

ACTIVATED CARBON FROM RENEWABLE RESOURCES – LIGNIN

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The world consumption of activated carbon is approximately 1.1 million tons per annum. Only some 15-20% of this is manufactured using renewable resources. Lignins in kraft pulp black liquors are polyaromatic macromolecules with about 60 wt% carbon contents, derived from renewable resources. Recently, an efficient process for the recovery of lignin from kraft black liquor has been developed, “LignoBoost”; this lignin has a carbon content of ~66 wt%. In 2010, a research consortium of Sodra, Jacobi Carbons and Innventia, initiated the “LignActiv” project to establish the commercial and environmental sustainability of the manufacture of activated carbon from this lignin. This paper reports initial studies on the carbonization and activation behaviour of “LignoBoost” lignin subjected to laboratory scale physico-chemical activation processes. The paper describes the yields and physical properties of lignin-based chars and provides an initial evaluation of the nanoporous structure of the resultant “LignActiv”-activated carbons.

Keywords: lignin, LignActiv, activated carbon, carbon footprint, renewable resources

INTRODUCTION

Activated carbon is one of the most widely applied filtration media in the world, vital to both air and water treatment. As a structurally disordered carbon form, activated carbon is porous at nanometre scale. The unique adsorptive properties of activated carbon result from the interaction of the attractive forces that exist between the atoms making up the walls of the nanopores and the contaminant molecules at atomic level. Its large adsorptive capacity results from the complex, three-dimensionally contorted, interconnected, porous network that exists within the activated carbon grains. The internal surface area and pore volume are several orders of magnitude greater than the external surface area and volume of grains themselves. Commercial activated carbon possesses a high internal surface area – typically around $1000 \text{ m}^2\text{g}^{-1}$, and large internal pore volume – $0.3\text{-}3 \text{ mL g}^{-1}$. Porosity within adsorbents has been categorized by IUPAC according to width.¹ The largest pores – the Macropores (access pores) are 1000 nm to 50 nm wide, the intermediate pores – the Mesopores (transport pores) between 50-2 nm wide, and the smallest pores (with the greatest adsorption energy) – the Micropores are <2 nm wide; their inter-

connection and distribution are illustrated in Figure 1.

Basically, the manufacture of activated carbon is a two-stage process of carbonization and activation by chemical or physico-chemical means. Activation proceeds by the removal of the carbon atoms from the nanostructure of the precursor accessing and interconnecting the inherent structural porosity. Chemical activation is achieved by soaking/impregnation of the precursor in chemicals that dehydrate the precursor, with some carbon volatile loss. Subsequent heating to 450-750 °C (charring) and removal/recovery of the activating chemical results in an “activated”, porous, carbon product. The chemicals most often used are phosphoric acid, zinc chloride or potassium hydroxide. The kinetics of chemical impregnation and the rinsing/recovery stages of chemical activation are favoured by the use of small particle sizes, so that the chemical processes are used, almost exclusively, to manufacture powdered activated carbon products.

The physico-chemical process differs from the chemical one by the use of high temperature gasification to remove skeletal carbon from a previously carbonized char, to

access and connect structural porosity. Initial carbonization, “char manufacture”, is generally carried out within the 500-750 °C range, in the absence of oxygen, char production being dominantly carried out in pit or retort kilns. Activation utilises large gravity fed vertical or horizontal rotating kilns to contact the char with an oxidizing gas, most often steam. The steam/char gasification reactions are complex, producing a number of gaseous reactants in the kiln environment: CO₂, H₂O, CO, CH₄ and H₂, H₂O, CO₂ being dominant. Gas composition is determined by temperature, in the 800-1000 °C range, with H₂ favoured at higher temperature. The net of all steam gasification reactions is endothermic, while the manufacturing processes require the use of some additional fuel.

