THE OPTIMUM VALUE INDEX IN THE YIELD OF CARBON THROUGH CONTINUOUS INCREASE OF PRESSURE IN THE PYROLYSIS OF PITCH-DERIVED CARBON-CARBON COMPOSITE

by

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ABSTRACT

In this work, a brief summary of the production of pitch from coal tar and petroleum residues has been presented. The increased yield of carbon through increase in pressure during pyrolysis of pitch has also been analyzed. Results show there is a limit to the increase in carbon yield of pitch as pressure is increased. This limit or optimum value of pressure is found to correspond to 95.6% *yield of carbon. Experiments reveal that any further increase in pressure beyond this value would result in (i) Energy waste from pressure increase (ii) Counter production effect whereby carbon yield is brought down to as low as* 91.5% *instead.*

Keywords: Pyrolysis-of-pitch; pitch-derived-carbon-carbon-composite; Optimum-value-pressure-index

1.0 INTRODCTION:

At present, about 63% by volume of the carbon-carbon brake materials produced worldwide is used in aircraft braking system. The Super Temp Division of B.F. Goodrich Inc. in the United States of America originally developed carbon-carbon brake materials. Trials were carried out in 1973 on a VCIO aircraft followed a year later by standard fitment to Concorde SST [1]. As at the time they were first introduced, the costs of the brakes were around £550kg^{-1}. As a result, their use could only be considered economically viable on supersonic transports and high-performance military aircrafts. Advances in technology have, however, now reduced the cost to about £100-£150kg $^{-1}$meaning that it is now commercially advantageous to employ carbon-carbon brakes on civil subsonic aircraft. Furthermore, the use of carbon-carbon has been exploited for a number of land vehicles such as racing cars, high-speed trains and battle tanks [2].

Apart from the use of carbon-carbon composites for brakes and braking systems, it is employed in the construction of rocket motors for re-entry vehicles from space. When a rocket blasts into space with velocities exceeding 27,000kmh^{-1} the heat generated at the leading edges can lead to temperatures as high as 1400^{o}C. Re-entry temperatures can be even higher; approaching 1,700°C and well beyond the operational temperatures of metals [3]. On a weight-for-weight basis, carbon-carbon composites can endure higher temperatures for longer periods of time than any other ablative material. Thermal shock resistance permits rapid transition from -160^{oC} in the cold of space to close to 1,700^{oC} during re-entry without fracture [4].

2.0 THEORETICAL REVIEW:

2.1 Pitch-Derived Carbon-Carbon Composites:

The fabrication of carbon-carbon composites is achieved by the impregnation of fibre tows, weaves or skeletons (3-D structures of felts) with the thermosetting resins or by chemical vapour infiltration with gaseous hydrocarbons. All of these processes are slow, expensive and offer limited carbon yield and also they fail to exploit fully the strength of the reinforcing fibres [5]. While vapour infiltration methods require low reaction rates to maintain a uniform deposition throughout a porous body, the resin-based process, on the other hand, requires a number of cycles of impregnation and carbonization to attain useful levels of density. Great deal of work has been carried out to investigate the suitability of pitches derived from: (a) coal tar (b) petroleum and (c) polyaromatic thermoplastic resins as matrix precursors, the aim of which is to harness the advantages of high carbon yield and ease of graphitization offered by these materials and to achieve lower processing cost [6].

2.2 Coal-tar pitch:

Coal-tar is a by-product of the coking of bituminous coals to produce cokes. Metallurgical cokes are produced at high temperatures (900-11 OO°C) while low temperatures (about 600°C) yield domestic smokeless fuels. The low-temperature process gives a smaller amount of tar than the high-temperature process. Pitch is obtained from the coal-tar by distillation and heat treatment processes. Typical coal-tar distillation data are given in table 2.1 [7].

Table 2.1: Typical coal-tar distillation data

Product	Boiling range ^oC	Weight (%)
Light oil	Below 200	1
Naphthalene oil	200-230	12
Creosote oil	230-300	6
Anthracene oil	Above 300	20
Pitch	Residue	61

Smith et al, in bituminous materials.

2.3 Petroleum pitch:

Petroleum pitch is a readily available product, which can be obtained from the bottom of catalytic crackers. Like coal-tar pitch, it is the heavy residue obtained from a catalytic cracking process, from a steam cracker tar, a by-product of the steam cracking of naphtha or gas oils to produce ethylene or any residues from crude oil distillation or refining.

