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Pyrocatalytic Degradation of Industrial Waste Lignin Using H_3PO_4 for the Production of Activated Carbons

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Abstract
In this work pyrolysis of industrial waste lignin has been carried out with and without using H_3PO_4 as a catalyst. The pyrolysis reactions were carried out at 350-400 ºC with the heating rate of 10ºC per min. in N_2 gas atmosphere. For pyrocatalytic degradation crude lignin was used instead of pure lignin to obtain residual carbon. The residues obtained were washed properly and studied. The activated carbon obtained was characterized by proximate analysis, CHNS, FTIR, SEM analysis and the BET surface area of char has been studied. It was found that the residual coke after pyrolysis of lignin with H_3PO_4 shows 72.71% of carbon. The FTIR study of activated carbon shows the structural changes occurred during the pyrolysis of lignin. Comparative study of I.R. showed flattening as well as lowering the intensities of maximum peaks in the activated carbons.SEM image of activated carbon shows the porous surface, which act as active sites, where the adsorption takes place. H_3PO_4 activated carbon of lignin has BET surface area 618.77 m^2/g. It was observed that industrial waste lignin is a good raw material for the preparation of activated carbon.

Keywords Lignin, activated carbon, pyrolysis, H_3PO_4.

Introduction

The rapidly increasing cost, dwindling resources and uncertain supply of oil have lent a sense of urgency to the need for developing new technologies for the use of alternative raw materials as a petroleum substitutes. It is now clear that mankind will make a greater demand on renewable resources in the future to meet the needs for energy and particularly for carbon-based chemicals in the wake of eventual depletion of fossil oil and natural gas reserves. Lignin will have an important place in the chemical industry, when it starts shifting from a petrochemical base to coal and renewable materials.

Enormous quantity of wood material is utilized by pulp and paper industries using several pulping processes such as soda process, sulfite process and sulfate process. Lignin thus removed from the wood is a major waste product of pulp and paper industries in the form of black liquor. This industrial waste lignin can be used as a precursor for activated carbon production. In fact this waste lignin has a high carbon content and molecular structure similar to bituminous coal. Hence lignin can be an ideal precursor for activated carbon and the data that is available confirm that lignin is particularly interesting material to use.[1]

Lignin is crosslinked aromatic macromolecule with the high molecular mass. It is relatively hydrophobic and aromatic in nature. Lignin is an amorphous, polyphenolic material arises from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, p-coumaryl, coniferyl and synapyl alcohols. The structure is well suited for its use as a raw material for the production of phenolic chemicals as well as activated carbon.[2]

Recently carbon has been one of the magnificent elements which have revolutionized material science. From the carbon we can obtain the best porous adsorbed (activated carbon) with excellent properties for large scale applications. Activated carbon is the common term used for the group of adsorbing substances of crystalline form, having a large pore structures that make carbon more adsorbent.[3]

Activated carbon is a high-porosity material which is useful in adsorption of both gases and solutes from aqueous solution. Therefore it has been widely used for the separation of gases, the recovery of solvents and removal of organic pollutants from drinking water and as a catalyst support.[4]

Few researchers have studied thermal degradation of lignin under different conditions with or without oxygen. Study of pyrolysis kinetics for lignocellulosics reveals that lignin component starts decomposing at lower temperature than the carbohydrates, but covers the whole temperature range up to 900 °C. Lignin is the main biomass component responsible for the coke formation. However in oxidizing atmosphere the coke yields are lower. Carbonization and solidification with maximum surface area of the coke is obtained at 350-400 °C [5]. At lower temperature, volatile products are released due to dehydration, dehydrogenation, deoxygenation and decarboxylation reactions resulting from the breaking of weaker bonds and condensation reactions [6]. At higher temperature,

rearrangements take place producing volatiles (Syngas, CO and H_2) and reactive free radical reactions occur when stronger bonds are broken [7]. Phenolic components are the main volatile products that are released during the pyrolysis stage between 250-400 ºC along with syngas. TGA experiments of different lignin shows that the amount of C-C bonds in lignin enhances the coke residue formation.

