



PREPARATION OF ACTIVATED CARBON FROM INDUSTRIAL WASTE LIGNIN BY CHEMICAL ACTIVATION

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Abstract-

Lignin is a waste which is generally used only for its fuel value; therefore it can be of interest to prepare a higher value product such as activated carbon. Activated carbon can be obtained through chemical activation of industrial waste lignin by using various activating agents such as H_3PO_4 , K_2CO_3 , $ZnCl_2$, KOH , Na_2CO_3 etc. Lignin is a waste which is generally used only for its fuel value, therefore it can be of interest to prepare a higher value product such as an activated carbon from lignin. Activated carbon is a high-porosity material which is useful in adsorption of both gases and solute from aqueous solution. Under appropriate condition of activation it is possible to obtain materials with surface area and pore volume approaching $2000\text{ m}^2/\text{g}$ and $1\text{ cm}^3/\text{g}$ respectively and these material have capacities for aqueous phase adsorption of metallic pollutants that are comparable to those of commercial activated carbon. To optimize the preparation method, the effect of the main process parameters such as impregnation ratio, activation temperature and activation time were investigated. The present review compiles the work done over the last few decades on the use of lignin for the preparation of activated carbon. As there is lots of problem of utilization of industrial waste lignin which is generated as a by-products in the process of conversion of wood chips to pulp in manufacturing of paper, the development of methods to re-use waste materials is greatly desired and the production of activated carbons from wastes is an interesting possibilities. Relatively little work has so far been published and there is considerable scope for more detailed studies on the preparation, characterization and adsorption application of lignin-based activated carbons. Moreover the review also examines the surface chemicals properties of lignin based activated carbons.

Key words- Lignin, Activated carbon, Chemical Activation, Surface area, BET Surface area.



Introduction:

Lignin is the second most abundant natural raw material and nature's most abundant aromatic (Phenolic) polymer whose main function is to cement the cellulose fibres in plant (Unlike cellulose lignin is a highly cross linked polyphenolic polymer without any ordered repeating units). The conversion of wood chips to pulp for manufacturing paper generates huge quantities of by-products lignin. It is generally obtained from black liquor, a waste discharged from paper mills in large quantities, which poses a major disposal problem. Currently much of the lignin produced in paper industry is consumed as a fuel. Although there are some marginal applications such as an adhesive or tanning agent, no major large scale applications have so far been found. Another possible application for excess lignin is as a precursor for activated carbon production. Although lignin is an excellent bio-fuel, it may have higher value application in manufacture of activated carbon.

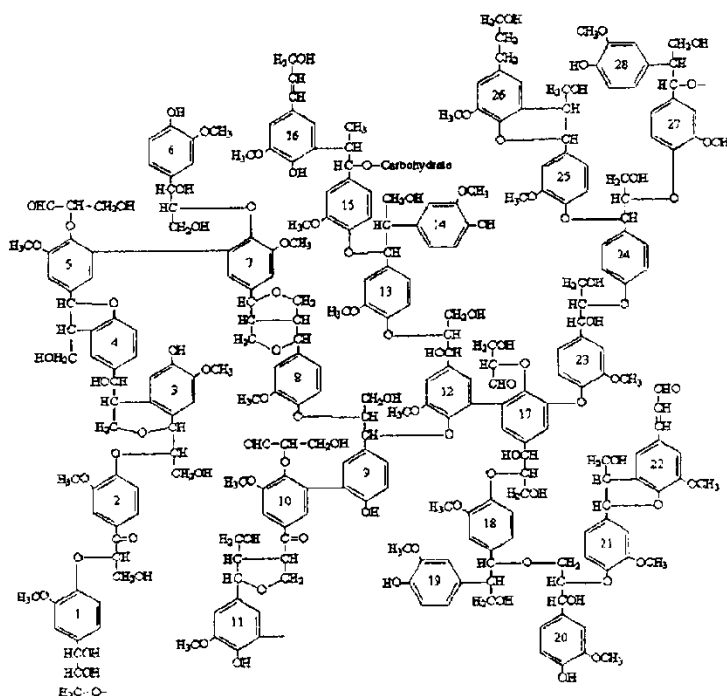
Lignin is a highly stable biopolymer built from three highly cross linked phenyl propane¹⁻³(C₆-C₃)units of p-coumaryl alcohol, coniferyl alcohol & sinapyl alcohol which are bonded together with over two-thirds being ether bonds(C-O-C) and rest being (C-C)bonds . The content of lignin ranges from 20-40% in plants.

