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Liquid Phase Depolymerization of Neyveli Lignite Over Phosphotungstic Acid

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Neyveli lignite was depolymerized with phenol using phosphotungstic acid as catalyst at 185 ºC. The degree of depolymerization was determined by estimating the pyridine soluble portion in the product. Maximum pyridine extractability was 60.61 %. The effect of reaction parameters such as catalyst loading, phenol content and reaction time were studied for high degree of depolymerization. The IR spectrum of depolymerized lignite showed an intense peak for phenolic C-O stretching vibration in support of depolymerization. ^{1}H NMR spectrum of depolymerized lignite also showed an increase in intensity for the signals due to aromatic ring. The TGA results illustrated reduced decomposition temperature for depolymerized product. The present study reveals phosphotungstic acid as an active catalyst for depolymerization of Neyveli lignite.

Key Words: Depolymerization, Neyveli Lignite and Heteropoly acid.

INTRODUCTION

Coal is generally an organic rock like natural product. An understanding of the chemical structure of coal is an essential part of projecting its successful use as a source of chemicals and for conversion processes. As the solubility of coal in organic solvents is very low due to its complexity, methods are required to enhance the extractability of coal in organic solvents. Depolymerization is one of the methods suggested to convert the high molecular weight polymeric material into low molecular weight products. The latter can be characterized by various spectroscopic techniques. Hence it is possible to relate the structure of the depolymerized products to that of the starting material. Thus depolymerization assumes greater significance towards the elucidation of coal structure[1].

Lignite is chemically simple and the conditions of depolymerization are much suited to lignite as the unit structure of the lignite is maintained[2].

Ever since its introduction in the early 1960s, acid catalyzed depolymerization has been a widely used method of converting coal into soluble products and exploiting them for structural elucidation. Heredy and Neuworth[3] reported that coal could be depolymerized by reacting it with phenol-BF_3 complex at 100 ºC. The basis for the method is that coal contains aromatic structures bonded by methylene bridges which are sufficiently reactive to participate in an acid-catalyzed *trans*-alkylation reaction. Ouchi *et al.*[4] modified the depolymerization reaction by substituting *p*-toluenesulphonic acid for BF_3 catalyst and enhanced the reaction temperature from 100-185 ºC. A very high yield of depolymerization was obtained under these conditions and the pyridine extractability was increased to over 90 %. Similarly depolymerization of Neyveli lignite was attempted by Kannan and Nadar[5] with *p*-toluene sulphonic acid as catalyst at 185 ºC. They reported that the extractability of depolymerized Neyveli lignite was higher than 90 %. Ouchi *et al.*[6] also examined the depolymerization reaction with sulphuric acid as catalyst and obtained 83 % pyridine extractability. Comparative studies on the solvolytic extraction of Neyveli lignite and Assam coal through alkaline treatment and acidic depolymerization were carried out by Sharma and Singh[7].

Inspite of higher extractability in pyridine, generally it is believed that sulphonic acid and sulphuric acid catalysts are highly toxic and cause severe corrosion problems[8]. Considerable efforts are being made to find suitable environment friendly solid acid catalysts which can be used successfully to carry out the depolymerization reaction. Heteropolyacids are examples for super acid catalysts and hence they are chosen as active catalysts for depolymerization of Neyveli lignite. Because of their strong acidity due to Keggin phase, depolymerization is expected to occur at a higher rate than *p*-toluene sulphonic acid and sulphuric acid. In addition, these catalysts

have not been exploited to our best of knowledge for depolymerization of Neyveli lignite.

Among the heteropoly acids, phosphotungstic acid is better than others as its protons are strongly acidic and thermal stability[9] is relatively higher than others, for example silicotungstic acid. It is also reported that phosphotungstic acid is a better catalyst than silicotungstic acid based on the thermodyanamic parameters[10].