As lignin is a three dimensional branched polymer with aromatic phenolic units, it degrades slowly and leads to the formation of coke as a major degradation product. An intensive study on coke formation and its relationship with lignin was carried out by some researchers [8-12].

Aqueous distillate is the next major component of pyrolysis of lignin. As reported earlier the main constituents in addition to water are methanol, acetone and acetic acid [13-15].

The yellow oil liquid and tar are other components of pyrolysis of lignin. It contains mixture of low molecular weight phenolic compounds [16-18].

In this work pyrolysis of industrial waste lignin has been carried out using H_3PO_4 as a catalyst. The pyrolysis reaction was carried out at 350-400 ºC with the heating rate 10 ºC per min. in N_2 gas atmosphere. For pyrocatalytic degradation crude lignin was used instead of pure lignin to obtain residual carbons. The residue obtained was washed properly. The activated carbon obtained wascharacterized by proximate analysis, CHNS, FTIR and SEM analysis. Also the BET surface areas of char has been studied.

Experimental

1. Isolation of lignin from black liquor

100ml of black liquor was acidified with 20% sulphuric acid. The precipitate obtained was thouroughly washed with water and filtered. The residue was dried and weighed.

2. Pyrolysis of lignin in N_2 atmosphere (without H_3PO_4)

The lignin was extracted from industrial waste black liquor which is used for the pyrolysis reactions. (100 g) of lignin was taken in 500 ml, 3 necked round bottom flask and was heated using Heating Mantle up to carbonization temperature in presence of N_2 flow at the rate of 10 ºC per min. for 2 hours. The pyrolysis temperature achieved was in the range to 350 ºC to 450 ºC which was monitored using thermocouple. Gaseous products (fumes) emerging out during degradation were allowed to escape out. To avoid secondary reaction, the fragmentation products are rapidly removed from the hot zone of reaction mixture by using continuous flow of nitrogen gas. After emergence of gases the next fraction contains aqueous distillate, yellow oily liquid and dark brown tarry materials were collected separately. After carbonization, the sample was cooled down under N_2 flow. The carbonized sample was washed several times with hot distilled water and the sample was dried at 110 ºC in an oven. The dried sample was crushed into powder and sieved with 150 microns test sieve.

3. Pyrocatalytic degradation of lignin using H_3PO_4 in N_2 atmosphere

The pyrolysis of lignin has been carried out using H_3PO_4 as an activating agent. Lignin was mixed with various activating reagent separately along with little water and this mixture was dried at 110 ºC to prepare the impregnated sample. The impregnation ratio was estimated from the following equation.[4]

$$Impregnation\ ratio = \frac{Weight\ of\ sample\ after\ impregnation - Weight\ of\ lignin}{Weight\ of\ lignin}$$

In this study impregnation ratio was 1.0 i.e the lignin and activating agent was mixed in 1:1 proportion.

100 g of lignin was impregnated with 57.46 ml (100 g) of H_3PO_4. The impregnated sample was taken in 500 ml, 3 necked round bottom flask and was heated using Heating Mantle up to carbonization temperature in presence of N_2 flow at the rate of 10 ºC per min. for 2 hours. The pyrolysis temperature achieved was in the range to 350ºC to 450 ºC which was monitored using thermocouple. The gases are allowed escape out and the distillates obtained during pyrolysis were collected separately. After carbonization, the sample was cooled down under N_2 flow. The carbonized samples were washed several times with hot distilled water till complete removal of activating agent. [4, 10, 11]The supernatant liquids tested for the removal of H_3PO_4. Final washing was done by plenty of distilled water and sample was dried at 110 ºC in an oven. The dried samples were crushed into powder and sieved with 150 microns test sieve. Prepared sample of activated carbon was taken for the further analysis.