2.4 Properties/composition of pitches as a result of source and /or method of processing:

Pitches are compact mixtures containing many different individual organic compounds and their precise composition and properties vary according to the sources of pitch and the method of removal of low molecular weight fractions. It has been found that two-thirds of the compounds so far isolated from coal-tar pitch are aromatic carbon the remainder being hetero cyclic. Like the coal- tar pitch, the chemical and physical characteristics of the petroleum pitch are very much dependent on the process and condition employed in their production - especially, the process temperature and heat-treatment time. Generally, longer times and higher temperatures produce pitches with increased aromaticity and higher anisotropic contents. Petroleum pitches are usually less aromatic than coal-tar pitches. Typical properties of the various types of pitches are shown in Table 2.2 [8].

Table 2.2: Characteristic of typical carbon matrix precursor pitches from two different feedstocks

Property	Petroleum Pitch		Coal-tar Pitch	
	1	2	1	2
Softening Point(^{o}C)	117	110	101	113
Coking value (wt% at 550°C)	54	56	57	60
Aromatic carbon (%)	82	80	89	88
C/H ratio	1.44	1.57	1.77	1.76

J. Newmann in Petroleum derived carbons.

2. 5 Characterizations of Pitches:

Like in every carbon science, a definite system of nomenclature exists for the characterization of pitches. These include:

1. The fractions, which are insoluble in quinoline or pyridine, are usually denoted as ά resins' or 'QI'.
2. The fractions which are soluble in quinoline but insoluble in Benzene or toluene usually are denoted as 'b resins' or 'BI'
3. The fractions which are soluble in Benzene are usually denoted as 'BS' or the 'crystalloid' fraction

The theoretical evaluation of the carbon yield of a pitch is based on the law of mixtures, which means that the carbon yield of a pitch is the sum, total of contributions of its three components namely: QI, BI and BS respectively obtained by solvent fractionalization. The carbon yields of $\propto$ and β resin fractions are believed to be almost constant and independent of the origin of the pitch [9], being approximately 95% and 85% respectively. The carbon yield of the BS fraction is known to vary from, 30 - 55% depending on the softening point (SP) of the pitch. The higher the (SP), the higher will be the average molecular weight of the BS fraction, and as a consequence, the higher will be the contribution towards the carbon yield of the pitch. The relationship of the carbon yield of a pitch can therefore be written as:

$$CY = QI\,X\,0.95 + (BI - QI)X0.85 + BSXK$$

where CY is the carbon yield, QI, BI and BS are defined already. K is a constant such that $0.3 < K < 0.55$ which is dependent on the SP of the pitch [10].

2.6 Carbon Yield From Pitch:

Pitch can be regarded as a suitable matrix precursor for carbon-carbon composites only if high carbon yields are obtainable. This yield depends very much on the composition of the precursor pitch and the conditions of pyrolysis. The conditions of pyrolysis itself depends on (a) Decreasing of the heating rate (b) The application of pressure during the process and (c) The use of chemical additives prior to thermal decompositions all of which will increase the carbon yield of the pitch. Each of the above pyrolysis variables serves to improve the carbon yield in pitches by restricting the evolution of volatile molecules present in the original pitch. The retention of these species in the carbonizing liquid as the temperature is raised allows them to participate in the aromatic growth and polymerization processes [12].

2.7 The Pyrolysis of Pitch:

Pitch is converted to carbon by a process of pyrolysis. This mechanism involves carbonization, which is a process of aromatic growth and polymerization [11] Fig I shows a schematic representation of this process whereby a small aromatic structure may ultimately attain the three- dimensional order of graphite.

