

ACTIVATION OF BIOMASS FIBRES USING ALKALI METAL SALTS

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SUMMARY

Low grade flax fibre in the form of a non-woven fabric was carbonised and then activated at 800°C in the presence of potassium salts (KOH, K₂CO₃ and KCl). The influence of varying the activating agents and their chemical ratio / impregnation procedure on the porosity of the carbon products was investigated. Wet impregnation with KOH and K₂CO₃ produced microporous activated carbon fibre (ACF) with BET surface areas in excess of 1000m²/g. High chemical ratios were found to favour the development of porosity. Activation with KCl caused no porosity development when compared with an untreated sample. The drying stage following wet impregnation was found to be an important factor when using KOH. Extended drying times in air reduce the effectiveness of the activation, apparently due to the carbonation of the hydroxide. This suggests that KOH is a superior activating agent to K₂CO₃. Substitution of wet impregnation with a dry mixing procedure proved successful only for KOH activation whereas K₂CO₃ was ineffective. This was explained in terms of the contrasting melting points of the two chemicals and shows that wet impregnation modifies the behaviour of K₂CO₃ as an activating agent. The results show that the flax precursor potentially offers a low cost alternative to other ACF precursors.

1. INTRODUCTION

Activated carbon fibre (ACF) can offer a number of advantages over the more traditional powdered and granular forms of activated carbon. One of the most important reported benefits of ACF is the high adsorption capacity and fast adsorption rates relative to other activated carbon materials [1-4]. Furthermore, ACF can be consolidated into a wide range of textiles, felts and composites which allow greater flexibility in the forms of materials which may be produced. The result of this is carbons which are easier to contain and handle than powdered or granular forms [5]. However, despite the undoubted potential of ACF, its use in commercial applications is currently restricted due to its high cost.

Recent work at the University of Leeds has focused on the preparation of ACF in the form of a non-woven fabric using hemp and flax fibre as the precursor. These biomass materials represent a renewable, low-cost fibre source and may therefore provide a potential alternative to the traditional ACF precursors. Initial work using physical

activation with steam has produced fibrous carbons with apparent surface areas up to $900\text{m}^2/\text{g}$ [6].

There has also been much recent interest in the production of activated carbons by chemical activation using alkali metal compounds such as KOH and K_2CO_3 . This method generally produces microporous carbons with high surface area and significantly higher yield than physical activation procedures [7-10]. The current paper involves the production of a fibrous non-woven ACF from flax using chemical activation with alkali metal salts. The effects of varying the activation agent and chemical ratio were investigated. In addition, the influence of the impregnation procedure on the development of porosity is highlighted.

2. EXPERIMENTAL

2.1. Pyrolysis

Flax fibre char was produced at 800°C in a vertical tube furnace under flowing nitrogen ($300\text{ml}/\text{min}$) with a heating rate of $2^\circ\text{C}/\text{min}$ and 1 hour soak time. Pre-carbonisation was found to be required to maintain the precursor's fibrous morphology upon activation.

2.2. Char Impregnation

Wet Impregnation – 1.00-1.50g quantities of flax char were impregnated with alkali metal compounds. The impregnation ratio was defined as ratio of activating agent:char by weight. The required quantity of chemical was dissolved in 50ml of distilled water and the precursor was soaked in this solution for 30 minutes at room temperature. The mixture was then dried at 110°C for 24 hours prior to activation.

Dry/Physical Preparation – 1.00-1.50g quantities of flax char were covered with selected ratios of dry alkali metal compounds and activated immediately. (It should be stressed that the activating agents were not added to the char as a solution).

2.3. Activation of flax chars

The prepared chars were activated for 2 hours in a vertical tube furnace at 800°C under flowing nitrogen ($300\text{ml}/\text{min}$). The heating rate was $5^\circ\text{C}/\text{min}$. Following activation, the samples were allowed to cool (again under N_2) to room temperature and were then washed sequentially with hot and cold distilled water until the pH of the wash water reached 7-7.5. The carbons were then dried at 110°C for 24 hours and stored in a desiccator prior to analysis.