The estimates for the world consumption of activated carbon vary,² being around 1.1 million tons per annum, and growing at 9% p.a. The distribution of this total amongst specific carbon precursors is also variable, but some 80-85% (ca. 0.9 million tons) of the total production is claimed to be derived from non-renewable coal-based resources.^{2,3} The remaining production is derived from renewable resources, such as wood and coconut shell, the latter being dominant at ca. 200000 tons, which requires approximately 1.8 million tons of coconuts.³

Carbon dioxide is the dominant greenhouse gas, contributing to the carbon footprint of the manufacture of both coal and coconut-based activated carbons. Figure 2

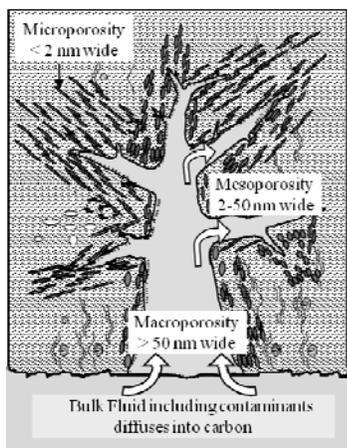


Figure 1: Caricature of the pore structure of activated carbon

Recently, an efficient process for the recovery of kraft lignin from the pulping (black) liquor has been developed – the

shows that the production of activated carbon from coal has a positive carbon footprint, releasing ca. 6 tons of CO₂ per ton of activated carbon produced, returning the carbon previously sequestered over geological time to the present atmospheric inventory. Figure 2 also shows that the production of coconut shell-based activated carbon has a negative carbon footprint. The manufacture of coconut-based carbon fixes the CO₂ that would have been released from the decay of the coconuts as a solid product – the activated carbon. The mass of activated carbon, pro-rated to the carbon sequestered by coconut palm growth more than offsets the emissions from coconut-activated carbon production and transportation.

Cognisant of the increasing demand profile and relative carbon footprint of different raw materials, active carbon manufacturers are actively seeking to extend the application of “renewable” raw materials. The high carbon content of lignin makes it a potentially attractive feedstock. As a polyaromatic hydrocarbon macromolecule with a carbon content between 61-66%, lignin may provide the high carbon yields required for commercial manufacture of activated carbon. The kraft pulping industry produces large quantities of lignin as a by-product. Generally, this lignin is dissolved in the process liquor (black liquor) and used as fuel for the recovery of process chemicals and energy provision elsewhere in the pulping operation.

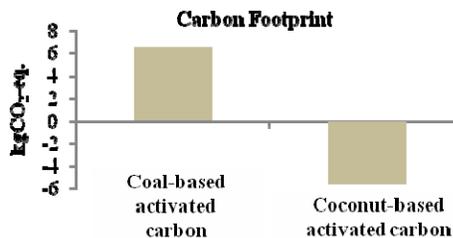


Figure 2: Carbon footprint for activated carbon manufacture, coal and coconuts

“Lignoboost”.⁴ In this process, the black liquor from kraft pulping is acidified with gaseous carbon dioxide, precipitating the

lignin, which is dewatered, slurried in acid and washed. The use of CO₂ reduces the process carbon footprint. The available fuel quality lignoboost lignin contains low levels of impurities, such as ash (0.8-1%) and carbohydrates (1-2%), and high carbon contents of ~66 wt%. Although this lignin is an excellent bio-fuel, it may have higher value application in the manufacture of activated carbon. In 2010, a research consortium of Sodra, Jacobi Carbons and Innventia began the “LignActiv” project, to establish the commercial and environmental sustainability of the manufacture of activated carbon from the lignin produced by the “Lignoboost” process.

A review⁵ of lignin as a raw material for activated carbon described the preparation of activated carbon from 12 previous studies, split equally between chemical and physico-chemical activation routes. Amongst the physico-chemical activation studies, none applied the actual industrial activation conditions of a steam/CO₂ environment at ~900 °C. Hence, this paper reports initial studies on the carbonization and activation behaviour of lignin produced using the “Lignoboost” process by a commercial physico-chemical activated carbon manufacturing process. The paper describes the carbonization and activation behaviour of pelleted and granular lignin, detailing the nanoporous structure of the resultant “LignActiv” products.

RESULTS AND DISCUSSION

Table 1 shows the properties of the as-received lignin, both in pellet and granular forms, carbonized at 950 °C, at 5 °C min⁻¹, under flowing Nitrogen.