EXPERIMENTAL

Lignite samples: The depolymerization was carried out with Neyveli lignite sample. The sample was powdered, sized to *ca.* 100 mesh and used after drying at 105 ºC in vacuum for 24 h.

Solvents and reagents: The solvents and phenol used were purified by standard methods[11]. The other chemicals used are of standard purity.

Depolymerization procedure: Lignite sample was depolymerized employing the procedure of Ouchi *et al.*[6] 1 g of lignite, 1 g of phosphotungstic acid and 15 g of phenol were placed in a 250 mL round bottom flask. The mixture was refluxed for 18 h with stirring under nitrogen atmosphere. After 18 h refluxing, the unreacted phenol was removed by steam distillation. The mixture was cooled and the floating solid was filtered, washed repeatedly with distilled water and dried in vacuum at 105 ºC for 24 h. The depolymerized lignite was soxhlet extracted using pyridine. The solvent from the solution was evaporated in vacuum to obtain soluble products.

The FT infrared spectra were recorded in Bruker Optics-Alfa model spectrophotometer by placing the substance over a Zn-Se reflector. The proton NMR spectra were recorded in chloroform-d in a Bruker Avance 300 MHz ultrashield high resolution spectrometer. Thermogravimetric analyses were carried out for raw lignite, depolymerized lignite and pyridine soluble portion of depolymerized lignite in a TA instruments-thermogravimetric analyzer model -Q50 unit for a temperature range of 40º-700 ºC in an inert atmosphere at a heating rate of 20 ºC min^{-1}.

RESULTS AND DISCUSSION

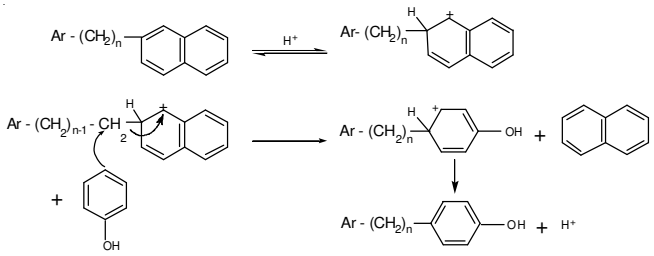
The pyridine extractability of raw lignite and depolymerized lignite are presented in Table-1. The pyridine extractability of raw lignite is much lower than that of depolymerized Neyveli lignite. It is evident that the reaction of lignite with phenol resulted in depolymerization and during depolymerization the polymeric coal molecule is broken into smaller fragments.

TABLE-1
PYRIDINE EXTRACTABILITY OF RAW NEYVELI LIGNITE AND DEPOLYMERIZED LIGNITE

Sample	Pyridine extractability (wt %)
Raw lignite	11.00
Depolymerized lignite	60.61

Depolymerization of Neyveli lignite was proposed to proceed[12] as given in the reaction **Scheme-I**.

Aromatic rings in Neyveli lignite are protonated by the catalyst at α or β position to form arenium ion. The arenium ion makes electrophilic attack on phenol and cleaves the bond of methylene groups to it as shown in the reaction **Scheme-I**. It thus results in depolymerization of Neyveli lignite.



Scheme-I

Depolymerization of Neyveli lignite was carried out at 185 ºC with varying amount of phenol and 1 g of Neyveli lignite. In all the experiments, 1 g of phosphotungstic acid was used as the catalyst. The reaction was carried out for 18 h and the level of depolymerization was determined by the extractability of depolymerized lignite with pyridine. The results of pyridine extractability of depolymerized lignites for different amounts of phenol are presented in Table-2.

TABLE-2
EFFECT OF PHENOL CONTENT ON EXTRACTABILITY

Weight of phenol (g)	Pyridine extractability (wt %)
04	21.15
05	34.50
06	37.30
07	38.46
10	49.43
15	56.00
20	38.91

The data indicate that with increase in amount of phenol, the pyridine extractability increases upto 56 % for 15 g of phenol and then decreases. Hence the optimum amount of phenol was 15 g for 1 g of Neyveli lignite and 1 g of catalyst.

