

Catalytic Alkylation of Depolymerized Neyveli Lignite

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Catalytic alkylation of depolymerized Neyveli lignite was carried out with various alcohols as alkylating agents in presence of phosphotungstic acid as a catalyst. Alkylation was evident from the higher extractability of alkylated depolymerized lignite in various solvents. Hence it is proved three dimensionally bonded alkyl chains for coal structure cleaving of which by alkylation permits additional depolymerization. The IR and NMR spectra also conformed the alkylation reaction. A suitable alkylation mechanism is proposed. Thermogravimetric analysis results revealed enhanced thermal stability for alkylated depolymerized products.

Keywords: Alkylation, Depolymerization, Neyveli lignite, Heteropoly acids.

INTRODUCTION

Coal has been a material of intensive research for many years, as it is composed of valuable extractable chemicals. The progress of research is hampered by the macromolecular nature of coal. So, in order to free the simple chemicals and then to understand bonding mechanism disrupting its macromolecular structure called depolymerization, becomes inevitable. Methods that have been practiced to break the coal structure, particularly lignite, include pyrolysis, oxidation and depolymerization¹. Depolymerization of Neyveli lignite using phosphotungstic acid as a catalyst, carried out in our laboratory², yielded a residue that helped to have only a semi-quantitative understanding about the structure of Neyveli lignite. In order to gain more insights into the chemical structure of coal, further studies are required to enhance depolymerization.

Catalytic alkylation of coal has been practiced by different researchers and some simple earlier processes in respect of it are highlighted. Friedel-Crafts alkylation of coal with alkyl chlorides in the presence of AlCl_3 was reported by Kroger and Vries³. The acid catalyzed addition of olefins to coal was also studied by Kroger *et al.*⁴ and confirmed an increase in aromaticity as a result of alkylation. Schlosberg *et al.*⁵ studied alkylation of coals at high pressure and they reported alkylation as a beneficial pretreatment for coal liquefaction. Mondargon *et al.*⁶ reported alkylation of Taiheiyu coal using ZnCl_2 and FeCl_3 catalysts with various alcohols. Friedel-Crafts alkylation reaction of Assam coal was studied by Sharma *et al.*⁷ which

resulted in an increase in the extractability of coal in quinoline. Krishnamurthy and Nadar⁸ carried out reductive alkylation of Neyveli lignite and they deduced some important structural parameters.

In spite of many such reports the coal structure appears still complex. Hence, in continuation of such previous reports we in the present study planned to carry out depolymerization of Neyveli lignite using phosphotungstic acid and subsequent alkylation of the resulting residue with alcohols. It was expected that alkylation could reduce inter chain interaction, enhance diffusion of catalyst into the polymer matrix and facilitate additional cleavage of chains. Such an attempt has not been reported to the best of our knowledge.

EXPERIMENTAL

The solvents were purified by standard methods⁹ and all the chemicals used were of standard purity. The Neyveli lignite was powdered, sized to 100 mesh and dried at 105 °C in a vacuum oven for 24 h. It was depolymerized using phosphotungstic acid as a catalyst by a reported procedure². Alkylation of depolymerized lignite was carried out using alcohols. In a typical procedure 0.5 g of depolymerized lignite, 0.2 g of phosphotungstic acid, 1 mL of alkylating agent and 10 mL of tetrahydrofuran were taken in a 15 mL Teflon coated autoclave. The reaction mixture was heated at 200 °C in an air-oven for 18 h. Then the mixture was transferred to a 100 mL beaker and the solvent was evaporated on a water bath. The resulting

semi-solid was dissolved in methylene dichloride and transferred to a separating funnel. It was washed with distilled water to extract the catalyst. The aqueous layer was discarded and the methylene dichloride in the organic layer was removed by evaporation. The recovered solid was dried in an air oven at 105 °C for 3 h. *n*-propanol, iso-propanol, *n*-butanol, iso-butanol, *tert*-butanol, *n*-pentanol, iso-pentanol, *n*-hexanol and *n*-octanol were used as the alkylating agents.