These lignins differed markedly from the usual coal or coconut precursors for activated carbon manufacture in that they are thermoplastic and melt completely on heating above 180 °C. Carbonization results in complete fusion of the individual pellets or grains, producing light weight carbon foam. The 950 °C carbon yield of the lignin forms differ only slightly at ~40 wt%, comparing well with that of coconut at ~30 wt%. However, due to foaming, the apparent density of the carbonized lignin was only half that of the coconut-based carbon. Also, carbonization releases large amounts of sulphurous gases, the sulphur content of lignin decreasing from 2.1 to 0.7 wt% on carbonization. Hence, although the fixed

carbon and carbon yields from the lignin precursors appear attractive relative to other renewables, *e.g.* coconut, their melting and the resulting low apparent density would likely preclude their use in commercial activation processes.

Air oxidation or baking has been used as a pre-treatment in the commercial preparation of activated carbon from fusible bituminous coal precursors, being applied to lignin in an attempt to control melting and foaming during carbonization. Available fuel grade Lignin pellets, 8-10 mm in diameter, proved unsuitable precursors for oxidative stabilization. Their large size introduced diffusion limits to oxygen penetration, making them mechanically unstable; also, they continued to exhibit bulk melting on carbonization. Granular lignin proved to be a better precursor, as the loosely aggregated powder clumps allowed easy oxygen diffusion into the large grains. Oxidation of granular lignin at 165 °C for 72 h limited melting to only local grain fusion, resulting in coherent particles with an apparent increase in yield to 49 wt% at 950 °C.

The success of oxidation in preventing general melting of lignin allowed the preparation of granular carbonized products, facilitating a comparison of the char bulk properties. Two particle sizes were prepared by pre-crushing separate charges of ~400 g each of the granular lignin, at 6x12 and 12x20 USS mesh. These were “baked” at 165 °C for 72 h and carbonized at 950 °C. The carbonized grains exhibited some intergranular melting with numerous “melt bead” shaped particles, but the carbonized mass did not fuse.

Table 2 compares the physical properties of the granular lignin char with those of a coconut precursor. Overall, the physical properties of lignin carbons were poor in comparison with coconut char, particularly hardness (56 and 58% for 6x12, and 12x20 USS particle sizes). Granular carbons had a “popcorn” beaded appearance, low density and hardness. It is unlikely that such friable granules will withstand the mechanical attrition that occurs during activation in commercial activation kilns.

Table 3 shows the properties of activated carbons prepared from lignin – “LignActiv”, crushed and sized to that typical for commercial activated carbon manufacture 3x5 USS, ~ 5.8 mm in diameter, carbonized at 950 °C. The samples were activated in

separate experiments using CO₂ at 850 °C and CO₂/steam atmospheres at 900 °C. The lignin carbon proved un-reactive toward CO₂, but activated readily in CO₂/steam. The extent of activation for the LignActiv products was measured as weight uptake of

butane gas, *via* the ASTM D 5742 method. The butane activity of the CO₂/ steam activate proved quite variable at 23 to 28 wt%, reflecting the variability inherent for batch activation, offering good yield at only 17 wt% loss on activation.

Table 1
Comparison of lignin and coconut-based carbon properties

Carbon property	Granular lignin	Pelleted lignin	Raw, dry coconut
Char yield at 950 °C, wt%	40	39	29
Char properties at 950 °C			
Carbon apparent density (ASTM D 2854)	0.28	0.29	0.56
Carbon activity (ASTM D 5742)	12	14	4
Carbon iodine number (ASTM D 4607)	314	395	135
Carbon total ash (ASTM D 1506)	1	1.1	1.5
Sulphur content, wt%	N/D	0.7	0.01

Table 2
Physical properties of carbonized lignin and coconut at 12x20 USS

Property	Granular lignin	Coconut
Carbon apparent density (ASTM D 2854)	0.31	0.56
Carbon activity (ASTM D 5742)	18	4
Carbon ball pan hardness (ASTM D 3802)	58%	92%

Table 3
Effect of activation conditions upon LignActiv properties

Property	Lignin carbon	Activated CO ₂ , 850 °C, 1 h, 150 mL/min	Activated steam, 900 °C, 30 min, 150 mL/min, CO ₂ /steam
Butane uptake, wt%	2	6	28
Activation loss, wt %	--	0	17

