Thermochimica Acta, 62 (1983) 237–248
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THERMOGRAVIMETRIC CHARACTERIZATION OF THE SUITABILITY OF VARIOUS PITCHES AS MATRICES FOR CARBON–CARBON COMPOSITES

I. CHARIT, H. HAREL, S. FISCHER and G. MAROM

Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem (Israel)

(Received 28 August 1982)

ABSTRACT

The present study has been undertaken in view of the importance of the right choice of carbon precursor for the matrix of carbon–carbon composites. It presents a correlation of the carbonization process as measured by thermogravimetric means with simple fractionization characteristics of coal-tar pitch. The correlations, based on results of six different pitches, link properties such as the fractional composition and the C/H ratio with the carbon yield of a pyrolysis up to 900°C. They also set criteria by which the "best" pitch may be selected. Further examinations of the effect of variabels such as the rate of pyrolysis, the contributions of individual fractions, and the addition of crosslinking agents such as sulfur, are carried out with the selected "best" pitch.

INTRODUCTION

Carbon–carbon (C–C) composites are made from carbon fibers in a carbon matrix. These composites can be used as structural materials at high temperatures, as they maintain high strength and good thermal shock resistance up to 3000°C [1].

The final structure and mechanical properties of the C–C composites depend upon various factors, such as the type of carbon fiber, the precursor of the carbon matrix, the fiber–matrix interface and the processing method [2,3].

The first stage of preparing a C–C composite is to impregnate carbon fibers with a carbon precursor, such as coal-tar pitch, to form prepregs. The prepregs are formed to shape in a mould and pressed to the desired thickness and fiber volume loading. The next stage is to carbonize the matrix. The carbonization process infers weight loss leaving many voids and cracks which are detrimental to the physical properties of the composite. Therefore, it is usual to reimpregnate the composite with a carbon precursor and recarbonize until the desired level of densification is reached [4,5]. For a

0040-6031/83/0000–0000/$03.00

non-graphitizable matrix, thermoset polymers such as phenolics or furfuryl alcohol are used for carbon precursor. For graphitizable matrix the traditional precursors are coal or pretroleum tar pitch [5,6]. Recently, replacements such as liquid aromatics [7] and aromatic polymers [8] have been used. Also, a number of catalysts and crosslinking agents such as $AlCl_3$, peroxides, and sulfur have been examined as to their ability to improve the carbon yield [9,10].

In view of the importance of the right choice of carbon precursor and the carbonization process, this study was carried out to correlate the carbonization process, as measured by thermogravimetric means, with simple fractionization characteristics of coal-tar pitch.

EXPERIMENTAL

The experimental work was carried out with six pitches designated by the numbers 1–6, and characterized by the softening points of 100, 55–60, 65, 107–118, 85 and 70°C, respectively.

The resolution of the pitches into four fractions was carried out by either one of the following two methods. In the first, toluene was used initially to separate the toluene solubles (TS) and the toluene insolubles (TI), followed by applying *n*-pentane to the TS's to extract the soluble oils fraction from the insoluble γ-resin, and by applying pyridine to the TI's to extract the soluble β-resin, leaving the insoluble α-resin. The second method used the same solvents in a series of successive extractions starting by applying *n*-pentane to the whole pitch to extract the soluble oils, and followed by applying toluene and then pyridine to extract the γ-resin and the β-resin, respectively, leaving the pyridine insoluble α-resin.

Each extraction was carried out for eight hours at the boiling temperature of the solvent, using a weight ratio of solvent to solid of over 50 : 1. The solvents were evaporated under a low pressure, and the precipitates were dried to a constant weight in an oven at 40°C.

Thermogravimetric analysis was carried out using a Mettler model 194 thermoanalyzer, under N_2 at a flow rate of 240 ml min^{-1}, with 80.00 mg samples, at heating rates of 6°C min^{-1} (unless otherwise stated).