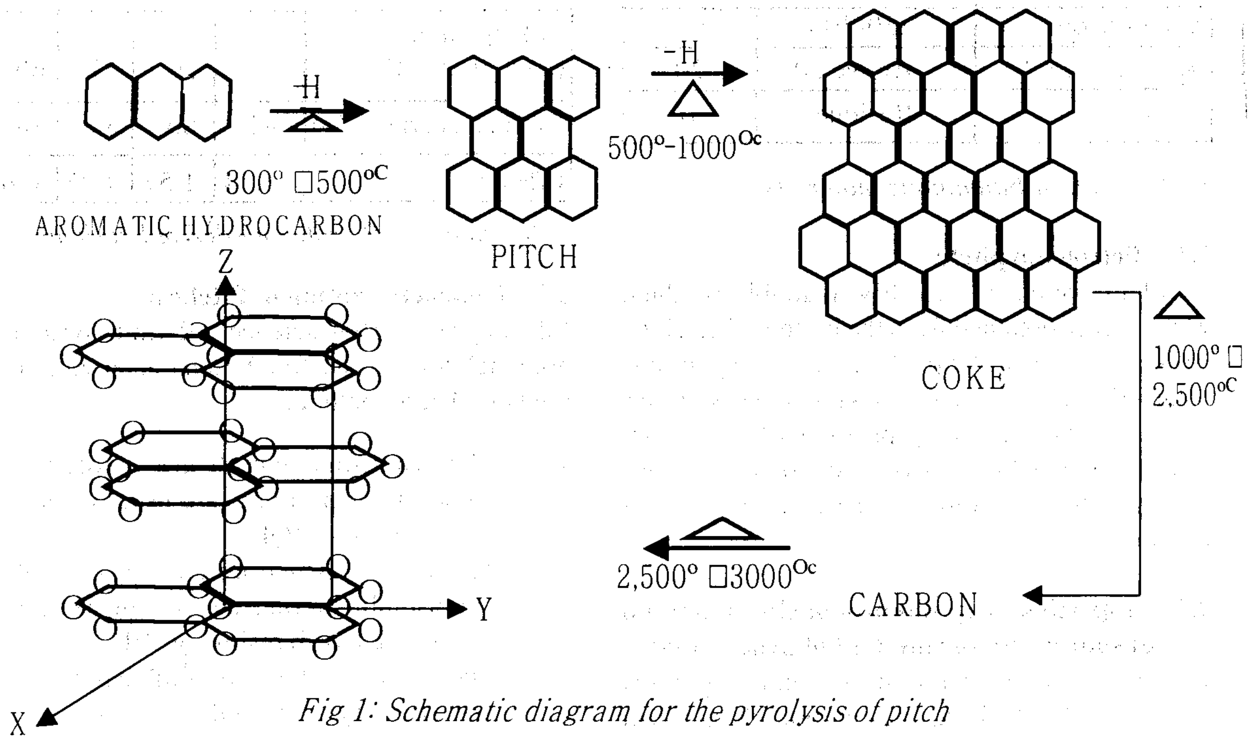

Fig 1: Schematic diagram for the pyrolysis of pitch

2.8 THE INFLUENCE OF PRESSURE IN PITCH-DERIVED CARBON-CARBON COMPOSITES

It is know that at atmospheric pressure the carbon yield obtained from pitches are only about 50% by weight. It has also been found that when oxygen is used to stabilize the pitches carbon yields can be produced in excess of 70% by weight [13] yields as high as 90% and above can be obtained, however, by carbonizing the pitch under high pressure [14] but, the uninvestigated question remains: how far or to what extent will increase in pressure continue to yield increase in carbon in pitches? This is the thrust of this work.

2.9 THE OPTIMUM VALUE INDEX IN THE YIELD OF CARBON THROUGH CONTINUOUS INCREASE OF PRESSURE DURING PYROLYSIS:

Equipment and Process Requirements:

A hot isostatic press (HIP) is employed. The design consists of a large externally water-cooled pressure vessel within which is situated a furnace surrounded by thermally insulating material usually called: 'thermal barrier' (see fig 2).

3.0 EXPERIMENTAL METHOD:

The work piece is placed inside the furnace central (see fig 2 again). A high isostatic inert gas is passed over the work piece, which effectively impregnate and density carbon-carbon composites during the melting and carbonization stages of the pyrolysis circle (refer to fig 1). The range of pressure applied here falls between 0.07MNm^{-2} and 700MNm^{-2}

4.0 RESULTS:

1. At atmospheric pressure the yield of carbon obtained from pitch fell within the 50% by weight (already referred to).
2. But as pressure increased carbon yield of pitch continued to increase until it came to a final maximum of about 95.6% by weight of carbon - at a corresponding pressure of 356MNm$\cdot^{2}$.
3. From this point further increase in pressure showed, rather, *a decline in carbon yield.* This decline continued further to as low as 91.5% by weight (corresponding to about 704MNm$\cdot^{2}$ pressure value, see fig 3).

4, Further tests could not continue because of lack of adequate equipment to generate higher pressure ranges needed for the experiments.

