

The Effects of Pre-Oxidation of Cellulose on the Properties of Chars for Methane Storage

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Introduction

In the present economic climate and with ecological awareness at a high, the need for cheaper more environmentally friendly fuels has never been greater [1]. Natural gas is an abundant and relatively clean burning fuel. It is conventionally stored at high pressures for transportation and for use as an alternative vehicle fuel, (Compressed Natural Gas (CNG) pressure is 3000psi). Adsorbed Natural Gas (ANG) systems, which involve adsorption of gas onto porous media, (operating pressure, 500psi), have emerged as a viable alternative to CNG for use as a storage system for natural gas as a vehicle fuel. The methane is stored in the micropores ($<20\text{\AA}$) of the adsorbent where the physical forces are such that the methane is at a higher density than that of liquid methane. Weaker forces in the meso (20-200 \AA) and macro-pores ($>200\text{\AA}$) mean that compressed gas at 500psi only is stored in them. Since a finite volume (i.e. storage vessel) of adsorbent can be utilised, it is important that the adsorbent not only possesses high levels of microporosity, but that it is also of a high enough density. Activated Carbons contain high levels of microporosity and can be produced with satisfactorily high densities to be good adsorbents for methane storage. However, the process of creating an activated carbon generally involves gasification of the char with CO_2 , O_2 or H_2O in order to increase the overall surface area. This treatment tends to widen the porosity and thus produce higher levels of meso- and macro-pores. By paying more attention to the precursor and the effects of altering its structure on the carbon produced, it may be possible to produce a more uniform microporosity. It was therefore decided to take pure cellulose and change its structure through air oxidation, observing any changes in the porosity of the resultant carbon produced.

Cellulose can be viewed as a linear condensation polymer consisting of D-anhydroglucopyranose units linked by β -1,4-glycosidic bonds [2]. The structure observed for the fully extended cellulose polymer is that of a flat ribbon with laterally protruding hydroxyl groups able to form both inter- and intra-molecular hydrogen bonds. Well-ordered areas of the cellulose structure contain hydrogen bonding between adjacent hydroxyl groups and the disordered areas show water bridging between adjacent chains [3]. The physical structure of cellulose has been studied using a variety of techniques including Differential Scanning Calorimetry (DSC). The difficulty in finding a first order phase transition in cellulose at a temperature lower than that of decomposition, ($\sim 500\text{K}$) has been noted by Hatakeyama *et al* [4].

There has long been interest shown in the partial oxidation of cellulose by chemical means through the use of different reagents, mainly as a means of preventing damage to the cellulose structure during processes such as textile fibre and wood pulp bleaching [2]. However, utilisation of the product formed from physical oxidation through simple heating in an oxygen or air atmosphere of cellulose seems to have been somewhat neglected as a research field, probably because of its degrading effects on the cellulose

polymer. The oxidation of alkali cellulose by gaseous oxygen in order to reduce the degree of polymerisation of wood pulp for viscose rayon production has been the major application of this type of oxidation process, with a controlled degradation of the polymer being desirable.

Cellulose derivatives in the form of biomass are the most common source materials for the production of active carbons. A wide variety of cellulose derivatives varying from coal, lignite, peat, wood through to agricultural waste products are used commercially [5]. The range of activation conditions and methods is equally wide using lower temperature chemical activation [6], higher temperature steam or CO₂ activation [5], or a combination of both. The production of active carbons generally involves pyrolysis of cellulose bases in a highly oxidizing environment with the result that the pyrolysis is performed on oxidized cellulose.

The objective of the present paper is to investigate the effects of pre-oxidation of pure cellulose on the nature of chars produced by pyrolysis in N₂. This is achieved by characterization of the fresh and oxidized cellulose by a variety of common polymer analytical techniques, solid state NMR, (DSC) and elemental analysis. Mass losses during pyrolysis of the fresh and oxidized cellulose was monitored by thermogravimetric analysis (TGA). Characterization of the resulting chars was by nitrogen adsorption at 77K and BET analysis to yield surface area.

Experimental

Cellulose powder (20 micron) was obtained from the Aldrich Chemical company and used as supplied. Oxidation was performed at 473K for varying time in a forced circulation oven in air. Pyrolysis was performed in a tube furnace in a flowing nitrogen atmosphere. The carrier flow rate was 1 lmin⁻¹ and the sample size ~5g.