4. Characterization of activated carbons

The activated carbons obtained after pyrolysis of lignin with and without H_3PO_4 as an activating agent were characterized by various techniques as follows

a) Proximate analysis [19]

In proximate analysis the moisture, volatile matter, ash content and fixed carbon content was determined by standard method using Lab Hosp Oven and Lab HospMuffule Furnace.

b) CHNS analysis

The elemental analysis of activated carbons obtained by pyrolysis of lignin was carried out in Thermo Finnigan CHNS Analyzer.

c) FTIR analysis

The infrared spectrums of activated carbons were recorded on Nicolet MAGNA 550 in spectral range 4000- 400 cm-1 using 64 scans at 4 cm^{-1} resolution.

d) SEM analysis

The porous structure of activated carbon was examined using scanning electron microscope, type JEOL Model JSM-6390 LV at an accelerating voltage 20 kv with SEI image mode and 1 µm resolution.

f) BET (Brunaur- Emmette-Teller) surface area of activated carbons

The adsorption isotherm of N_2 was measured on activated carbon at 77K by use of constant volume adsorption apparatus (SMART SORB 92/93). Before measuring the isotherm, activated carbons were heated at 200 ºC for 2 hrs. in vacuum to clean its surface. The surface area of activated carbon was calculated by the BET method using the adsorption isotherm of H_3PO_4 activated carbon of lignin was studied.

Results and Discussion

Lignin with H_3PO_4 activating agent shows 57.63% yield of activated carbon, whereas without H_3PO_4 it was 39.9% obtained. The activated carbons (char residue) obtained were examined using proximate, CHNS, FTIR, SEM BET surface area analysis methods.

Proximate analysis of activated carbons (Table.1) shows good percentage of fixed carbon. The H_3PO_4 activation gives 58.58% of fixed carbon, whereas pyrolysis of only lignin gives 60.94% of fixed carbon. The H3PO4 activated carbon shows high volatile matter i,e 30.6%, whereas activated carbon of lignin shows low volatile matter i,e 27%. CHNS analysis shows high percentage of carbon for activated carbons. Activated carbon are having small amount of chemically bonded hydrogen and oxygen in the form of various functional groups that usually gives acidic character to the solid carbons, which is usually indicated as ash or residue after ignition. The presence of O, H S and N in activated carbon has important effects on adsorption .[43] Table 2 shows the presence of C, H, O and N content in activated carbons.

FTIR method[21-25] is very useful to determine surface active groups like (C=C) aromatic stretching, carboxyl (-COOH), C=O stretching conjugated, -OH stretching, ether bridge etc. in activated carbons. A comparative spectrum of lignin and lignin coke is shown in Fig.2. The I. R. spectra of activated carbon of lignin with H_3PO_4 is shown in Fig.3. The FTIR studies of activated carbons show the structural changes occurred during the pyrolysis of lignin. Comparative study of I.R. (see Fig.2) showed flattening as well as lowering the intensities of maximum peaks in the activated carbons. Peak found at 3420 cm^{-1} attributed to -OH stretching. Peak at 2920 cm^{-1} is assigned to C-H stretching methyl/ methylene group. C=C stretching in alkynes obtained at 1696 cm^{-1} whereas C=C stretching (nonconjugated) was found at 1636 cm-1. Peaks at 1542 cm^{-1}, 1557 cm^{-1} and 1525 cm^{-1} are attributed to aromatic ring vibrations. C-H bending vibrations in CH_2 occurred at 1422 cm^{-1}. Medium intensity peak at 1378 cm^{-1} has been assigned to C-H deformation in CH_3. C-O stretching in ether has been found at 1162 cm^{-1}. 1113 cm^{-1} shows O-H association in C-OH. Peak obtained at 1028 cm^{-1} shows C-O stretching in O-CH_3 and peak at 672 cm^{-1} assign to the -CH=CH- stretching. Peaks at 607 cm^{-1}, 520 cm^{-1} 1nd 443 cm^{-1} attributed to the bending modes of aromatic compounds. The carbonyl group in lignin is lost during carbon formation. It may attribute to thermal cleavage that leads to the loss of carbon dioxide during the treatment [26]. The peak for C-O stretching in ethers was found in lignin and in activated carbons. FTIR study of activated carbon shows the presence of surface functional groups which plays a key role in the surface chemistry of activated carbons [1, 27].