Though increase in amount of phenol increased pyridine extractability (56 %) upto 15 g, at 20 g of phenol a drastic decrease (38.91 %) is noted. The decrease was attributed to the dissolution of the catalyst that destroys the Keggin phase[13].

In order to establish the optimum weight of catalyst for depolymerization, the amount of catalyst was varied from 0.25 to 2.5 g for 1 g of lignite and 15 g of phenol. The reaction was carried out at 185 ºC and the results of pyridine extractability of depolymerized lignites are presented in Table-3.

TABLE-3
EFFECT OF CATALYST CONTENT ON EXTRACTABILITY

Weight of the catalyst (g)	Pyridine extractability (wt %)
0.25	30.71
0.50	38.13
0.75	43.24
1.00	60.61
1.50	65.00
2.00	71.00
2.50	44.92

The data indicate the increase in pyridine extractability with the increase in catalyst content from 0.25-2.0 g, but at 2.5 g of catalyst, a large decrease in pyridine extractability

(44.92 %) was observed. The decrease was attributed to the agglomeration of the Keggin phase[8]. So, the optimum loading of catalyst was 1 g though 2 g of the catalyst gave 71 % pyridine extractability. Since the weight of lignite was 1 g, the loading of catalyst more than 1 g was not considered for its optimization though enhancement in pyridine extractability is noted.

In order to find out the influence of reaction period on depolymerization, the reaction was carried out at different reaction times and the results of pyridine extractability of depolymerized lignites are presented in Table-4. The data indicate that depolymerization increases with increase in time and attain the maximum conversion of 59.60 % at the end of 18 h. Thereafter the pyridine extractability remains almost constant. Hence the optimum time for depolymerization was 18 h.

TABLE-4
INFLUENCE OF REACTION TIME ON EXTRACTABILITY

Duration (h)	Pyridine extractability (wt %)
12	38.13
18	59.60
24	60.91
36	60.54

Kannan and Nadar[5] reported more than 90 % pyridine extractability for depolymerized Neyveli lignite with *p*-toluene sulphonic acid as catalyst. But with the present catalyst of phosphotungstic acid, 60.61 % pyridine extractability was obtained. Inspite of lower pyridine extractability, it is advantageous as the catalyst is not hazardous and technically simple to handle[14].

IR Spectra: The IR spectra of raw lignite, depolymerized lignite and the pyridine soluble portion of depolymerized lignite are shown in Fig. 1.

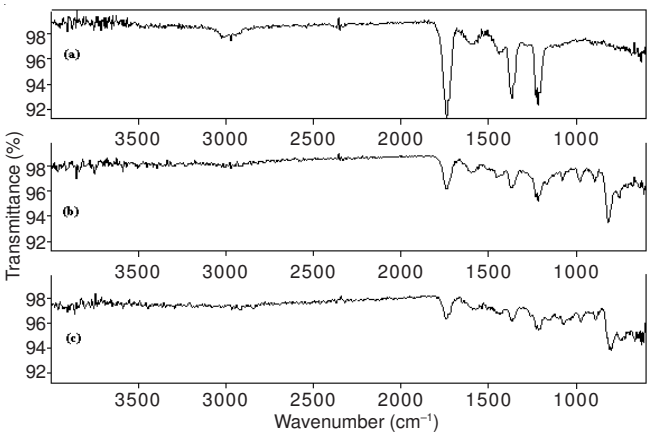
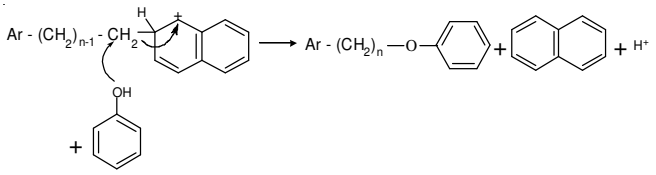