The FTIR spectra were recorded in a 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 BrukerAvance 300 MHz ultrashield high resolution spectrometer. Thermogravimetric analyses were carried out for alkylated lignites in a TG/DTA instruments-thermogravimetric analyzer model EXSTAR 6200 for a temperature range ambient-1100 °C in an inert atmosphere at a heating rate of 20 °C/min.

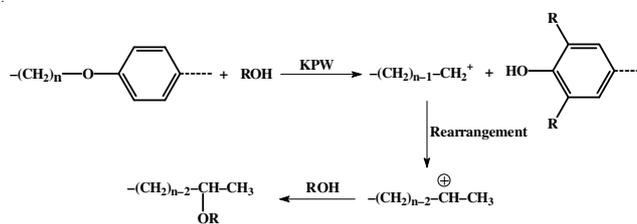
RESULTS AND DISCUSSION

The extractability of raw lignite, depolymerized lignite and alkylated depolymerised lignite in different solvents are presented in Table-1. Both the depolymerization and alkylation after depolymerization increased the extractability, but the latter better than the former. It confirms that alkylation after depolymerization facilitates breaking of the macrostructure of coal into highly soluble simpler ones. Hence, it is verified that single depolymerization is not adequate to significantly break the structure of coal. The introduction of alkyl groups into the depolymerized lignite is also verified crucial to further disrupt the coal structure.

The extractability of raw lignite, depolymerized lignite and nitric acid treated¹⁰ depolymerized Neyveli lignite are given in Table-2. It is evident that the nitric acid treated depolymerized lignite showed higher extractability compared to depolymerized lignite. Hence, nitric acid could easily diffuse into the coal matrix helps in further opening up of the coal structure. As alkylation and nitric acid treatment of depolymerized lignite showed nearly similar level of extractability, both the processes are suggested to have the same chemical transformation. In addition, the nitric acid treatment oxidises aliphatic portions of the coal structure to carboxylic acid functional groups.

IR spectra: The IR spectra of depolymerized lignite and alkylated depolymerised lignites are studied. In the spectrum of propylated depolymerized lignite showed the peaks at 2926 and 2859 cm⁻¹ were due to asymmetric and symmetric stretching vibrations of -CH₂- groups. As the broad peak above 3000 cm⁻¹ was very weak, free phenolic -OH groups might be very few, but there might be a trace amount of water, as there was a peak at 1611 cm⁻¹ due to its bending mode. The aromatic

ring vibrations at 1600 and 1500 cm⁻¹ were not clearly resolved and the aromatic C-H stretching vibrations just above 3000 cm⁻¹ were also very weak. The peak at 1725 cm⁻¹ was due to C=O stretching vibration of keto group. The CH₂ bending vibrations occurred at 1369 and 1453 cm⁻¹. The phenolic C-O-C stretching vibration was seen at 1184 cm⁻¹. The peak at 1065 cm⁻¹ was due to C-O stretching vibration of ether groups. As it was very intense, the process is expected to yield high proportion of ether linkages. The group of peaks below 1000 cm⁻¹ was due to aromatic C-H bending modes. Comparison of this spectrum with that of depolymerized lignite confirms alkylation. The spectra due to other alcohols, showed similar features, hence alkylation is also verified in them. Based on the high extractability and intense C-O-C vibration, the following changes are suggested to coal structure. As shown in the reaction in **Scheme-I**, the aromatic rings are subjected to usual electrophilic alkylation and the alkyl chains are cleaved to form ethers.



Scheme-I

In the IR spectrum of nitric acid treated depolymerized lignite the shoulder above 1654 cm⁻¹ was due to C=O stretching vibration of acid groups. The peaks at 3413 and 3543 cm⁻¹ were due to -OH stretching vibrations of acid and alcohol. So, some of the ether linkages might be hydrolysed to form alcohols during nitric acid treatment. Formation of alcoholic groups could enhance the extractability in pyridine, which is verified from the results presented in Table-2.