DSC was performed on a Mettler DSC 30 system. Temperature calibration was by the melting points of Indium, Lead and Zinc standards. Temperatures are accurate to ±0.5K. Enthalpy calibration was by integrating the melting endotherm of an Indium standard supplied by Mettler. It was estimated that enthalpies were accurate to ±0.05 J/g. Standard aluminium pans were used with two pin holes to allow evaporation of water and the removal of pyrolysis products. The sample size was 10mg. The polymer was spread in a monolayer over the base of the aluminium pans to maximize heat transfer to the cellulose. The procedure was as follows. The samples were dried *in situ* at 373K for 30 mins and then quenched to the starting temperature of 300K. DSC was then performed at 10K/min to a temperature of 523K using a nitrogen carrier. The samples were again quenched to 300K and DSC performed at 10K/min to 523K. The cycling procedure was repeated a further three times to identify only reversible phase changes in the samples.

25 MHz ¹³C solid state nmr spectra of oxidised cellulose samples were obtained using a Bruker MSL100 spectrometer equipped with a 7-mm double-bearing probe for cross polarisation (CP) and magic angle spinning (MAS). The samples were spun at a speed of 5kHz, which is sufficient to reduce the side-band intensities to below 5% of those of the central aromatic bands in coals [7]. Typically four thousand scans were accumulated with high-power ¹H decoupling in CP experiments employing a contact time of 2ms and a recycle delay of 1.5s. Dipolar dephasing was carried out on one sample to estimate the fraction of non-protonated aromatic carbon present after oxidation. Delays of between 0-200μs were introduced immediately before acquisition during

which the ^1H decoupler was switched off. Those carbons bound to hydrogen are rapidly dephased while non-protonated and rotationally mobile (methyl) carbon dephase more slowly. The attenuation of the non-protonated aromatic carbon signal with increasing dephasing time follows a single exponential law. Thus by plotting $\ln(\text{aromatic signal area})$ versus dephasing time and extrapolating the best line fit through data in the region 60-200 μs to time zero, one can obtain an estimate of the fraction of non-protonated aromatic carbon. All FIDs were processed using exponential line broadening factors of 20Hz prior to Fourier transformation.

TGA was measured in a Stanton Redcroft TG750. A heating rate of 10 K/min was used and an air carrier. The typical sample size for TGA was $\sim 10\text{mg}$.

Surface area determinations were made from N_2 adsorption at 77K with a BET analysis. Samples were outgassed in situ to 10^{-4} Torr at a temperature of 398K for at least 12 hours before the adsorption was determined volumetrically in a Micromeritics Accusorb 2100E machine.

Results and Discussion

Chemical Composition Variation

Table 1 shows the ultimate analyses of the cellulose following the oxidation procedure described above. The O/C ratio decreases rapidly from 24 hours to 75 hours of oxidation and then shows a slight increase up to 456 hours. The initial decrease in oxygen content can be attributed to dehydration and, at the later stages of oxidation, loss of CO and CO₂ on de-polymerisation of the cellulose. The slight increase in oxygen content from 75 hours to 456 hours is thought to be due to oxygen chemisorption by the cellulose. The H/C ratio decreases with an initial fast rate from 24 hours up to 75 hours of oxidation followed by a slower rate of H loss with time of oxidation and appears to be approaching some limiting value. Solid State ^{13}C NMR measurements were made to investigate the chemical changes on oxidation further. Figure 1 shows the NMR measurements on the oxidized cellulose samples. The aromatic/aliphatic ratios were determined by integrating the aromatic and aliphatic peaks which are indicated in Figure 1. The observed peaks were comparable to the accepted allocation of signals for cellulose [8]. The unoxidized cellulose showed no significant aromatic functionality, which is consistent with the accepted structure of cellulose [2]. However, even relatively mild oxidation was sufficient to produce a small aromatic content. This was corroborated by a colour change from white in the unoxidized cellulose to light brown in the 24 hour oxidized sample. The variation of the aromatic/aliphatic ratio with time of oxidation is shown in Figure 2. Initially, the ratio decreased slightly from a value of 0.152 for 24 hour oxidation to 0.106 following 50.5 hours of oxidation. The aromatic/aliphatic ratio then displayed a monotonic increase with time of oxidation up to 456 hours.