RESULTS AND DISCUSSION

Characterization and evaluation of the pitches

The first stage in the characterization of the various pitches investigated here was to determine their fractional composition. This was done by a series of extractions resolving each pitch into four separate fractions denoted by α,

TABLE 1

The fractional composition of the six pitches

No.	C/H ratio	Oils (%)	γ-Resin (%)	β-Resin (%)	α-Resin (%)	Total (%)
1	21.6	6.5	55.0	12.3	24.8	98.6
2	13.8	28.3	63.2	7.1	0.3	98.9
3	20.5	17.8	53.6	7.3	20.0	98.7
4	24.1	9.6	52.1	11.5	25.3	98.5
5	13.1	14.6	71.5	12.0	0.7	98.8
6	22.0	12.5	58.6	11.5	17.2	98.8

β and γ-resins and oils. The extraction procedure resulted in values of the proportional contents of each of these fractions for every pitch. Such knowledge of the fractional composition was highly relevant to the evaluation of the pitches since each fraction was expected to generate a different contribution to the total carbon yield of the carbonized pitch.

The results of the extraction separations are shown in Table 1. It is seen that the compositions of the pitches differ greatly. The contents of the lighter fractions (oils + γ) range from 61.5 to 91.5%, and those of the heavier ($\alpha + \beta$) range from 7.4 to 37.1%, pitch no. 1 being the most promising with regard to the expected carbon yield.

At this point it was essential that the carbon yield of every pitch at 900°C be determined. Hence, the loss of pitch material during carbonization was determined with the thermoanalyzer for the six pitches. The thermogravimetric (TG) and the differential thermogravimetric (DTG) results are presented

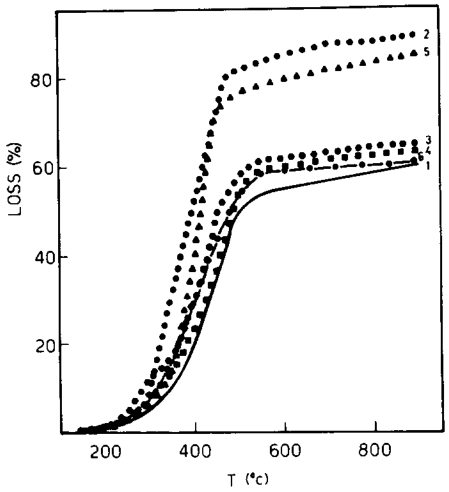

Fig. 1. Thermogravimetric traces of the six pitches.

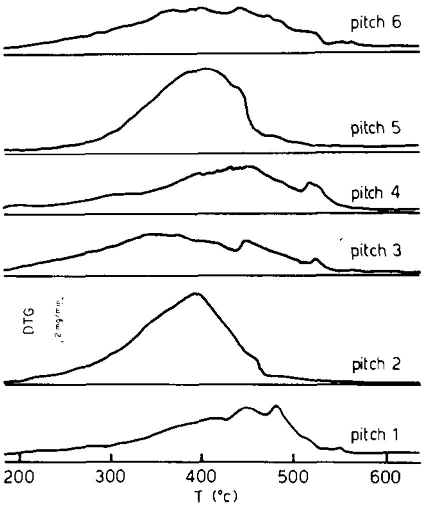

Fig. 2. Differential thermogravimetric traces of the six pitches.

in Figs. 1 and 2. It is seen that the different pitches exhibit similar TG trends, however the weight losses at 900°C vary from 60–90%. (The nominal scatter of the weight loss results for repeating experiments was ±3%.) It is also seen that the weight loss at 550°C is already as high as 90–95% of that at 900°C, while at 350°C it is in the range 16–38%. The DTG results exhibit two typical trends, one which is an indication of more gradual pyrolyses, and another which reflects pyrolyses taking place over a shorter temperature interval (pitches no. 2 and 5).

In view of the results of both the fractional compositions and the residual weights at 900°C, pitch no. 1 out of the six is evidently the most promising as a carbonization precursor. In order to establish the so far intuitive correlation between the thermal stability and the relative content of the

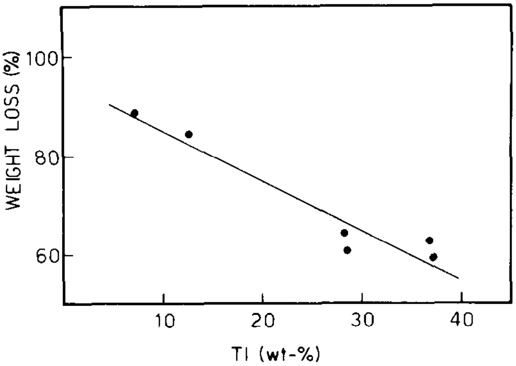

Fig. 3. The weight loss at 900°C as a function of the toluene-insoluble contents.

