquor, 50 mL, was acidified with hydrochloric acid, 50 mL (pH = 4.5). The suspension was warmed to coagulate the lignin and subsequently filtered. It was washed with cold water, dried and weight 5 g.

The crude lignin 5 g was dissolved in minimum quantity of 1,4-dioxane and the dissolved lignin was reprecipitated from water. It was filtered, dried and 3.5 g.

(ii) Oxidation of lignin with alkaline nitrobenzene by thermal method

Lignin 10 g, aqueous sodium hydroxide 1 N, 300 mL, and nitrobenzene 50 mL, were transferred into a round-bottomed flask. The contents were refluxed at boiling temperature for 4 h and allowed to cool; the organic layer was removed by extraction with benzene. The aqueous layer was acidified and undergraded lignin was precipitated. The acidic suspension of lignin with degraded products was again subjected to complete extraction with benzene. Evaporation of benzene afforded a mixture of phenolic compound, 0.9 g.

Analysis of mixture: The above mixture, 9 mg was dissolved in pure methanol 100 mL. The solution was analyzed through HPLC (Fig. 2). The mixture

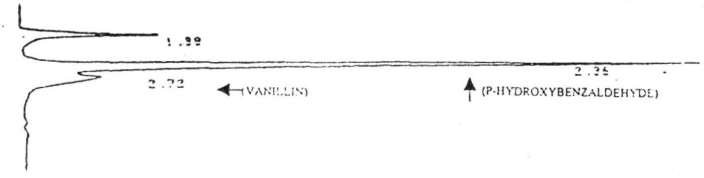

Fig. 2. Chromatogram showing low molecular weight compounds obtained from thermal degradation of industrial waste-lignin

was found to contain *p*-hydroxybenzaldehyde (68.96%) and vanillin (17.24%)

Conditions of Analysis: Wavelength: 285 nm; mobile phase: methanol: water (70 : 30) v/v; flow rate: 1 mL/min.

(iii) Oxidation of lignin with alkaline nitrobenzene using microwave energy

Lignin 10 g, aqueous sodium hydroxide 1 N, 300 mL, along with nitrobenzene 50 mL, were transferred into a round-bottomed flak (Borosil). The flask was properly fitted in the modified microwave oven[7, 19, 20] and the contents were irradiated with microwaves for 50 min at full power by pulse irradiation method applying two water condensers to ensure safe refluxion. After cooking the contents, the mixture of phenolic compounds was obtained by the simpler method as used in the case of thermal degradation.

(iv) Analysis of the mixture: The above mixture 9 mg, was dissolved in pure methanol 100 mL, and the solution was analyzed through HPLC (Fig. 3). The mixture was found to contain *p*-hydroxybenzaldehyde (54.6%) and vanillin (15.5%) in addition to some other unidentified peaks.

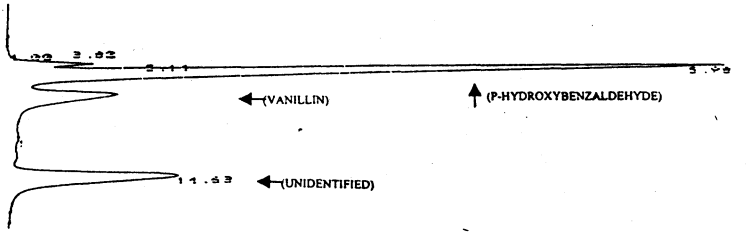

Fig. 3. Chromatogram showing low molecular weight compounds Obtained from Microwave assisted degradation of Industrial waste-lignin.

Conditions of Analysis: wavelength: 280 mm; mobile phase: methanol : water (60 : 40) v/v; flow rate : 0.5 mL/min.

RESULTS AND DISCUSSION

The industrial waste-black liquor afforded around 10% w/w crude lignin. Crude lignin on purification yielded about 95% pure lignin. Its oxidative degradation with alkaline nitrobenzene under microwave energy showed greater degree of degradation of lignin than that of thermal method. Thermal method showed about 8% degradation while microwave irradiation method has afforded 12% degradation at normal pressure. Further, the time required for the oxidative degradation using the thermal method has been greatly reduced. Microwave technique is found to be simpler, fast and more effective as far as the overall efficiency is concerned. Even though, the microwaves can be used in industry for processing foodstuffs, material processing, to break down sludge produced by still mills and other industries and for the treatmetn of hazardous materials from weapon components and radioactive waste of rubber tires and fluorescent bulbs, etc. This study confirms the known advantages of use of microwave in several organic reactions beyond doubt. Particularly, in this case the system which involves aqueous solutions, the use of microwave is very safe, convenient, high

yielding and environmentally benign.