SEM images of activated carbons shows the porous surface, which act as active sites, where the adsorption takes place[28-29]. The activated carbon formed by H_3PO_4 shows good porosity of carbons. The SEM images of lignin and Activated carbons are given in Fig.4.

BET surface area[30,31] was found to be 618.77 m^2/g for H_3PO_4 activated carbon. From the results it was observed that the activating agents increase the surface areas of carbon. The result shows good agreement with the results obtained by Puaet al.[32] and Moreno-castilla[33]. Fig.5 shows the N_2 adsorption curves for H_3PO_4 activated carbon. From the above results it can be conclude that the pyrocatalytic method enhances the surface characteristics of activated carbons.

Conclusion

It can be concluded that, pyrolysis of lignin in presence of chemical activating agent H_3PO_4 increases the surface area of activated carbon to a greater extent. SEM images confirm the porous structure of activated carbons. The BET surface area of H_3PO_4 activated carbon shows good surface characteristics. The FTIR study shows the presence of the presence of few functional groups in the prepared activated carbons which may act as sites for biosorption of various organic and inorganic pollutants. The overall study indicates that, the industrial waste lignin has the potential for the production of low cost activated carbon having better surface characteristics.

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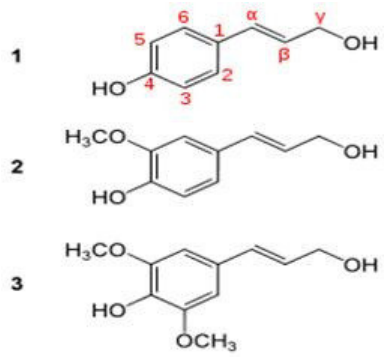

Figure .1 Structure of monomers p-coumaryl (1), coniferyl (2) and synapyl (3) alcohols