2.4. Characterisation of products

The pore structure of the activated carbons was characterised using an Autosorb 1-C gas adsorption instrument (Quantachrome Instruments) using adsorption of N_2 at 77K and CO_2 at 273K. Apparent surface areas were obtained using the BET equation and micropore volumes using the DR method. DFT micropore size distributions were determined using the Quantachrome DFT software kernels. Mesopore volumes were assessed by the BJH method.

2.5. Activation gas analysis

Analysis of product gases (CO, CO₂, and H₂) from the activation procedure was carried out using a Gas Chromatograph (Varian C3380) equipped with a thermal conductivity detector.

3. RESULTS AND DISCUSSION

3.1 The influence of impregnation ratio

Activated carbons were prepared over 2 hours at 800°C with varying KOH ratios (0.5, 1, 2 and 4) and the influence of the impregnation ratio on the porous properties of the activated products was assessed. Figure 1 shows the N₂ adsorption isotherms which are of type 1 (IUPAC classification), indicating that the carbons prepared are microporous, a common feature of KOH activated carbons.

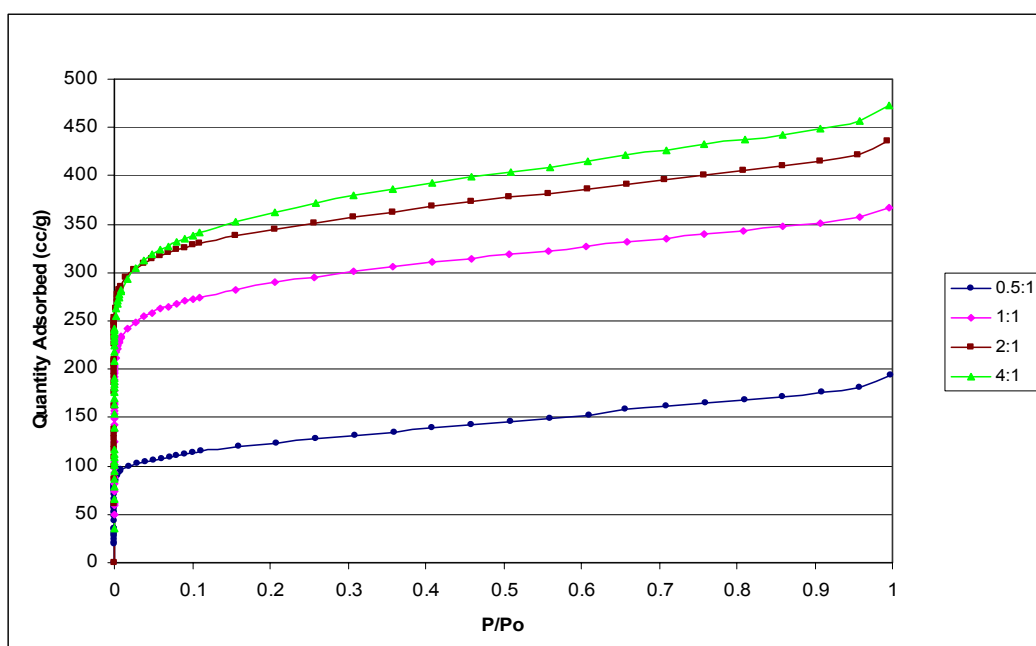


Figure 1: N₂ adsorption isotherms at 77K. Effect of impregnation ratio

Table 1 displays the porous texture data. Increasing the KOH ratio has a considerable effect on the activation process with the porosity of the samples increasing markedly with increased chemical addition. As the KOH:Char ratio is raised from 0.5 to 4, the knee of the isotherms begin to widen indicating a more heterogeneous size distribution and a greater contribution from larger micropores and the smaller mesopores. Accordingly, an increase in the mesopore volume is noted. At low KOH ratio, the narrow micropore volume (DR-CO₂) exceeds that of the wider micropores (DR-N₂). This indicates the presence of very narrow micropores that are inaccessible to the N₂ adsorbate. The carbonised flax precursor also shows this property. At high KOH ratio there is a far greater contribution from the wider microporosity and this is reflected in the corresponding DR values for the two adsorbates. Numerous other studies [7-10] have also observed this trend when activating with KOH and a wider pore size distribution is obtained as the intensity of the activation is increased. This is accompanied by a

decrease in product yield and suggests that the consumption of material from the char is largely responsible for the formation of porosity, similar to the physical activation process using carbon dioxide or steam.

