

THE PRODUCTION OF VARIOUS CARBONS FROM NORTHERN IRELAND SPRUCE BARK, AND THE VALIDITY OF LANGMUIR AND FREUNDLICH ISOTHERMS FOR NITROGEN AT LOW PRESSURES

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Introduction

Activated carbons have been around for years, and used in many varied applications, including the manufacturing processes to produce sugar, whiskey, reclamation of solvents, catalysis, and to adsorb gaseous species. It was for this later purpose that the original extensive interest was devoted to activated carbons, for it to be used in gas masks during World War I.

To allow for the accurate computer modelling in technological purposes, the properties of the medium must be known for various conditions. Nitrogen gas has been used in a preliminary study of the various carbons produced as to their actual isotherms observed at 21 °C, and a comparison of these to Langmuir and Freundlich Isotherm Theories. An examination into percentage burn off rates for the various samples during their production was also investigated.

Experimental

The materials under consideration were produced from local Spruce tree bark. Some of these samples were treated with ZnCl₂ solutions to achieve metal salt impregnation. The samples were firstly ground to a suitable size in a hammer mill, and then sieved to give a particle size range of 1-2 mm.

The chemical pre-treatment method involved 100 g of the pre-sieved particles being placed in a suitably large container, where upon 1 litre of either 1% or 2% wt/wt ZnCl₂ solution was added, and was mechanically stirred for 1 hour. The mixture was then poured into a 1 mm mesh size sieve and was washed with 1 litre of deionised water; this was to remove any residual ZnCl₂ and any particles smaller than 1 mm mesh size, due to the friable nature of the samples. The resulting material was spread across a tray, and placed inside an oven at 80 °C to dry overnight.

In the production of chars, a known dry mass of the required sample (approximately 80 g) was placed in a sealed metal container which

had an air lock during operation (this allowed gases out during the pyrolysis process, but prevented atmospheric air entering the container during the cooling off period). This was heated in a furnace (which has an approximate constant heating ramp of 5 °C/min) up to the required temperature for sample pyrolysis. This temperature was then held for half an hour, after which the furnace was turned off and allowed to cool overnight. The temperatures at which the furnace was set were 600, 700, 800 and 900 °C. The sample was then removed and its final weight recorded. The codes for the samples produced were as follows:

Code	
2a	untreated bark, unpyrolysed
2b	untreated bark, pyrolysed @ 600°C
2c	untreated bark, pyrolysed @ 700°C
2d	untreated bark, pyrolysed @ 800°C
2e	untreated bark, pyrolysed @ 900°C
2f	1% ZnCl ₂ , bark, pyrolysed @ 600°C
2g	1% ZnCl ₂ , bark, pyrolysed @ 700°C
2h	1% ZnCl ₂ , bark, pyrolysed @ 800°C
2i	1% ZnCl ₂ , bark, pyrolysed @ 900°C
2j	2% ZnCl ₂ , bark, pyrolysed @ 600°C
2k	2% ZnCl ₂ , bark, pyrolysed @ 700°C
2l	2% ZnCl ₂ , bark, pyrolysed @ 800°C
2m	2% ZnCl ₂ , bark, pyrolysed @ 900°C

Percentage burn off is a measure of the reduction of the initial sample mass to a final mass after pyrolysis, due to a combination of the volatile components being driven off and the combustion of materials present. Percentage burn off can be calculated using the following equation.

$$\text{Percentage Burn Off} = \frac{(\text{initial} - \text{final})(\text{mass} / \text{g})}{(\text{initial})(\text{mass} / \text{g})} \times 100$$

The experimental apparatus to carry out Static Equilibrium Isotherms consisted of an air tight glass vessel with ports to allow temperature and pressure measurement, a port to allow gas to be injected into the system and a port connected to a vacuum source. A known mass of adsorbent

was placed in a P.T.F.E. pan, which was placed in the vessel before being sealed and evacuated. The system was outgassed at 80 °C and re-evacuated at regular intervals for 8 hours. The system was then allowed to cool to the desired experimental temperature (21 °C), where upon a final evacuation was carried out before experimental work continued. A known volume of gas was injected into the vessel and the initial pressure change was recorded. The system was then allowed to reach equilibrium, and the equilibrium pressure was recorded. This procedure was repeated until the relative pressure reached approximately 1, or until no more pressure change was observed at equilibrium.

Results and Discussion

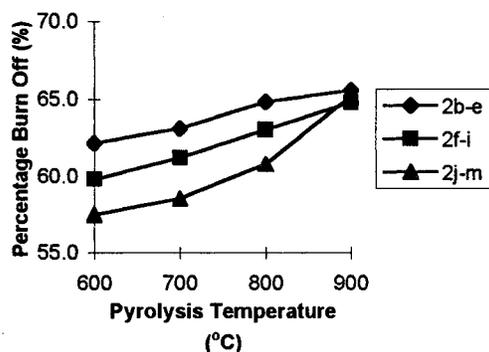


Figure 1: Graph to show percentage burn off for samples 2b-m.

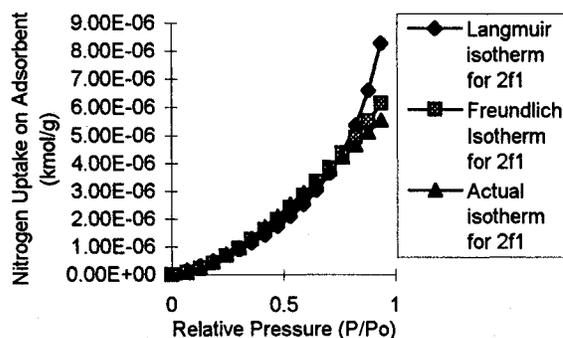


Figure 2: Graph showing a typical actual isotherm for the samples, and the respective Langmuir and Freundlich Isotherms at 21 °C.

In Figure 1 it can be seen that there was a general increase in percentage burn off for the samples as the pyrolysing temperature increased. However, although the percentage burn off tapers off to a near common point for the samples formed at a high pyrolysis temperature (900 °C), it appeared that the ZnCl₂ solution

inhibited the percentage burn off as the solution strength increased. This could be due to the metal salt acting to draw out water and aromatic materials in a “de-hydrating” action during the chemical treatment of the samples, and this would be more noticeable as the ZnCl₂ solution strength increased, which is seen in Figure 1.

It can be seen from Figure 2 that a typical isotherm for all samples, here 2f1 (chemically pre-treated with 1% wt/wt ZnCl₂ solution, and pyrolysed at 600 °C), was a Type III Isotherm. Type III isotherms generally only occur in adsorbents in which there are a wide range of pore sizes¹, or indeed in a macroporous adsorbent².

The Freundlich Isotherm theory most closely fits the actual isotherms observed, as compared to the Langmuir Isotherm theory, although the Langmuir plot did have a similar general trend. This is very plausible since the Langmuir theory is based on a purely theoretical model, whereas the Freundlich theory is an empirically based theory. The predicted final uptake at (P/Po)=1 for the Freundlich Theory is approximately 5% higher on average compared to the actual isotherm in comparison to the predicted final uptake at (P/Po)=1 for the Langmuir Theory which is approximately 45% higher.

Conclusions

- Type III isotherm indicates macroporous adsorbents produced during pyrolysis
- At pyrolysis temperatures of 900 °C, macropore formation creates uniform percentage burn off
- The Freundlich Theory is much more applicable than the Langmuir Theory for the adsorbents

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References

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2. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, 2nd Ed., Academic Press, 1982, p. 248.