The decrease in H/C values may be associated with initial dehydration, (the O/C ratio decreased concurrently with H/C), accompanied by increasing aromaticity combined with the onset of cross-linking and more dehydration as the extent of oxidation increases. The variation of chemical composition based on C 100 together with the NMR data enables reasonable chemical structures to be constructed.

Figure 2 shows that the initial decrease in H/C ratio can not wholly be explained by simply an increase in aromaticity. In fact the loss of hydrogen at this stage appears predominantly to be associated with an increase in crosslinkage of the cellulose

combined with dehydration.

The initial decrease in overall aromaticity of the oxidised samples up to 50.5 hours can be explained by the observed competitive generation of non-cellulose related aliphatics (at ~35ppm and 190ppm) in addition to the created aromatics (at~128,162ppm). An early indication of possible carbon crosslinking taking place is seen after 24 hours of oxidation (Figure 1a) when the C-6 signal (at ~70ppm) disappears. By 75 hours of oxidation, the cellulose structure has been completely altered (Figure 1b) and the cellulose peaks at have disappeared. The spectra at this stage consists of large aliphatic signals at 40ppm, due to alkyl groups, and 80ppm, due to ether groups, with a smaller aliphatic carbonyl signal at ~190ppm and aromatic peaks at 128ppm and 162ppm. The newly generated aromatic peaks at 128 and 162ppm dominate the NMR plots after 165 hours oxidation, with the new aliphatics at 40ppm and 80ppm taking a secondary role. The main aromatic peak centered at 128ppm corresponds to protonated and non-protonated aromatics (possibly bridgeheads for crosslinking), and the smaller peak at 162ppm corresponds to phenolic aromatics.

The general picture of changes on oxidation therefore appears to be an initial dehydration, occurring first at cellulose position C-6, with carbonyl production and generation of crosslinks with some aromatic production. This is followed by significant aromatic production with crosslinking by a mixture of short aliphatic groups and ether linkages.

Differential Scanning Calorimetry

The DSC plot, (Figure 3), for fresh cellulose shows a broad endotherm on run 1 from 330-400K due to the evaporation of water which was present on the surface of the polymer. After this water has been removed it can be seen that there is an endotherm indicative of a reversible second order phase transition probably due to a glass to rubber transition in the region 370-380K, which was obscured by the large evaporation endotherm. It has previously been observed by Hatakeyama *et al* [4] that dry cellulose exhibits no phase transition at a temperature below that of decomposition. This disagreement could arise from the fact that our own DSC sensor is somewhat more sensitive than that of Hatakeyama. Figure 4 shows the intensities of the glass transitions for the oxidised cellulose samples. The intensities of the Tg's are defined conventionally. It was noted that the Tg intensities decrease with increasing extent of oxidation. This may be due to an increase in cross-linking and density in the polymer which will make the structure considerably more rigid.

Oxidation and Carbonization

Table 2 shows the weight losses following oxidation and carbonization of the cellulose. The initial weight loss on oxidation up to 75 hours is extensive, with the loss from 75 hours to 456 hours being a lot smaller. The decomposition of cellulose in an oxygen atmosphere is well documented [9]. Initial weight loss is principally due to dehydration of water hydrogen bonded to the structure followed by dehydration of the actual cellulose structure, decarboxylation and general decomposition and depolymerisation of the cellulose. The weight loss after 75 hours being due mainly to hydrogen loss as the structure aromatises with some loss of CO and CO₂. The carbon yields shown in Table 2 are the percentage of carbon in the original cellulose that remains in the char. The theoretical maximum carbon yield, if all of the carbon in the cellulose were converted into carbon in the char, is 68%. the char yield obtained for the untreated cellulose on carbonisation at 1173K using a heating rate of 10K/min of 18.4% is comparable to that quoted by Brunner and Roberts [10]. Increasing the extent of

oxidation decreases the overall carbon yield as more of the initial carbon in the cellulose structure is burnt away to form CO and CO₂ during the oxidation stage before carbonisation.