KOH ratio [KOH:C]	BET area [m ² /g]	DR (N ₂) [cc/g]	DR (CO ₂) [cc/g]	Mesopore Vol. [cc/g]	Yield [wt. %]
Untreated	361	0.141	0.165	0.087	95
0.5:1	447	0.175	0.220	0.109	86
1:1	1086	0.423	0.402	0.120	78
2:1	1312	0.511	0.467	0.139	68
4:1	1385	0.521	0.460	0.164	54

Table 1: Porous texture data: The influence of impregnation ratio

The DFT pore size distribution plots (figure 2) are of a similar overall shape for each of the carbons with the contribution from a given pore size generally increasing with the impregnation ratio. For the 4:1 carbon, the narrow micropore volume can be seen to decline to less than that of the 2:1 sample while the contribution from the wider micropores has increased substantially. This is in agreement with the data in table 1.

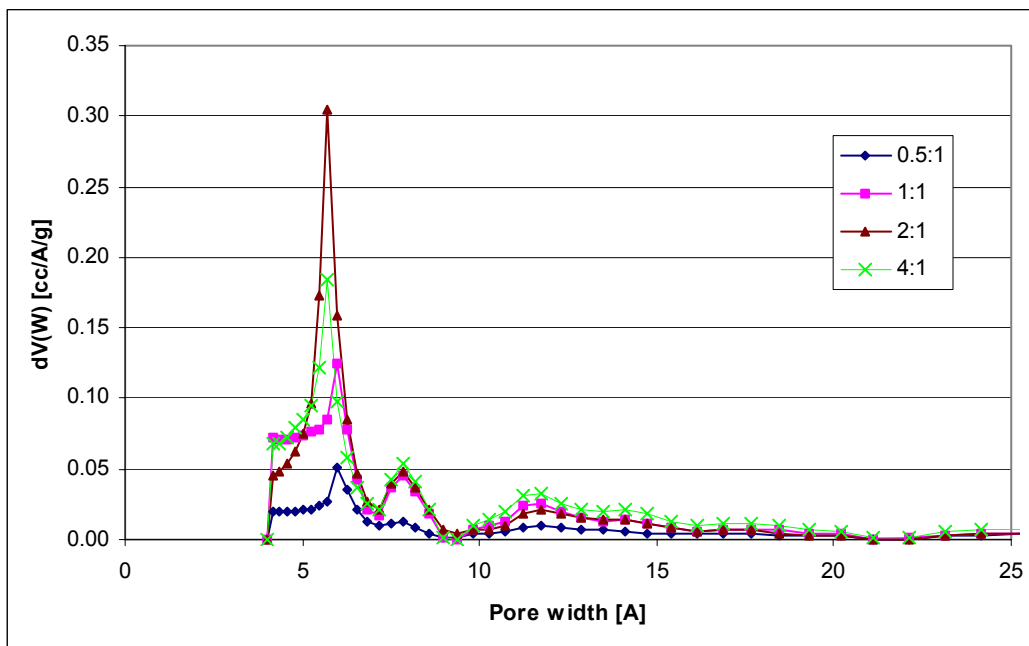


Figure 2: DFT micropore size distribution. Effect of impregnation ratio

3.2 Activation with other potassium salts

The effect of using different potassium salts for the activation procedure was examined. Flax char was activated at 800°C for 2 hours with both potassium carbonate and

potassium chloride. To ensure the atomic ratio of potassium to carbon remained similar to the 1:1 KOH impregnated samples, the weight/weight ratio used was adjusted accordingly. For K_2CO_3 , a 1.23:1 ratio was used and for KCl the ratio was 1.51. The N_2 adsorption isotherms are shown in figure 3 and the porous texture data are included in table 2.