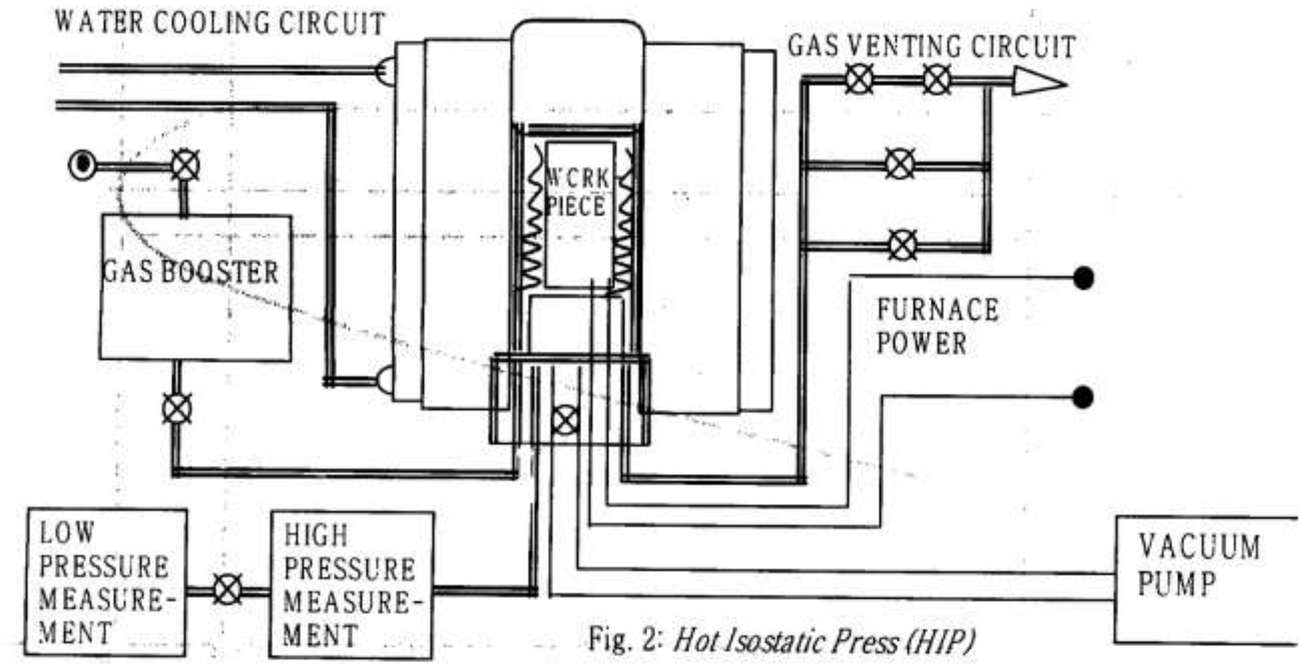

Fig. 2: *Hot Isostatic Press (HIP)*

5.0 DISCUSSION:

For the resulting graph, a combined linear and parabolic model can be obtained if we remember that for the equation of a straight-line with a slope intercept form:

$$y = m \times + b \qquad (1)$$

where m is the slope or gradient, b is the intercept value on the y-axis. Similarly, for the parabolic section, we know that:

$$(y - k)^2 = 4a(x - h) \quad ....(2)$$

where h and k represent the x and y co-ordinates of the vertex of the parabola and which must be a non zero real number. In this case, h and k represents 95.6% and 356 M N m^{-2}

respectively from the graph (see the vertex of the parabola in fig 3). Combining equations (I) and (2) requires that first equation (1) is written as:

$$y = 2\sqrt{a(\times - h) + K} \quad (3)$$

$Then$

$$Y_{combined} = y_{straigt\ line} + y_{Parabola} \quad (4)$$

$$i.e\ Y_{combined} = m \times + b + 2\sqrt{a(\times - h) + k} \quad (5)$$

which is a combined characteristic model of the graph of fig 3. It is worthy to note here that h and k remain constants at 95,6% and 356MNm^{-2} respectively as further increase in pressure (y - values) are applied while corresponding drop in percentage of carbon yield are obtained (i.e x-values), The value: b is a constant also of about 0.12MNm^{-2} obtained simply by producing the straight-line part of the graph to meet the y-axis at an intercept Further values of x (i.e. percentage yield of carbon) can be obtained by extrapolation through further increase in the values of carbonization pressure beyond what the experimental equipment can allow or simply by plugging values into this equation, This, however has not been done here because it falls outside the immediate purpose of this work which is to identify the optimum pressure value and its corresponding carbon yield.

6.0 CONCLUSION:

The above result clearly shows that there is an optimum pressure at which (for the particular pitch in question: whether coal-tar-derived, petroleum- derived, etc) the continual increase in pressure would no longer produce corresponding increase in the carbon yield of pitch.