Table 4
Mercury and nitrogen pore size data for LignActiv products

Carbon	BET N ₂ surface area, m ² g ⁻¹	Total micropore volume, mL g ⁻¹	Combined Hg+N ₂ mesopore volume, mL g ⁻¹	Total macropore volume, mL g ⁻¹	Apparent density, 0.54psi Hg G mL ⁻¹
Lignin char, 2% butane	550	0.205	0.016	2.85	0.286
LignActiv, 28% butane	750	0.279	0.04	1.28	0.476
Coconut, 24% butane	1022	0.378	0.12	0.959	0.525

Table 4 compares the pore structure of the lignin char and CO₂/steam activate LignActiv, as determined from mercury intrusion and nitrogen adsorption pore size characterization techniques. It is immediately apparent from Table 4 that significant pore structural differences occur between the lignin-based carbon and LignActiv. LignActiv appears less macroporous and more microporous than its precursor carbon, in fact more similar to that of the coconut shell activate. Possibly, these differences

reflect pore collapse in the LignActiv product, due to thermal annealing on activation.⁶ Such annealing could be triggered by the removal of the carbon atoms, which previously propped open the wider porosity in the structure, due to preferential gasification. However, both the lignin carbon and the LignActiv product exhibit micropore volumes that differ markedly from those indicated by their butane uptake capacities. In the case of lignin char, a micropore volume of 0.2 mL g⁻¹

should result in a butane uptake of 10-12 wt%, and not in the measured 2 wt%. For LignActiv, a micropore volume of 0.28 mL g⁻¹ should result in a butane uptake of 15-18 wt%, and not in the measured 28 wt% uptake.

It should be noted that both the Mercury and Nitrogen porosimetry techniques determine pore size distribution for a sample size of only 0.13 g, whereas for butane, the uptake to an ASTM D 5742 sample size is typically of 5-8 g. Possibly, the relatively small sample size used by the porosimetry techniques has highlighted differences, due to activation variation within samples, *i.e.* sample size effects. Although the “bulk”, ca. 5 g samples of lignin-based carbons, exhibited butane uptake activities at 2 and 28%, the much smaller 0.13 g sample size used for porosimetry measurements has randomly determined the pore size distribution for component particles with lower butane uptakes than that of the “bulk”, *e.g.* ca. 12% butane on the precursor Lignin carbon, and ca. 18% for the LignActiv sample. The contribution of sample size should always be considered when analyzing porosity data. The interpretation of porosimetry should always be made cognisant of the bulk properties, and further work is planned for evaluating the pore size distribution of larger, ca. 10 g samples, of carbonized lignin and LignActiv carbons homogenized by grinding to overcome such issues.

CONCLUSIONS

The preliminary assessment on the use of “Lignoboost” lignin as a precursor for activated carbon by physico-chemical processes, “LignActiv”, supports the following conclusions:

- Lignin exhibits char yields at ca. 40 wt%, greater than those from other renewable resources, such as coconut shells. However, its thermoplastic foaming properties result in weak, low density carbons unsuitable for physico-chemical activation.
- Oxidative pre-treatment in air at 165 °C successfully crosslinked lignin, preventing general melting, which is only effective for particle sizes smaller than the available fuel grade lignin pellets. Crosslinking improves carbonization yields to ca. 50 wt%.

- Carbons from oxidized lignin exhibited apparent densities and hardness too low to be considered suitable for physico-chemical activation.
- Despite these limitations in their physical properties, laboratory activation of lignin carbons is possible by physico-chemical means, producing high activity products at low activation weight loss, *e.g.* ca. 20%.

Further study is planned to exploit the data provided by the preliminary work reported here. Attempts will be made to more extensively crosslink lignins during the Lignoboost process, so as to prevent bulk melting. The sulphur content of Lignoboost lignin will be further reduced, to avoid carbonization odour issues, and smaller particle size feedstock will be made available to more fully exploit the yield gains, etc. resulting from oxidative pre-treatments. These activities are targeted for the preparation of Lignin-based carbon chars, offering high weight yield, density and hardness to allow activation by commercial physico-chemical activated carbon production processes.

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