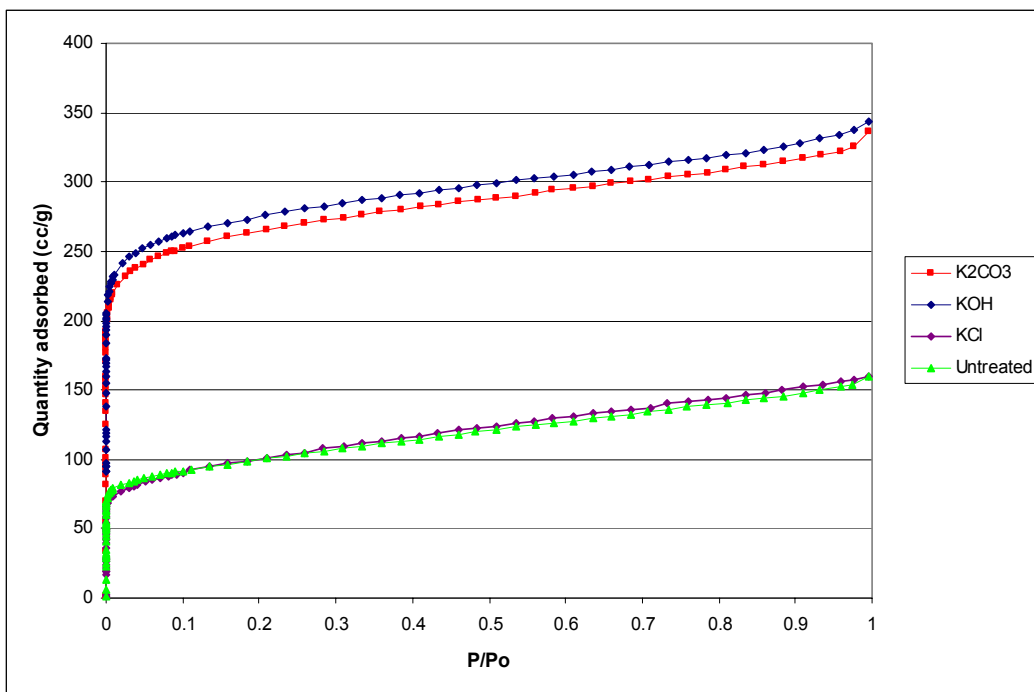


Figure 3: N_2 adsorption isotherms at 77K. Effect of activating agent

Activating Agent	BET area [m ² /g]	DR- N_2 [cc/g]	DH-meso. [cc/g]	Yield [%]
Untreated	361	0.141	0.087	95
KOH	1051	0.414	0.130	79
K_2CO_3	1017	0.402	0.126	74
KCl	365	0.138	0.092	89

Table 2: Porous texture data for activation with various potassium salts

The results show that the sample prepared with K_2CO_3 is very similar to the KOH sample whereas for KCl there is little difference in pore volume from that of the untreated char. The similarity between the KOH and K_2CO_3 activations was somewhat surprising as the effectiveness of the alkali carbonates as activating agents has recently been questioned [11]. Time resolved analysis of the gaseous products of activation (figures 4 and 5) confirmed that the activation process was proceeding in a very similar manner for each of the two potassium compounds.