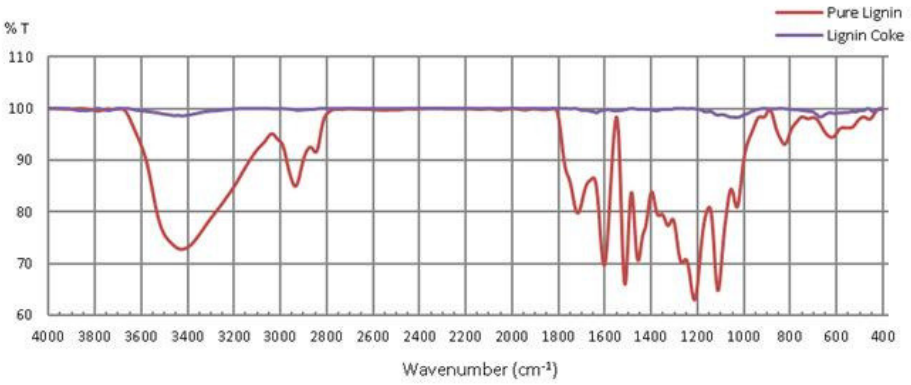

Figure.2 FTIR spectra of pure lignin and lignin coke

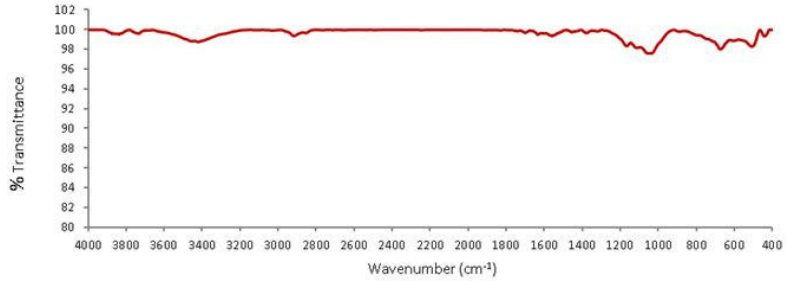

Figure. 3 FTIR spectra of activated carbon of lignin activated by H_3PO_4

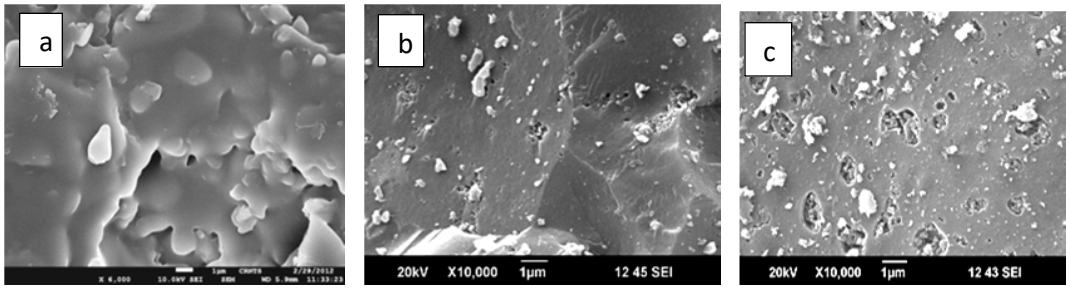

Figure.4 SEM image of a) ligninb) activated carbon of lignin c) activated carbon of lignin using H_3PO_4

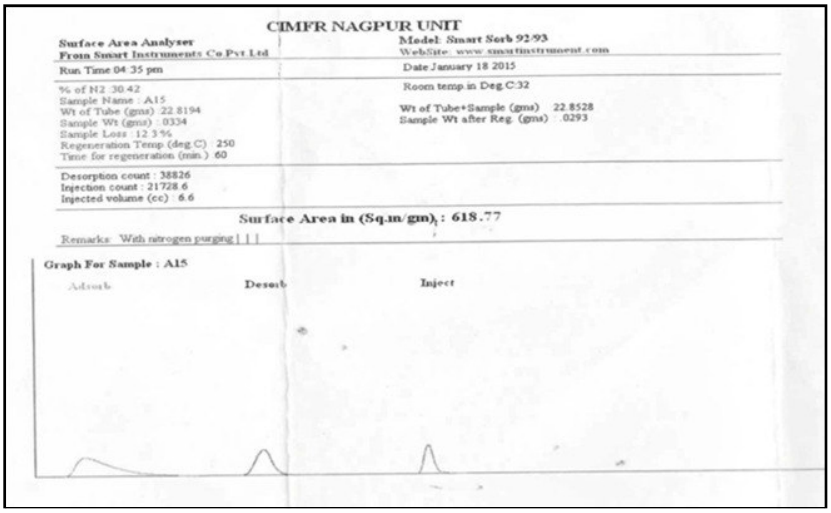

Figure.5 BET N_2 adsorption curve of activated carbon of lignin activated by H_3PO_4

Table 1: Proximate analysis of activated carbons

Sr. no.	Activated carbons obtained from pyrolysis of lignin	Moisture %	Volatile matter %	Ash %	Fixed Carbon %
1.	Lignin only	6	27	6.06	60.94
2.	Lignin with H_3PO_4	3.62	30.6	7.2	58.58

Table 2: CHNS analysis of activated carbons

Sr. no.	Activated carbons obtained from pyrolysis of lignin	C%	H%	N%	S%	O%
1.	Lignin only	70.74	2.93	0.88	1.34	24.11
2.	Lignin with H_3PO_4	72.71	2.36	0.56	1.28	23.09

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