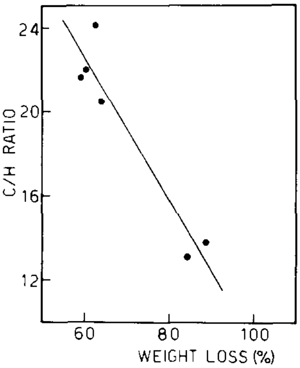

Fig. 4. The C/H ratio as a function of the weight loss at 900°C.

heavier fractions, a number of relationships have been examined graphically and statistically, and the following observations have been made. (i) High negative correlation exists between the weight loss at 900°C and the relative content of the heavier fractions ($\alpha + \beta$), the correlation coefficient being $r = -0.96$ (Fig. 3). (ii) A high negative correlation exists between the C/H ratio and the weight loss at 900°C, with a correlation coefficient of $r = -0.95$ (Fig. 4). The C/H ratio, presented for every pitch in Table 1 is a measure of aromaticity, thereby it is a measure of the potential carbon yield. (iii) A reasonable correlation with $r = 0.82$ exists between DTG (max), the maximum rate of pyrolysis, and the content of the toluene-soluble fractions (Fig. 5).

The correlations presented above show conclusively that the suitability of

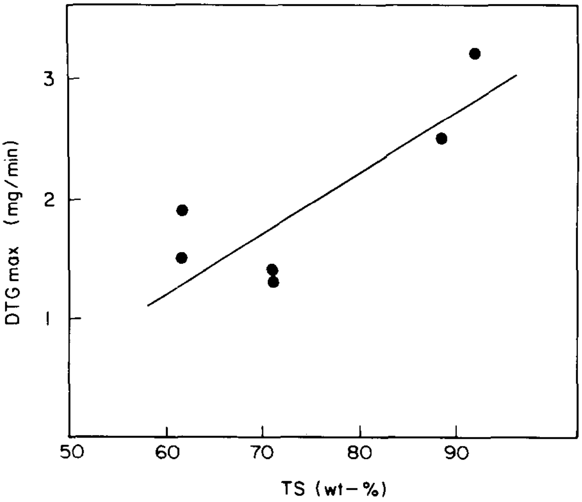

Fig. 5. The maximum rate of pyrolysis as a function of the toluene-soluble contents.

a particular pitch as a matrix for C–C composites depends on the content of the toluene-insoluble (TI) fractions ($\alpha + \beta$), and that in fact, a high content of toluene-insolubles is a prerequisite for a high carbon yield at 900°C. When this criterion is applied to the six pitches in Table 1, pitch no. 1 turns out to be the best candidate. In addition to that, pitch no. 1 is a preferable choice as a suitable matrix material for C–C composites because of its moderate rate of decomposition over a wide temperature range, with the highest value of T(max), the temperature at which the maximum decomposition rate occurs.

Based on the above observations and reasoning, pitch no. 1 was indeed selected for further studies of various aspects of increasing the carbon yield. Hence, the next section is concerned only with pitch no. 1.

The effect of the heating rate

The effect of the heating rate was studied with four rates of 2, 6, 15 and 25°C min^{-1}. The results presented in Fig. 6 show that in the temperature range 350–500°C there is a significant retardation of the weight loss with increasing heating rate. For example, at 450°C there is a difference of 27.6% between the rates of 2 and 25°C min^{-1}. However, at higher temperatures this difference diminishes gradually, and at 900°C it disappears completely, implying that the major part of the pyrolysis takes place up to 900°C regardless of the heating rate.

In view of these findings it was expected that the rates of weight-loss would be a function of the heating rate. This is indeed observed in Fig. 7, which shows the DTG traces of the four heating rates. Figure 8 shows that DTG (max) is highly correlated with the heating rate. It is therefore concluded that since the ultimate weight-loss is not affected by the heating

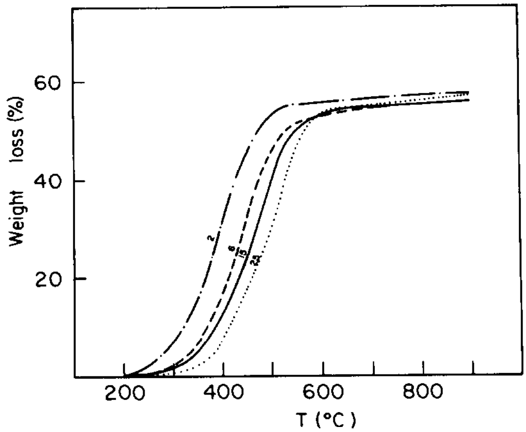

Fig. 6. The effect of the heating rate on the weight loss in the carbonization of pitch no. 1.