Enormous quantity of wood material is utilized by pulp and paper industries. Several pulping processes such as sulphite process and kraft process are used for delignification. The lignin thus removed from the woods is a major waste product of pulp and paper industries. Current global production of lignin is approximately 70 million tonnes. The significant environmental burden posed by this waste product could be alleviated to a large extent if the lignin could be converted chemically to produce value added fine chemicals and other by products. Its reuse in this manner would not only provide an environmental advantage in

reducing the amount of waste product, but at the same time it could provide an additional revenue source for the industries involved. The potential of lignin is not clearly valued because almost all are burned to generate energy and recover chemicals.

Considerable amount of research work has been reported on liginosulphonates and sulphonated kraft lignin in diverse areas⁴⁻⁵ such as animal feed binding, oil well drilling mud, soil stabilization, metal refining aids etc. Several methods such as hydrogenation⁶, alkali fusion and pyrolysis⁷⁻⁸ have been reported which can be commonly used for lignin degradation.

Low molecular weight compounds like vanillin⁹, p-hydroxybenzaldehyde¹⁰, syringaldehyde, some organic acids are obtainable from lignin degradation. Some progress has been reported showing the utilization of lignin as ion exchanger¹¹ and in the sorption mechanism for cation dyes and heavy metal ions.



Structure of lignin



Another approach of utilizing lignin as a co-reactant in phenol formaldehyde resin¹²⁻¹³ and as filler in many polymeric preparations to form lignin-polymer composites¹⁴⁻¹⁶ is on record. Recent studies have shown the potential of lignin to convert it into hydrocarbons and oxygenated high octane fuel additive with reformulated gasoline¹⁷.

The estimates for world consumption of activated carbon vary, being around 1.1 million tonnes per annum, and growing at 9% per annum. The distribution of this total amongst specific carbon precursors is also variable, but some 80-85% (0.9 million tons) of the total production claimed to be derived from non-renewable coal-based resources. The remaining production is derived from renewable resources, such as wood and coconut shell, the later being dominant at ca. 2, 00,000 tons, which requires approximately 1.8 million tons of coconut¹⁸.

Cognizant of the increasing demand profile and relative carbon footprint of different raw materials, activated carbon manufactures are actively seeking to extend the application of “renewable” raw materials. The high carbon contents of lignin make it a potentially attractive feedstock. As a poly aromatic hydrocarbon macro molecule and molecular structure similar to bituminous coal with carbon content between 61-66%, lignin may provide the high carbon yield required for commercial manufacture of activated carbon.

A certain amount of work¹⁹⁻²² has already been carried out on the production of activated carbon from lignin, as well as on the sorption of inorganic and organic substances on lignin derived activated carbon. Although the amount of published work is still comparatively small, the results so far obtained are promising and there is clearly a need for more detailed systematic studies.



Lignin: as precursor for char and activated carbons

1.1 Activated carbon

Activated carbons (ACs) have a very porous structure with large internal surface area ranging from 500- 2000 m² g⁻¹ and owing to this possess good adsorption capacities towards various substances. They have found applications in removing a wide variety of pollutants including both organic and inorganic substances from the liquid and gaseous phase.

There are two basic activation methods have been used.^[20]

1.1.1 Physical activation

Physical activation is a process in which the precursor is developed into AC using gases and is generally carried out in two step process. Carbonization is the first stage and involves the formation of a char, which is normally non-porous, by pyrolysis of the precursor at temperature in the range 600-900°C in an inert, usually nitrogen, atmosphere. Activation is the second stage and involves contacting in char with an oxidising gas, such as CO₂ or steam, in the temperature range 600-1200°C, which results in the removal of disorganized carbon and the formation of a well developed micropore structure.

1.1.2 Chemical activation

Chemical activation involves impregnation with chemical such as H₃PO₄, K₂CO₃, ZnCl₂, KOH, Na₂CO₃ etc. followed by heating under nitrogen flow at temperature range 450-700°C depending on impregnate used. Carbonisation and Activation will proceed simultaneously and the method will leads to the materials with higher micro pore volumes and larger surface area.