Fig. 1. Infrared spectra of a) Raw lignite, b) Depolymerized lignite and c) Pyridine soluble portion of depolymerized lignite

From the IR spectrum of raw lignite shown in Fig. 1a, it is evident that the peak at 3012 cm^{-1} illustrates the C-H stretching vibration of the aromatic ring. Absence of any peaks above 3050 cm^{-1} illustrates the absence of phenolic OH, alcoholic OH and carboxylic acids. Presence of alkyl group is evident by the peak at 2971 cm^{-1}. It is due to CH_2 stretching vibration. The intense peak at 1738 cm^{-1} is due to C=O stretching of a keto group. The aromatic ring skeletal vibration gives its peak at 1595 cm^{-1}. The CH_2 bending vibration occurs at 1437 cm^{-1} and 1367 cm^{-1}. Presence of phenoxy group is evident by the peak at 1217 cm^{-1}. It is due to phenolic C-O stretching vibration. Ether linkages might not be the part of lignite as there is no peak close to 1000 cm^{-1}. In other words there might be -Ph-O-Ph- linkages rather than -Ph-O-alkyl- linkages.

The IR spectrum of depolymerized lignite is shown in Fig. 1b. The spectrum depicts the similar features as that of Fig. 1a but there are additional peaks below 1000 cm^{-1}. The intense peak at 814 cm^{-1} is assigned to C-H bending vibration of phenoxide group. It illustrates the involvement of phenol in depolymerization of lignite. In addition there is a shoulder to a peak at 1216 cm^{-1}. It is due to the reacted phenolic C-O stretching vibration. The above peaks are important by which the depolymerization of Neyveli lignite is confirmed.

The IR spectrum of depolymerized lignite (Fig. 1b) shows a peak at 1076 cm^{-1} which might be assigned to an aliphatic -C-O- stretching of an ether group but this group was absent in raw lignite. Therefore this group might have arised in depolymerized lignite by an additional depolymerization mechanism. Phenol might have made nucleophilic attack on the -CH_2- group adjacent to the protonated aromatic ring as shown in the reaction **Scheme-II**. This attack might also result in depolymerization, but this mechanism has not been reported earlier to the best of our knowledge. Appearance of the peak due to Ph-O-CH_2- is a strong support for the existence of this mechanism in depolymerization.



Scheme-II

The IR spectrum of pyridine soluble portion of depolymerized Neyveli lignite is shown in Fig. 1c. The spectrum appears similar to that of Fig. 1b. The peaks due to aromatic C-H bending vibration close to 800 cm^{-1} are much intensified compared to Fig. 1b. Hence the fraction carrying phenolic groups is selectively dissolved in pyridine. Formation of a residue from pyridine soluble portion is a clear indication for depolymerization. In addition it also carries the peak due to Ph-O-CH_2- groups. Hence the product derived by nucleophilic attack with phenol is also soluble in pyridine.

^{1}H NMR: ^{1}H NMR spectrum of depolymerized lignite shown in Fig. 2a gives an intense peak due to aromatic ring protons close to 7.3 ppm. In addition there are also peaks on either side of the intense peak. They are also assigned due to different types of aromatic rings. The peaks between 1-2 ppm are due to alkyl protons. The ^{1}H NMR spectrum of pyridine soluble portion of depolymerized lignite is shown in Fig. 2b. This spectrum also shows the peak due to aromatic ring protons close to 7.3 ppm. In addition there are also other aromatic protons shown by weak signals close to the intense peak. The signals due to alkyl protons show slight variation compared to Fig. 2a. The intensity of peak at 1.597 ppm in Fig. 2a is drastically reduced in Fig. 2b. Hence this peak might be due to lignite

that is pyridine insoluble. Although the IR spectrum shows the evidence for Ph-O-CH_2- group, the signal due to -O-CH_2- group is not clearly seen between 3 and 4 ppm, but at 4 ppm, a minute peak appears which could be assigned to such groups.