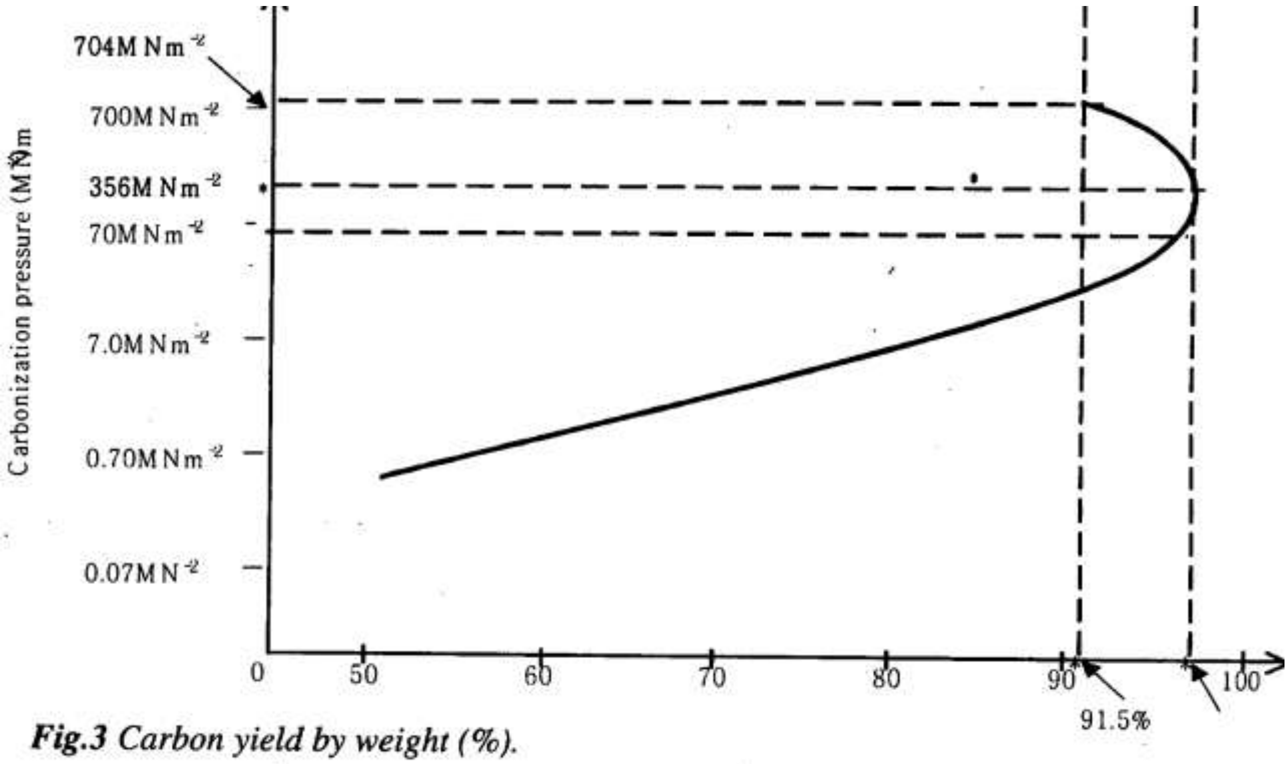

Fig.3 *Carbon yield by weight (%).*

The fact that the above experiment was carried out with coal tar-derived pitch does not mean that exactly the same pressure and at the same carbon yield by weight would be obtained using petroleum-derived pitch. However, what is common and of paramount importance is that there exist an <u>optimum value index-</u>which stands for that particular pressure or carbon yield in percentage by weight at which it is no longer reasonable to attempt to increase the yield of carbon in pitches through the increase in pressure during pyrolysis.

This optimum pressure value and its percentage yield in carbon, which is the primary thrust of this study, has been established in this work.

Secondly, this work has been able to develop a model in form of an equation which can be used to investigate the pressure increase versus carbon yield (i.e y versus x axes) behavior even beyond the pressure ranges the available test equipment can support.

Finally, the energy requirement to raise the system from atmospheric pressure to 356MNm-^{2} pressure value (which gave 96.5% yield of carbon) is found to be almost equal to the energy requirement to raise the system from 356MNm-^{2} to 704MNm-^{2} (which gave rather about 4% loss in carbon yield) - this shows a colossal waste of energy which, through the exposition offered by this work can be avoided.

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