TABLE-2
EXTRACTABILITY OF RAW, DEPOLYMERIZED AND NITRIC ACID TREATED DEPOLYMERIZED NEYVELI LIGNITES

S.No	Lignite Sample	Pyridine (wt. %)
1.	Raw Lignite	11.44
2.	Depolymerized Lignite	60.61
3.	Nitric Acid treated Depolymerized Lignite	89.56

¹H NMR spectra: The proton NMR spectra of depolymerized lignite and *n*-propylated depolymerized lignite are shown in Fig. 1 and 2a. The aromatic protons were evident by the peak between 7 and 7.5 ppm. The presence of alkoxy protons was evident by the peak between 3 and 4 ppm. Methylene and

TABLE-1
EXTRACTABILITY OF RAW, DEPOLYMERIZED AND ALKYLATED DEPOLYMERIZED NEYVELI LIGNITES

S.No	Lignite Sample	Pyridine (wt. %)	THF (wt. %)	Ethanol (wt. %)	Benzene-Ethanol (50 % v/v) (wt. %)
1.	Raw Lignite	11.44	07.90	01.99	08.36
2.	Depolymerized Lignite	60.61	20.39	13.07	27.77
3.	Alkylated Depolymerized Lignite	96.08	93.77	63.86	96.10

methyl group close to aromatic ring yielded a peak between 2 and 3 ppm. The broad peak between 2 and 0.5 ppm was due to terminal methyl group and those methylene and methyl groups far off from the aromatic ring. Comparison of this spectrum with that of depolymerized lignite shown in Fig. 1 confirms alkylation. The spectra due to other alcohols shown in Fig. 2b and 2c showed similar features.

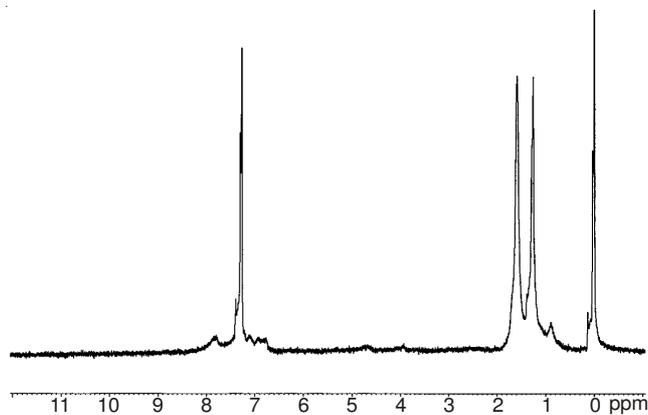


Fig. 1. Nuclear magnetic resonance spectrum of depolymerized Neyveli lignite

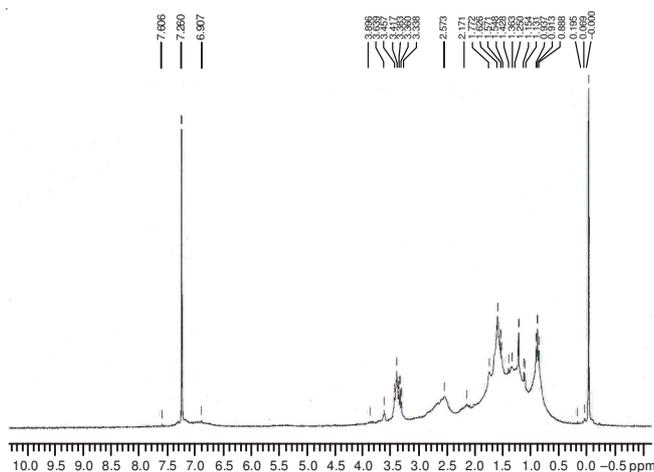


Fig. 2a. Nuclear magnetic resonance spectrum of *n*-propylated depolymerized Neyveli lignite