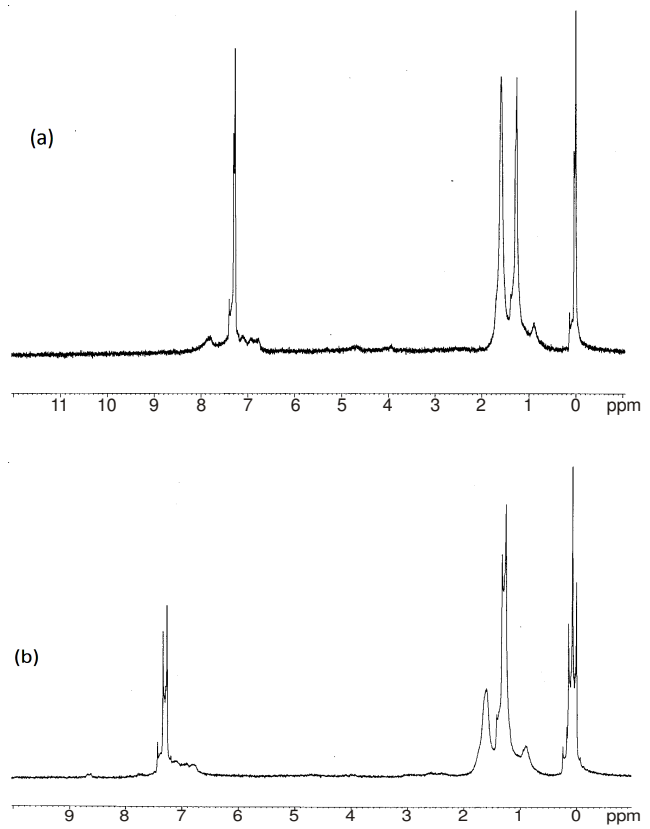
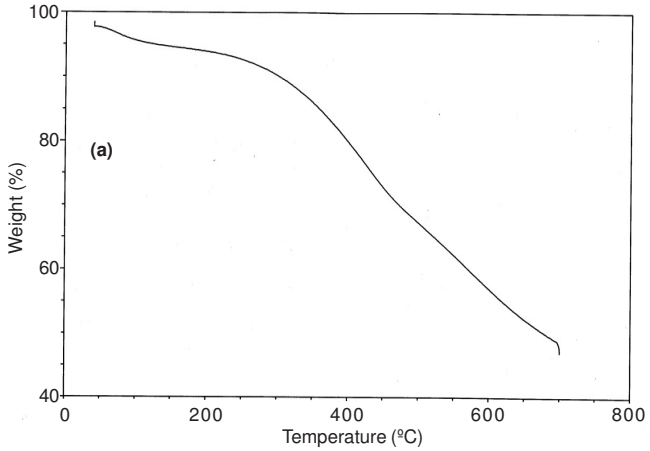


Fig. 2. Nuclear magnetic resonance spectra of a) depolymerized lignite and b) pyridine soluble portion of depolymerized lignite

TGA results: The TGA results of raw lignite, depolymerized lignite and pyridine soluble portion of depolymerized lignite are shown in Fig. 3a, 3b and 3c respectively. The thermogram of raw lignite showed a major weight loss starting at 200 ºC due to its degradation. The weight loss extended up to 700 ºC.

Thermogram of depolymerized lignite showed a major weight loss starting close to 175 ºC. Such a low temperature decomposition compared to that of raw lignite established depolymerization.