The extent of extractable low molecular weight compounds was found to be 12.35% on pure lignin basis. The HPLC analysis and the low molecular weight compounds showed the formation of *p*-hydroxy benzaldehyde (68.96%) and vanillin (17.24%) in the mixture by thermal method; similarly, *p*-hydroxy benzaldehyde (54.6%) and vanillin (15.5%) respectively by using microwave irradiation, on total low molecular weight compounds basis. The chromatogram (Fig. 3) clearly showed the formation of some more low molecular weight compounds, which could be detected due to non-availability of standards. Although, two individual conditions of analysis of mixture are used for two different systems, but conditions used for mixture obtained by microwave assisted degradation are found to be more appropriate, Further, from the general experience it also seems that some less polar low molecular weight compounds must have been formed as evident from the some of the peaks having relatively larger retention time. As from previous studies, prevention of characteristic Cannizzaro's reaction seems to be very much in agreement.

Conclusion

This piece of research work has provided a much needed HPLC analysis system which should be reasonably suitable for even fresh lignin researchers and chromatographers avoiding the use of buffer solution for the separation of peaks. Secondly, this separation technique may also provide the way for qualitative and quantitative analysis of two main compounds which has immense industrial importance. *p*-Hydroxybenzaldehyde is an important intermediate of dyes and polymers and is widely used in cardioactive drug (Hantzsch synthesis), in cynocoumarins and mercapto pyrimidines, an intermediate for antimetabolites; it is also a constituent of antihypertensive dihydropyrimidine drugs (Biginelli synthesis) and vanillin is a useful component in imitation flavouring of a vanilla in variety of food materials.

Overall, this piece of work has evolved some of the important aspects such as merits of microwave energy for such degradations. It prompts the need to device means to use microwave energy for industrial applications. A simpler method of detection of some important compounds formed during the oxidation of lignin explores the possibility of utilization of industrial-waste alkali lignin more fruitfully if other means of utilization of residues are carefully studied to produce the value added products or by producing precious fuels like coke.

Lastly, it also points out the upcoming challenges to improve the yields of low molecular weight compounds and their possible physical separation or the use of this mixture for the formation of phenol formaldehyde type resins, etc.

ACKNOWLEDGEMENTS

One of the authors J.D. Ekhe, is thankful to the UGC for financial assistance to the minor research project. Mr. L.P. Nagpurkar is also thankful to the UGC for providing a fellowship under FDP during the 9th Plan period to work on the Microwave assisted organic reactions.

REFERENCES

1. K.V. Sarkanen and C.H. Ludwig, *Lignin Occurrence Formation Structure and Reactions*, John Wiley & Sons Inc., New York-London, P.2, (1971).
2. C.P. Brewer, L.M. Cooke and H. Hibbert, *J. Am. Chem. Soc.*, **70,** 57 (1948).
3. M. Philips and M.J. Goss, *ibid.*, **125,** 241 (1938).
4. T.L. Fletcherv and E.E. Harris, *J. Am. Chem. Soc.*, **69,** 3144 (1947).
5. R.A. Abramovich, *Org. Prep. Int.*, **23,** 638 (1991).
6. D.M.P. Mingos and D.R. Baghu Crust, *Chem. Soc. Rev.*, **20,** 59 (1991).
7. S. Caddik, *Tetrahedron*, **51,** 10403 (1995).
8. R.S. Verma, *Green Chemistry* , 43 (1999) A Loupy, A. Petit, J. Hamelin, F. Texier-Boulet, P. Francoise and D. Mathe, *Synthesis*, 1213 (1998); A.K. Bose, B.K. Banik, N. Lavlinskaia, M. Jayaraman M.S. Manhas, Chemtech, **27,** 18 (1997), S.A. Galema, *Chem. Soc. Rev.*, **26,** 233 (1995).
9. G. Majetich and R. Hicks, *Radiat. Phys. Chem.*, **45,** 567 (1995).
10. C.R. Strauss and R.W. Trainer, *Aust. J. Chem.*, **48,** 1665 (1995).
11. K. Magara, J. Aruma and T. Koshijima, *Wood Res.*, **76,** 1 (1989).
12. M. Muray, D. Charlesworth, L. Swires, P. Riby, J. Cook and B.Z. Choudhary, *J Chem. Soc., Faraday Trans.*, **90,** 1990 (1994).
13. R. Dagani, *Chem. Eng. News*, **66,** 7 (1988).
14. M.V. Tse, M.C. Depew and J.K. Wan, *Res. Chem. Interm.*, **13,** 221 (1990).
15. S.T. Chen, S.H. Chiou, Y.H. Chu and K.T. Wang, *Int. J. Peptide Protein Res.*, **30,** 572 (1987).
16. A. Olkay, *J. Org. Chem.*, **27,** 1783 (1962).
17. Ma Wenxiu and Wu Weizhi, *Sepu.*, **14,** 62 (1996).
18. J.C. Pen, *ibid.*, **77,** 2931 (1995).
19. B.M. Khadilkar and V.R. Madyar, *Synth. Commun.*, **29,** 1195 (1999).
20. A.V. Naidu and M.A. Dave, *Asian J. Chem.*, **12,** 914 (2000).

(*Received:* 27 February 2002; *Accepted:* 9 May 2002) AJC-2698