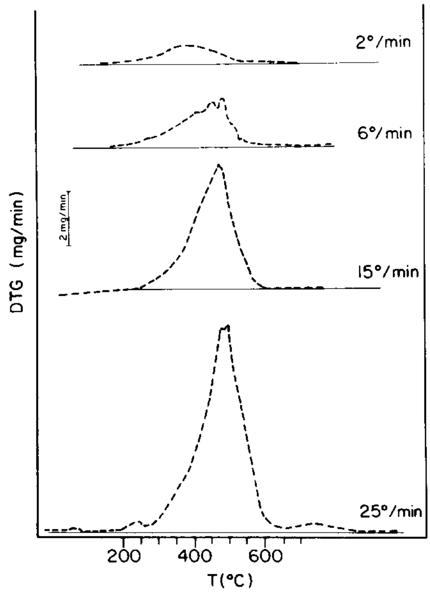

Fig. 7. DTG traces of four heating rates applied to pitch no. 1.

rate it is seemingly worthwhile to apply the higher rates. However, excessively high heating rates will result in high maximum pyrolysis rates, occurring over a very short period of time, and inducing a porous product.

Finally, isothermal carbonizations carried out at temperatures of 200, 300, 400 and 500°C also did not confer any improvement in the carbon yield. (Details of these experiments are given elsewhere [11]). However, the DTG

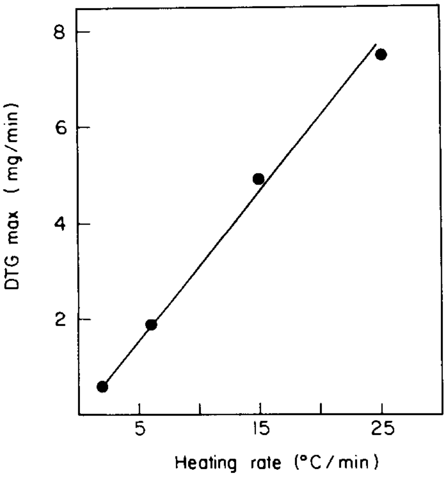

Fig. 8. The correlation between the maximum rate of weight loss and the heating rate (for pitch no. 1).

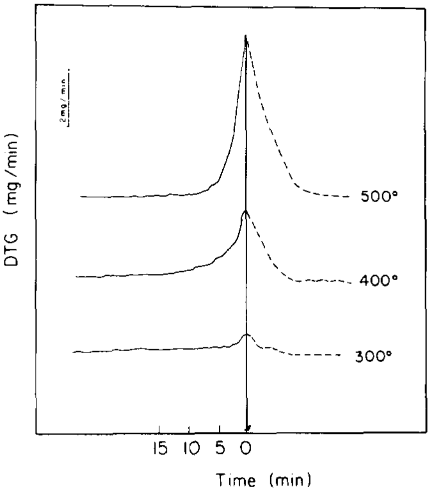

Fig. 9. DTG traces of three isothermal temperatures. The time scale starts from the instance of achieving the respective temperature (for pitch no. 1).

trends shown in Fig. 9 indicate that DTG (max) increases as the isothermal temperature increases, although at each experiment the pyrolysis rate decreases rapidly to a constant rate immediately after achieving the isothermal temperature.

The contributions to the carbon yield of the different fractions

In a previous section the correlation between the TI's and the carbon yield is pointed out. At this phase of the study it is important to examine in detail the behaviour in the carbonization process of each fraction separately, and to

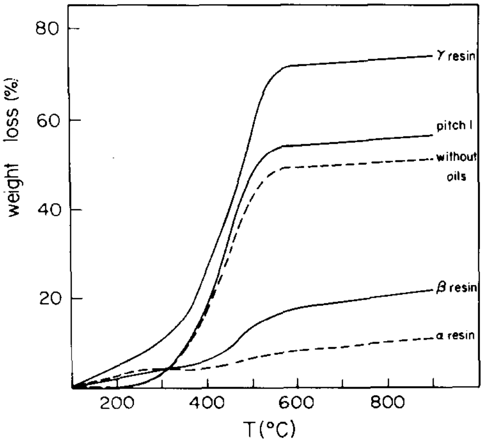

Fig. 10. TG traces of the different fractions of pitch no. 1.