1.2 Lignocellulosic precursors

Gergova et al. (1994) in their study of the production of ACs from agricultural by-products suggested that lignin char has more total pore volume as compared to cellulose char. Lignin is the main component responsible for most of the char produced^[23]. It was also studied that the one with higher lignin content produces a higher amount of char which in turn produces the highest amount of AC^[24]. Furthermore, the BET surface area was found to be comparable and with highest micropore surface area.

1.3 Activated carbon from lignin

As lignin is rich in carbon content and has a proven ability for sorption (Dizhbite et al., 1999; Demirbas, 2004; Basso et al., 2004; Laivani et al., 2000; Srivastava et al.' 1994; Ludvik and Zuman, 2000; Allen et al., 2005). A brief summery of work published and which is discussed in subsequently in Table 1.

Table 1.

Sr. No.	Lignin used	Activation	Conditions	Surface area (m ² /g)	Micropore volume (cm ³ /g)
1.	Kraft lignin	Physical: carbonisation- N ₂	C (300°C , 2h) +A(800°C + 40h)	1613	0.47
		Activation CO ₂	C (350°C , 2h) +A(850°C + 20h)	1853	0.57
2.	Lignin ^b	Physical: carbonisation-N ₂	C (500°- 900°C)	10-50	---
3.	Hydrolytic lignin	Physical: carbonisation- Ar activation - steam	C (600°C , 2h) + steam (800°C),	865	0.365
4.	Hydrolytic lignin	Physical: pyrolysis (fluidised bed) - air (with Al- Cu- Cr catalyst) activation - steam	Temp; pyrolysis- 700°C, Steam activation- 780°C	769	----
5.	Hydrolytic lignin	Physical: seam activation	700°C , 2h	----	0.33
6.	Indulin C ^a	Chemical: carbonised then activated	Lignin:	514	0.214

		with KOH	KOH::4:1 (700°C , 1h)		
7.	Lignin ^b	Chemical: H ₃ PO ₄ , K ₂ CO ₃ , ZnCl ₂ , KOH , Na ₂ CO ₃ , NaOH	Impregnation ratio 1 for all	-800 - 2000	----
8.	Kraft lignin	Chemical: ZnCl ₂	Lignin: ZnCl ₂ :: 1:2.3 (500°C, 1h)	-1800	1.039
9.	Kraft lignin	Chemical: H ₃ PO ₄	Lignin: H ₃ PO ₄ :: 1:2 (427°C, 2h)	1459	0.82
10.	Hydrolysis lignin	Chemical: carbonised then activated with KOH	Lignin: KOH :: 1:4 (850°C, 15min)	2753	1.37
11.	Kraft lignin	Chemical: H ₃ PO ₄	Lignin: H ₃ PO ₄ :: 1:1.4 (600°C, 1h)	1370	0.78

C- Carbonisation , A- activation, ^a From black liquors of kraft pulping

^b From stock black liquors of kraft pulping, acidulated with CO₂ to obtain the lignin.

Results and Discussion:

Although a large amount of lignin is unutilized, this work aims to present the findings on the use of industrial waste lignin as a precursor for preparation activated carbons. It is useful in adsorption of both gases and solute from aqueous solution. It indicates that properly sequenced treatments can ensure greater and better utilization of industrial waste lignin. Since large amount of renewable industrial waste alkali lignin is available, instead of isolating it from a particular species, the use of industrially produced lignin is considered more practical and rational for the purpose.

The work so far carried out indicates that lignin is relatively non-reactive and probably the component of lignocellulosic precursors primarily responsible for the micro porosity of activated carbons. Under appropriate conditions of activation it is possible to obtain materials with surface areas and pore volumes approaching 2000 m² g⁻¹ and 1 cm³ g⁻¹, respectively, and these materials have capacities for the aqueous phase adsorption of metallic pollutants that are comparable to those of



commercial activated carbons. Relatively little work has so far been published and there is considerable scope for more detailed studies on the preparation, characterisation and adsorption applications of lignin-based activated carbons. Continued research in this areas will no doubt yield an increased demand for lignin and lignin products in the future.

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