Thermogravimetric Analysis

Figure 5 shows the TGA plots for the oxidised cellulose samples. The samples show slight weight loss from 300-500K. This is probably due to loss of adsorbed H₂O. An increase in the oxidation period promotes greater weight loss in this temperature range from 300-500K. This phenomena can be explained by the presence of polar oxygen groups on the polymer surface of the more highly oxidised samples and hence, on heating in the TGA, these samples will subsequently show greater weight losses over the 300-500K temperature range. The onset of pyrolysis can be observed for the samples after 500K. Rapid weight loss can be observed for the fresh and more mildly oxidised samples probably due to depolymerisation, and scission of C-O and C-C bonds within the cellulose ring units, accompanied with evolution of more H₂O, CO and CO₂ [3]. The more highly oxidised samples loose weight less rapidly than the less oxidised cellulose. This is because an increase in oxidation period causes an increase in weight loss during the oxidation process due to the loss mainly of H and O and some C and associated with this is an increase in cross-linking of the polymeric structure. Therefore the more highly oxidised samples contain less volatile species and are in fact much strengthened by cross-linking and so will lose less weight during pyrolysis. Mass transfer through the more heavily crosslinked structure will also be slower, thus allowing more time for carbonisation.

Surface Areas of The Carbons

Table 2 shows the 77K N₂ BET surface areas of the cellulose carbons. A clear trend can be seen whereby the surface area of the carbon increases with an increase in oxidation of the polymer precursor. The increase is an exponential rise which levels off at 456 hours oxidation, with a surface area nearly 9 times that of the fresh cellulose carbon. The similar physical properties of methane and nitrogen result in there being a close relationship between 77K N₂ BET surface area per unit mass of adsorbent and methane uptake. Large N₂ adsorption capacities are indicative of high levels of microporosity.

Conclusions

The cellulose structure goes through radical changes on air oxidation at 473K until, after 456 hours the structure bears little or no resemblance to the original polymer. Initial oxidation promotes dehydration of the cellulose, resulting in some aromatic formation and crosslinking of the structure. Further oxidation encourages extensive aromatic production combined with increased crosslinking, resulting in a highly aromatic, highly crosslinked network with increased strength and resistance to weight loss. The extent of oxidation is linked to the surface area of the carbon produced from the cellulose precursors. Increased oxidation period produced carbons with higher N₂ BET surface areas. The fresh cellulose probably produces large pores with a generally open structure on carbonisation, with the more highly oxidised cellulose developing a narrower porosity. Although these surface areas are a good representation of probable methane uptake, it is a high priority to carry out methane adsorption isotherms on the carbons. It is also intended to develop the porosity of the carbons through CO₂ activation followed by characterisation of the carbons with Hg porosimetry and Small Angle X-Ray Scattering. The pre-oxidation procedure has been shown to be a good method for controlling the porosity of unactivated cellulose precursor carbons.

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Table 1 Ultimate Analysis of Fresh and Oxidized cellulose

Sample	wt %C	wt %H	wt %O	H/C (g/g)	O/C (g/g)	arom/aliph
Fresh	42.41	6.46	51.13	0.152	1.21	
(C 100)	100	188	90			
24 hr	43.30	6.64	50.34	0.154	1.17	0.152
(C 100)	100	184	87			
44 hr	50.01	5.16	44.83	0.103	0.90	0.143
(C 100)	100	124	67			
50.5 hr	51.27	4.64	44.09	0.090	0.86	0.106
(C 100)	100	108	64			
75 hr	58.39	2.96	39.65	0.051	0.69	1.694
(C 100)	100	61	51			
165 hr	53.64	2.86	43.50	0.053	0.81	4.341
(C 100)	100	60	61			
456 hr	52.99	2.48	44.53	0.047	0.84	7.099
(C 100)	100	56	63			

Table 2 Pyrolysis Yields and Carbon Surface Areas

Sample	Wt loss on Oxidation (%)	Wt loss on Carbonization (%)	Carbon Yield (%)	BET SA (m ² g ⁻¹)
Fresh	-	81.6	18.4	65
150°C, 24 hr	4.0	80.7	19.1	414
150°C, 168 hr	9.4	80.0	18.2	384
200°C, 24 hr	9.9	80.2	17.8	360
200°C, 44 hr	38.3	69.9	18.6	415
200°C, 50.5 hr	44.3	67.9	17.9	420
200°C, 75 hr	65.4	57.4	14.7	459
200°C, 165 hr	76.2	59.5	9.6	507
200°C, 456hr	72.7	59.4	11.1	541