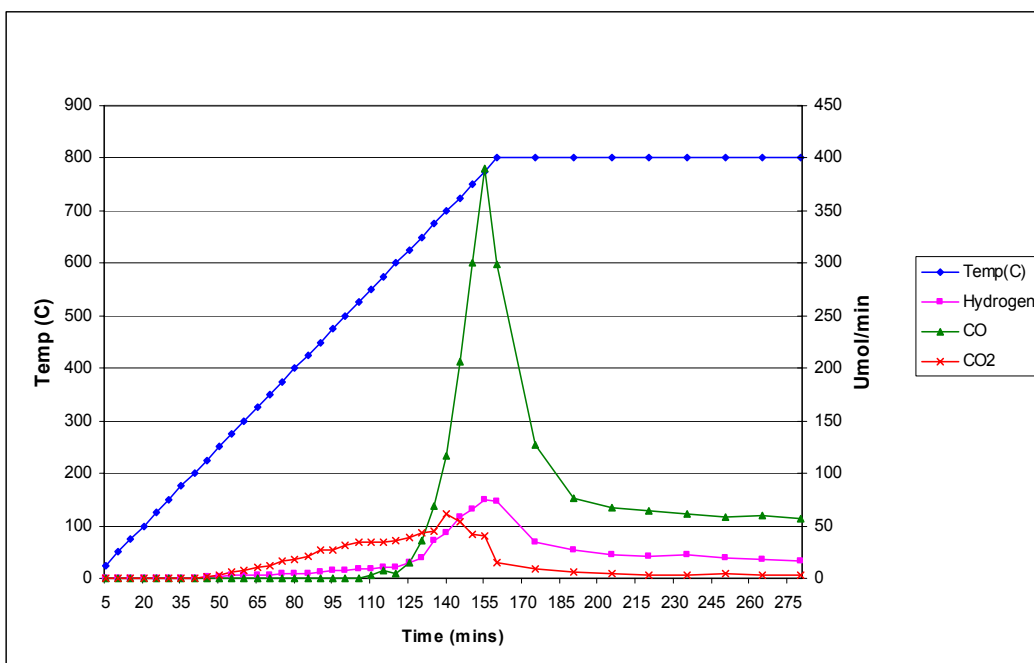


Figure 4: Off-gas analysis: 800°C char activation with 1:1 ratio KOH at 800°C

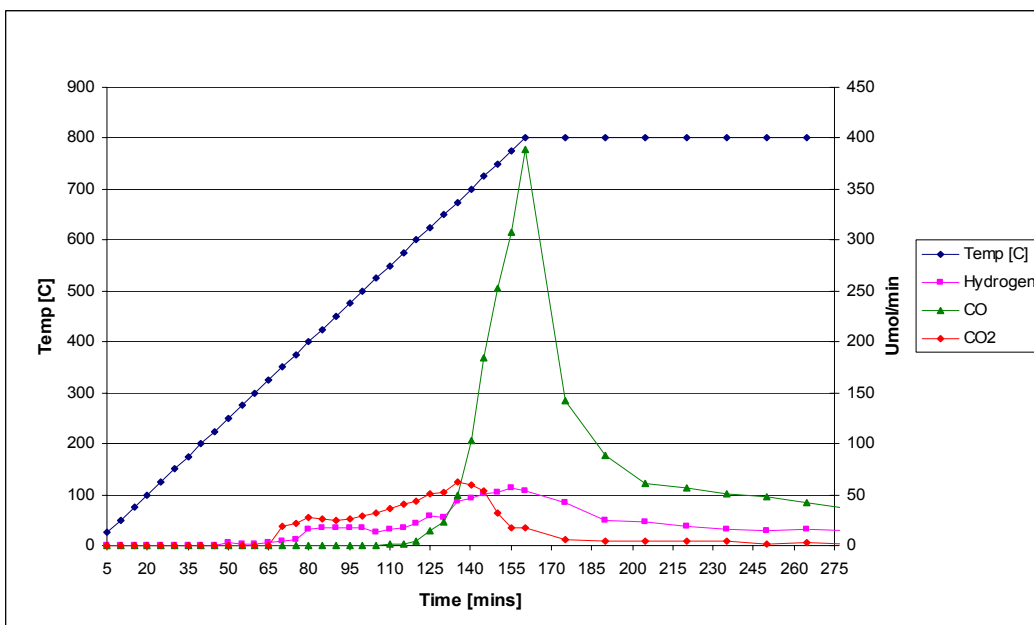
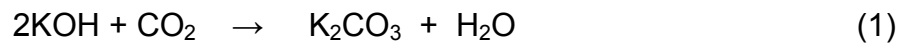


Figure 5: Off-gas analysis: 800°C char activated with 1:1 ratio K₂CO₃ at 800°C

At low temperatures, it is well known that conversion of KOH to K₂CO₃ takes place due to the carbonation reaction with CO₂ from the atmosphere according to equation (1).