TABLE 2

The weight losses at 900°C of the various fractions of pitch no. 1

Fraction and its content in pitch (%)	Weight loss at 900°C (%)	Contribution of fraction to total loss (%)	Contribution of fraction to carbon yield (%)
Whole pitch (100)	56.5	56.5	43.5
$\alpha + \beta + \gamma$ (92.1)	51.2	47.1	45.0
γ (55.0)	73.8	40.6	14.4
β (12.3)	21.9	2.6	9.7
α (24.8)	12.0	3.0	21.8

evaluate its individual contribution to the carbon yield at 900°C. Such knowledge may help improve the carbon yield through the controlling of the composition of the pitch.

Figure 10 presents the TG traces of the individual fractions. It can be seen that the ultimate weight losses of γ-resin is 74%. The oils fraction probably evaporates completely, since the pitch without oils loses 51.2% whereas the original pitch with an oils content of 6.5% loses 56.5% of its weight. The results are summarized in Table 2 in terms of the contribution of each fraction to the carbon yield at 900°C of pitch no. 1.

Additional data regarding the thermal behaviour of the different fractions is shown in Fig. 11. It is seen that the maximum pyrolysis rate, DTG (max) decreases as the weight of the fraction increases.

From the results in Table 2 we conclude that with a pitch free of oils and γ-resin it is possible to obtain a carbon yield of 85%. However, the elimina-

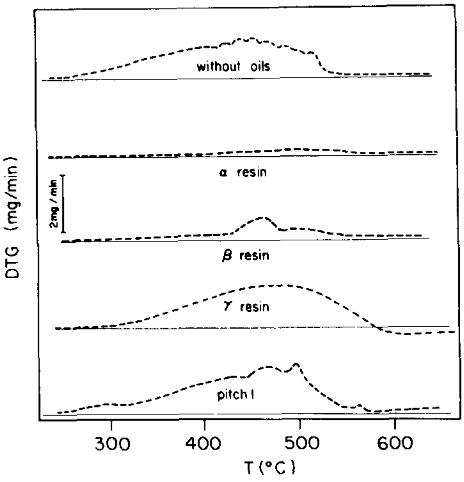

Fig. 11. DTG traces of the different fractions of pitch no. 1.

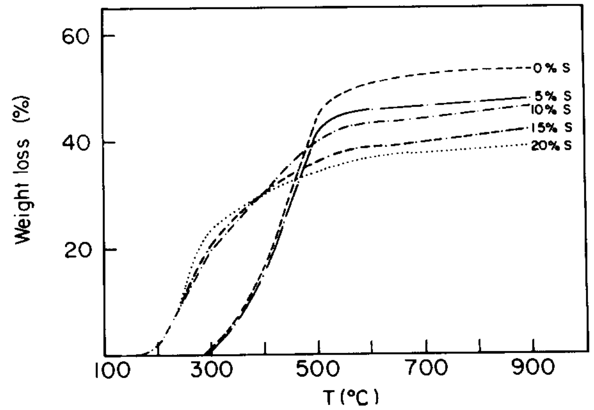

Fig. 12. TG traces of pitch no. 1 with four sulfur concentrations.

tion of these lighter fractions will result in deterioration of the processibility properties of the pitch, e.g. lower viscosity. Thus, an appropriate balance between the requirements of low viscosity and high carbon yield must be maintained. A possible way of doing that is by a combination of two steps: a partial elimination of the lighter fractions on the one hand and an addition of some crosslinking catalyst on the other, to enhance the molecular weight increase of the remaining lighter fractions during the initial heating period.