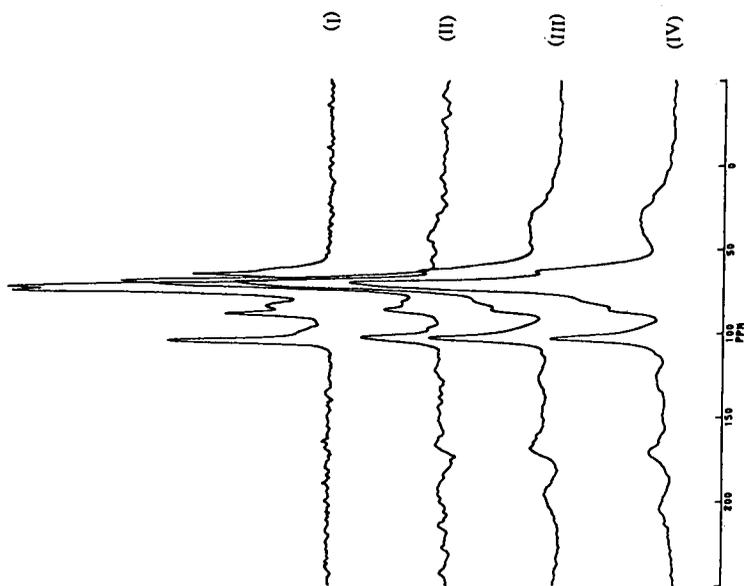


Figure 1(a) : ^{13}C NMR CP/MAS spectra of: Cellulose, (I) untreated, (II) oxidised at 473K for 24 hours, (III) oxidised at 473K for 44 hours, (IV) oxidised at 473K for 50.5 hours.

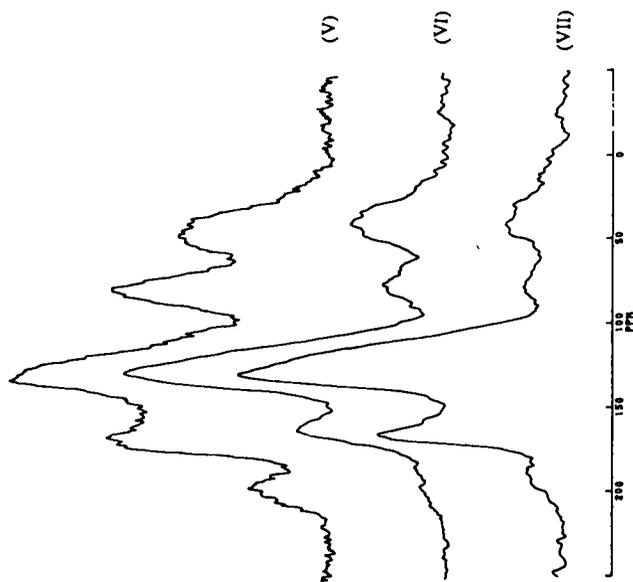


Figure 1(b) : ^{13}C NMR CP/MAS spectra of: Cellulose, (V) oxidised at 473K for 75 hours, (VI) oxidised at 473K for 165 hours, (VII) oxidised at 473K for 456 hours.

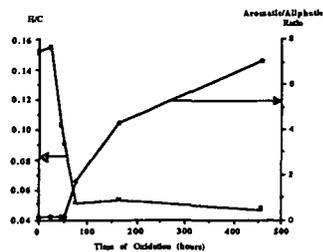


Figure 2 : Variation of H/C ratio and Aromatic/Aliphatic ratio with time of oxidation in air at 473K for cellulose powder. H/C values being derived from ultimate analysis and aromatic/aliphatic ratio from integration of the respective NMR peaks in Figure 1.

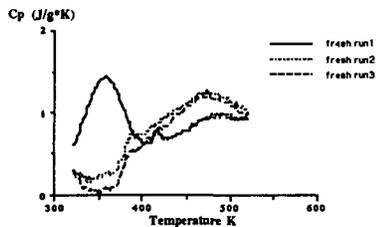


Figure 3 : DSC plot for untreated cellulose powder cycled from 323-523K in N₂ flow.

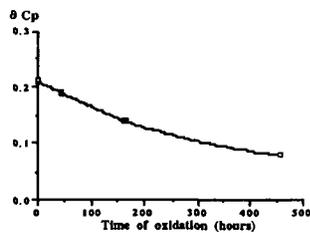


Figure 4 : Variation of δC_p glass transitions of cellulose powder with time of oxidation in air at 473K.