Due to the similarities during activation, significant conversion of KOH during the wet impregnation procedure was considered likely to have occurred. Elemental analysis of an impregnated sample prior to activation confirmed this suspicion. This indicates that the activations in this study were all, in effect, carried out using K_2CO_3 . To examine this effect in more detail further samples were prepared with 1:1 and 4:1 ratio KOH but dried in a vacuum oven to prevent the carbonation reaction (Eqⁿ 1). A significant increase in porosity development (table 3) was observed for these samples when compared to the corresponding air-dried systems, indicating that KOH is more effective as an activating agent for the flax char precursor than K_2CO_3 .

Sample	BET area [m ² /g]	DR-N ₂ [cc/g]	DR-CO ₂ [cc/g]	DH-meso. [cc/g]	Yield [%]
KOH (1:1)	1051	0.411	0.405	0.122	79
K ₂ CO ₃ (1.23:1)	1017	0.402	0.397	0.126	74
KOH (1:1)**	1197	0.460	0.442	0.129	64
KOH (4:1)	1385	0.521	0.460	0.164	54
KOH (4:1)**	1720	0.672	--	0.152	52

** Denotes samples dried under vacuum to prevent carbonation

Table 3: Porous texture data: The effect of the drying process

Other authors [10,12] have also reported similar results using different precursor materials. This shows that carbonation of KOH during the impregnation stage has a negative effect on the porosity development of activated carbons. The drying stage is therefore of particular importance if maximum porosity development is to be realised during KOH activation. Furthermore, a considerable change in the gaseous evolution (figure 6) was observed for the 1:1 sample.

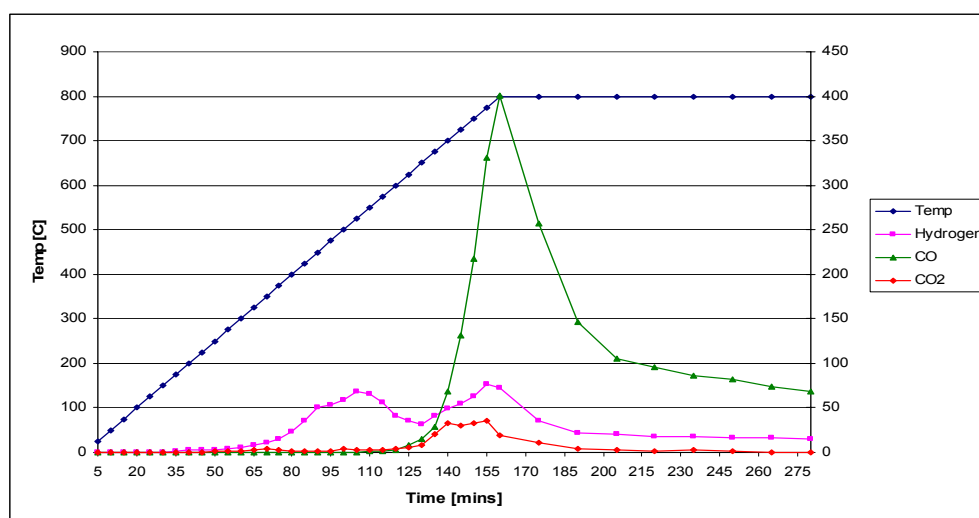


Figure 6: Off-gas analysis: 800°C char activation at 800°C, 1:1 ratio vac.dried KOH

This suggests a difference in mechanism, particularly in the lower temperature region (up to 600°C) of the activation. The yield data presented (tables 1-3) strongly suggests that the consumption of material (mainly carbon) from the char is responsible for the formation of porosity. A strong correlation between DR pore volume and yield of the activated carbons is shown in figure 7. The gas analyses indicate that the carbon is predominantly released as CO with the activating chemical presumably acting as an oxidising agent. The lack of oxygen in KCl explains its lack of effectiveness as an activating agent and formation of CO and CO₂ may only occur via the limited amount of oxygen present within the char.