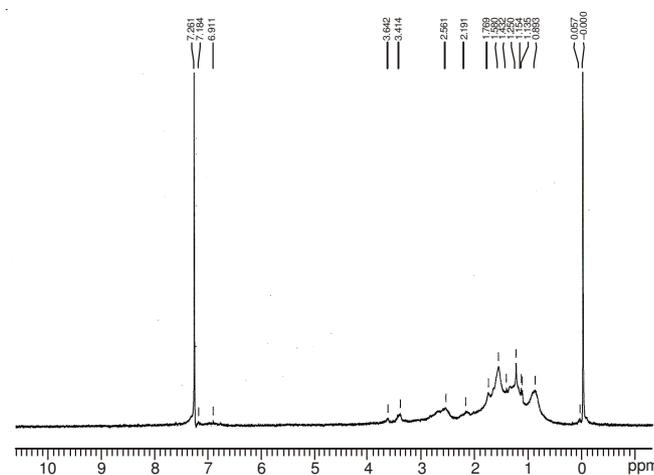


Fig. 2b. Nuclear magnetic resonance spectrum of iso-propylated depolymerized Neyveli lignite

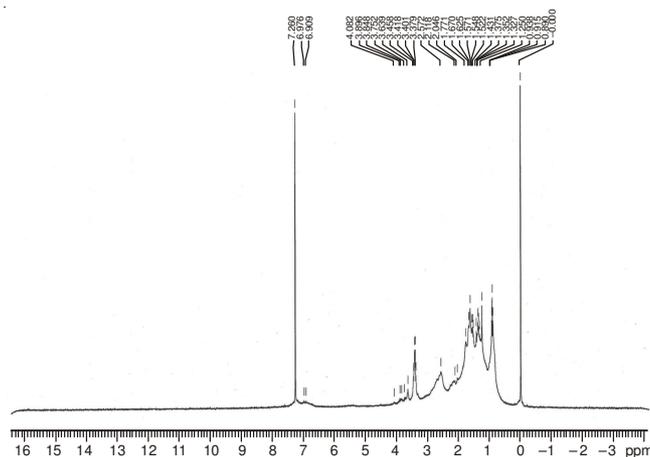


Fig. 2c. Nuclear magnetic resonance spectrum of *n*-butylated depolymerized Neyveli lignite

Thermogravimetric analyses: The thermograms of alkylated depolymerized liginites are illustrated in Fig. 3. The thermograms of products derived by propylation and isopropylation were nearly similar illustrating similar alkylated products in both. So, propyl cation might be rearranged to form isopropyl cation before alkylation. The butylated product showed higher thermal stability than other products. It is also free of adsorbed solvent in its matrix unlike propylated and isopropylated products.

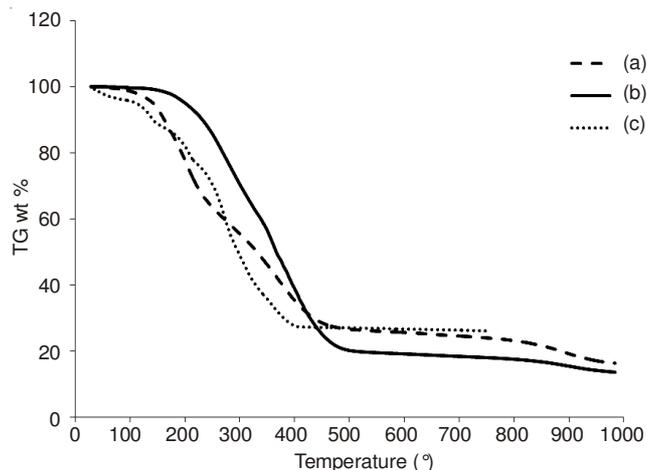


Fig. 3. Thermograms of (a) iso-propylated, (b) *n*-butylated and (c) *n*-propylated depolymerized Neyveli liginites