The effect of the addition of sulfur

A number of catalysts and crosslinking agents such as $AlCl_3$, peroxides, divinyl benzene and S have been examined as to their ability to improve the carbon yield at 900°C [11]. Of these, the results of the effect of the addition of S are reported here. Figure 12 presents the TG traces of pitch no. 1 with four S concentrations. Table 3 presents the effect on the weight loss of additions of 10% S to the α, β and γ-resins separately. It is seen that the

TABLE 3

The effect of the addition of sulfur (10%) on the weight loss of the various fractions of pitch no. 1

Temperature (°C)	γ-Resin		β-Resin		α-Resin	
	S	–	S	–	S	–
300	11.3	10.1	7.8	3.6	6.3	3.9
500	45.4	58.6	12.5	13.0	10.0	6.4
700	53.4	72.6	18.3	18.9	13.8	10.0
900	55.0	73.0	21.6	21.9	15.5	12.0

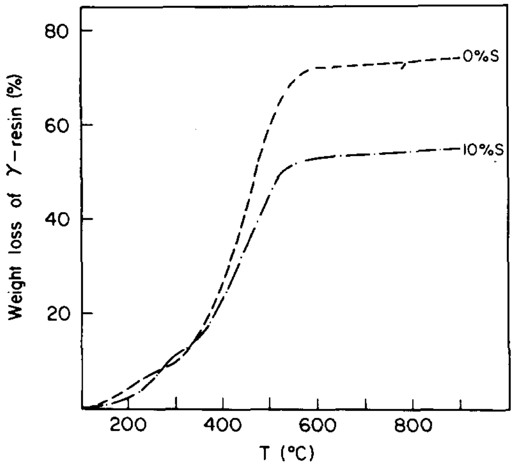

Fig. 13. The effect of the addition of sulfur on the weight loss of γ-resin of pitch no. 1.

weight loss decreases with increasing S content and that only the γ-resin interacts with the S, where a nominal improvement of 18% is obtained, as in Fig. 13.

Despite the observed high negative correlation between the weight loss and the S content, it is not recommended that the value of 10% is surpassed. This recommendation is based on the assumption that at least a part of the weight retention should be attributed to a weight of some remaining sulfur, which eventually would prevent the formation of a graphitic structure. Finally, experiments in preliminary isothermal treatments in the presence of S (to allow time for the crosslinks to form before the pyrolysis) have not produced any significant improvements in the carbon yield.

CONCLUSIONS

The thermogravimetric characterization of the suitability of various pitches as matrices for C–C composites results in the following conclusions. The carbon yield increases with increasing the C/H ratio of the pitch (showing in higher contents of the heavier $\alpha + \beta$ resins). The α and β-resins contribute almost their entire initial weight to the carbon yield, while the γ-resin loses 73.8% of its initial weight in the pyrolysis. Thus, the α and β-resins together are nominally responsible for 31.5% of the carbon yield of 43.5%, accounting for 72.4% of the weight retention, while the γ-resin is nominally responsible for only 14.4%, accounting for 33.1% of the weight retention. Additions of sulfur are effective, and result in increasing the contribution of the γ-resin to the weight retention.

REFERENCES

1 E. Fitzer and W. Huttner, J. Phys. D, 14 (1981) 347.
2 W. Fritz, W. Huttner and G. Hartwig, in A.F. Clarck, R.P. Reed and G. Hartwig, (Eds.), Nonmetallic Materials and Composites at Low Temperatures, Plenum Press, New York, London, 1979.
3 W.G. Bradshaw and A.E. Vidoz, Ceram. Bull., 57 (1978) 193.
4 B.L. Butler, T.R. Guess and D.A. Northrop, Sandia Laboratories Rep., SAND 75-0196, 1975.
5 R.C. Burns and J.L. Cook, in N.L. Deviney and T.M. O'Grady (Eds.), Petroleum Derived Carbon, A.C.S. Symp. Ser., 21 1970.
6 J.L. White, Prog. Solid State Chem., 9 (1974) 59.
7 W.E. Smith and B. Napier Jr., Union Carbide, Oak Ridge, Y-12 Plant, Rep. Y-2042, 1976.
8 E.W. Wewetka, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 14 (1973) 375.
9 I. Mochida, H. Judo, N. Fukuda, K. Takeshita and R. Takahashi, Carbon, 13 (1975) 135.
10 I. Mochida, K. Maeda and K. Takeshita, High Temp. High Pressures, 9 (1977) 123.
11 G. Marom, H. Harel and I. Charit, Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Rep. 8210 May, 1982 (in Hebrew).