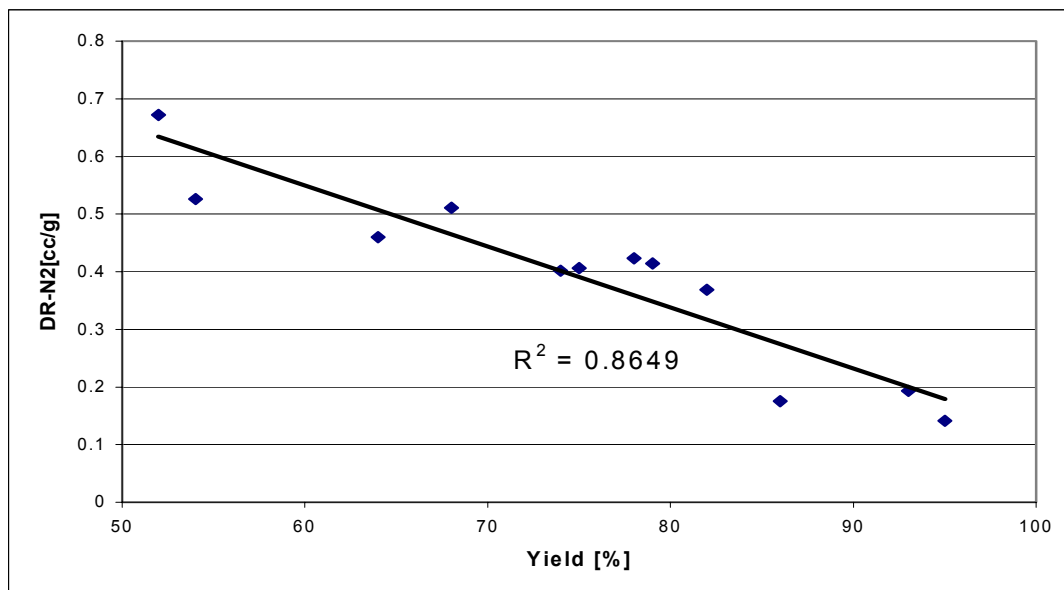
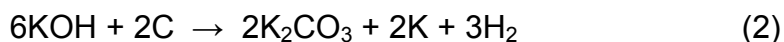


Figure 7: The relationship between product yield and DR pore volume

3.3 The effect of the impregnation procedure

The current paper has shown that K₂CO₃ is an effective activating agent when using wet impregnation with a flax char precursor. This has also been observed in other studies using different starting materials [10,12,13]. Conversely, a recent study [11] into the activation mechanism of anthracite using alkali metal compounds suggested that alkali carbonates were ineffective activating agents as the carbonate was a reaction product of the activation procedure (Eqⁿ 2).



However, a different method of impregnation was used in the said work, which involved dry physical mixing of the precursor with the activating agent. When employing a similar preparation procedure with the flax char some interesting results were obtained. The adsorption isotherms for these samples are shown in figure 8 and porous texture data displayed in table 4.