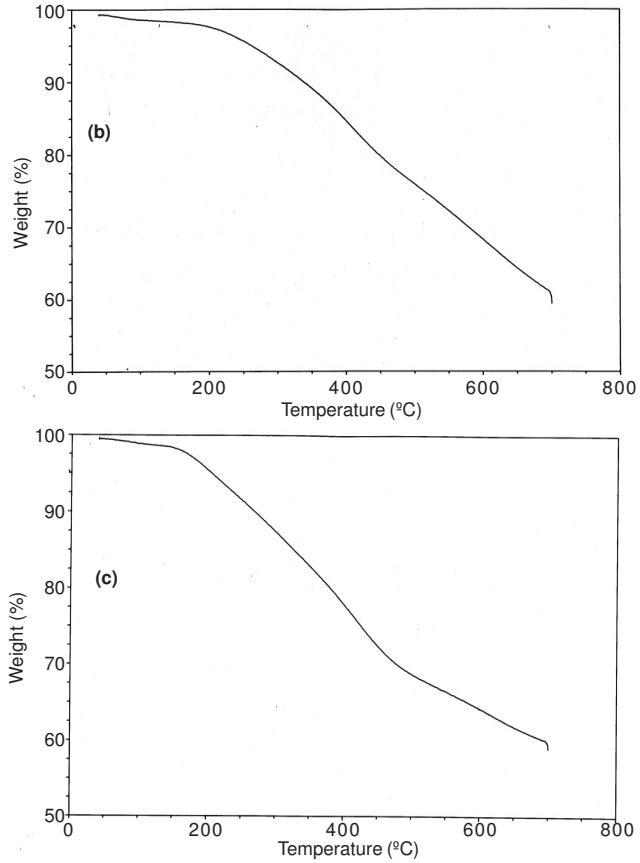


Fig. 3. Thermograms of a) Raw lignite b) Depolymerized lignite and c) Pyridine soluble portion of depolymerized lignite

The thermogram of pyridine soluble portion of depolymerized lignite showed a weight loss at 140 ºC. So, this fraction might be different from pyridine insoluble.

Conclusion

Depolymerization of Neyveli lignite was carried out with phosphotungstic acid as catalyst. The percentage of depolymerization was found to be 60.61 % based on the pyridine extractability. Thus, for depolymerization of Neyveli lignite phosphotungstic acid can be a convenient and eco-friendly substitute for *p*-toluene sulphonic acid.

REFERENCES

1. K. Imuta and K. Ouchi, *Fuel*, **52**, 174 (1973).
2. D.K. Sharma, *Fuel*, **67**, 186 (1988).
3. L.A. Heredy and M.B. Neuworth, *Fuel*, **41**, 221 (1962).
4. K. Ouchi, K. Imuta and Y. Yamashita, *Fuel*, **44**, 29 (1965).
5. P.A. Nadar and P. Kannan, *Indian J. Chem. Technol.*, **4**, 285 (1997).
6. K. Ouchi, K. Imuta and Y. Yamashita, *Fuel*, **52**, 156 (1973).
7. D.K. Sharma and S.K. Singh, *Fuel*, **68**, 717 (1989).
8. A. Popa, V. Sasca, E.E. Kis, R.M. Neducin, M.T. Bokorov and J. Halasz, *J. Optoelectron. Adv. Mater.*, **7**, 3169 (2005).
9. B.M. Devassy, G.V. Shanbhag, F. Lefebvre, W.B. Jack Fletcher and S.B. Halligudi, *J. Mol. Catal. A*, **230**, 113 (2005).
10. S. Shanmugam, B. Viswanathan and T.K. Varadarajan, *J. Mol. Catal. A*, **223**, 143 (2004).
11. A. Weissberger, Techniques of Chemistry, Organic Solvents, Physical Properties and Methods of Purification, Wiley Interscience, New York, vol. 2 (1970).
12. J.W. Larsen and E.W. Kuemmerle, *Fuel*, **55**, 162 (1976).
13. K.U. Nandhini, B. Arabindoo, M. Palanichamy and V. Murugesan, *J. Mol. Catal. A*, **243**, 183 (2006).
14. K. Tanabe, *J. Chin. Chem. Soc.*, **45**, 597 (1998).