The thermograms of alkylated depolymerized products with iso-butanol, *tert*-butanol and *n*-pentanol are shown in Fig. 4. The residue of *tert*-butylated product after an initial weight loss showed higher stability than the others. It is more stable than the raw lignite². It differs from that of *n*-butylated product shown in the previous figure. Hence, it is verified that *n*-butanol is not rearranged during alkylation unlike *n*-propanol. The thermograms of alkylated depolymerized products with iso-pentanol, *n*-hexanol and *n*-octanol are shown in Fig. 5. They showed decomposition close to 300 °C yielding residues decomposing at different temperatures. The iso-pentylated product retained solvent in its matrix, as there was weight loss below 200 °C. As the thermograms were different for different alkylated products, the TGA results also confirmed alkylation with all the alcohols.

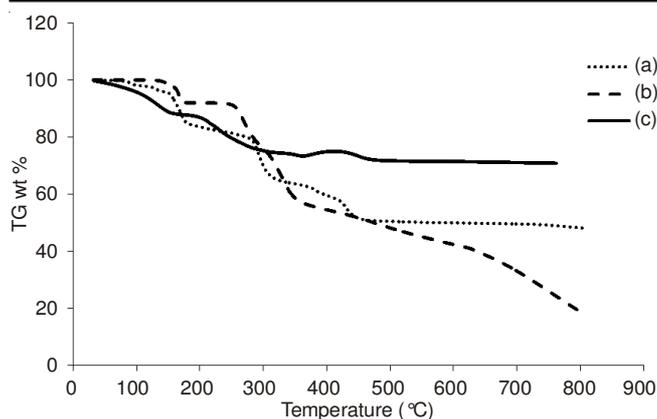


Fig. 4. Thermograms of a) iso-butylated, b) *n*-pentylated and c) *tert*-butylated depolymerized Neyveli lignites

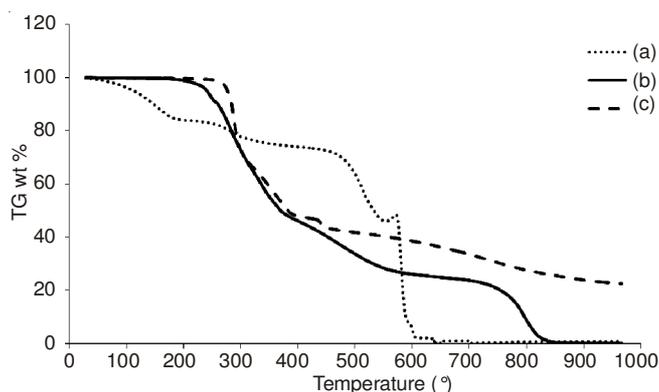


Fig. 5. Thermograms of a) iso-pentylated, b) octylated and c) *n*-hexylated depolymerized Neyveli lignites

Based on the above results of FTIR and NMR spectra in conjunction with TGA, it is inferred that the coal structure carries alkyl chains bonded to aromatic nuclei. The inter chain interactions might be of high magnitude to restrict depolymerization. It suggests that the alkyl chains might also be bonded three dimensionally. Such bonding has to be broken by depolymerization and subsequent alkylation. Lowering of inter chain interaction is important for diffusion of reagents

of depolymerization into the matrix. So, it is confirmed that surface alkylation provides enough space for diffusion of phosphotungstic acid for subsequent depolymerization.

Conclusion

Alkylation of depolymerized Neyveli lignite was carried out using phosphotungstic acid as a catalyst. The alkylated depolymerized lignite showed higher extractability than the depolymerized lignite. Hence, it is evident that alkylation aids further depolymerization by disrupting the coal structure. Coal has to be a matrix carrying three dimensionally bonded alkyl chain matrix. Their cleavage can be aided by alkylation which provides free space for diffusion of catalyst to exhibit its function of depolymerization. The effectiveness of alkylation reaction was understood from FTIR and ^1H NMR spectra. The TGA results were in support of the spectral results.

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