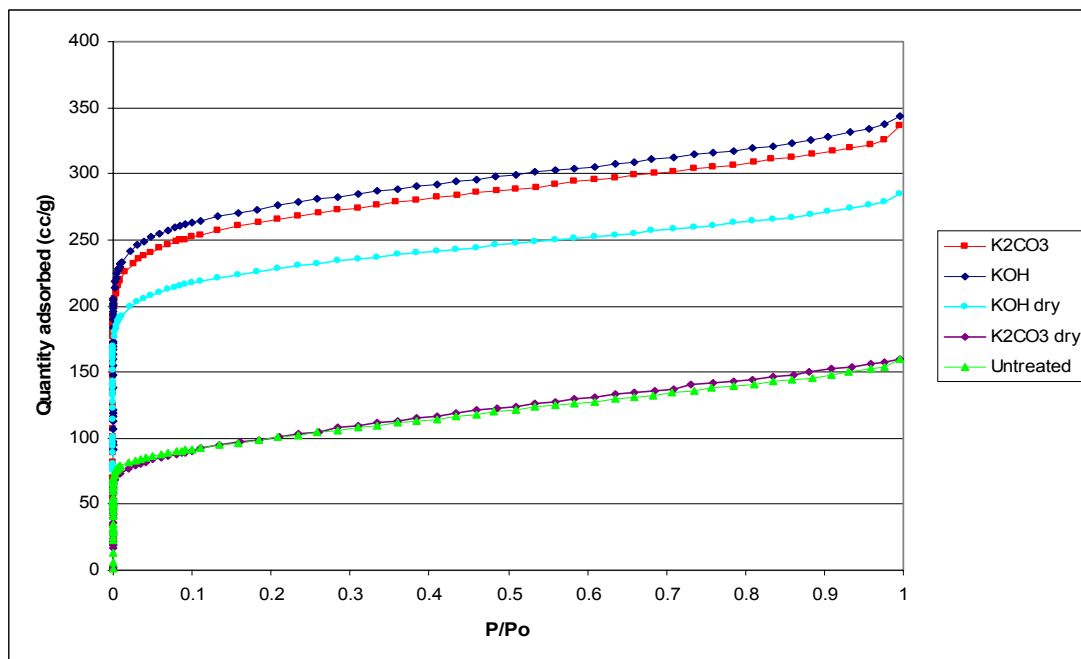


Figure 8: N₂ adsorption isotherms at 77K: Influence of impregnation procedure

Sample	BET area [m ² /g]	DR-N ₂ [cc/g]	DR-CO ₂ [cc/g]	DH-meso [cc/g]	Yield [%]
KOH (1:1)	1051	0.411	0.405	0.122	79
K ₂ CO ₃ (1.23:1)	1017	0.402	0.397	0.126	74
KOH (1:1) dry	892	0.369	--	0.103	82
K ₂ CO ₃ (1.23:1) dry	357	0.140	--	0.089	97

Table 4: Porous texture data: Influence of the impregnation procedure

Significant porosity development was observed for a KOH activated sample although this was found to be lower than with a wet impregnated sample prepared under the same conditions. Dry preparation with K₂CO₃ produced no change when compared to an untreated sample. Indeed, on removal of the K₂CO₃ sample from the reactor the activating chemical was still present and unchanged on the surface of the char whereas for KOH the bulk chemical had disappeared and formed a fine coating over the fibres of the char. This can be explained by examining the different melting points of the two activating agents. KOH has a melting point of around 360°C, thus allowing the activating chemical to establish intimate contact with the char above this temperature. In contrast, the melting point of K₂CO₃ is around 890°C which is above the activation temperature used in this study and activation cannot proceed. Wet impregnation with K₂CO₃ allows an intimate contact between the char and activating agent and appears to modify the behaviour of the carbonate allowing activation to proceed at temperatures below the melting point of pure K₂CO₃. Further investigations into the activation mechanism of flax char with both KOH and K₂CO₃ are currently underway.

4. CONCLUSIONS

The current paper has shown that chemical activation with KOH and K_2CO_3 may be used to produce a microporous carbon in the form of a non-woven fabric with surface areas well in excess of $1000m^2/g$. The waste flax fibre therefore offers a potentially low cost precursor for the production of ACF. As reported in previous studies, the development of porosity is enhanced by increasing the proportion of activating agent. The creation of the pore structure appears to be related to the gasification of the char precursor. The importance of the drying stage during wet impregnation has been demonstrated. Extended drying in air produced a negative effect on porosity development when activating with KOH. This was attributed to the formation of K_2CO_3 by reaction with CO_2 from the atmosphere. This carbonation reaction should be avoided to attain maximum porosity during activation. The wet impregnation procedure produced considerable porosity in the flax chars with both KOH and K_2CO_3 . The dry mixing method was effective only with KOH. This effect was explained in terms of the differing melting points of the two chemicals, with that of K_2CO_3 exceeding the activation temperature used in the study. However, wet impregnation with K_2CO_3 allows activation at temperatures below the melting point of the pure carbonate. This is facilitated by the intimate contact between the char and activating agent which develops during the wet impregnation procedure

5. REFERENCES

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