CHAPTER III

PREPARATION AND CHARACTERIZATION OF CARBON TEMPLATE AND OTHER RAW MATERIALS

3.1 Introduction

Pine wood is a rich source of lignocellulosic material which can be converted into carbon by pyrolysis. Major components present in wood are cellulose, hemi cellulose and lignin. Temperatures of their decompositions are different which ultimately results in to carbon. The amount and type of carbon produced is greatly affected by how these materials are heated or pyrolysed. When compacted in one product like wood, their pyrolysis behavior will be different which is also rate dependent. Thus, the pyrolysis behavior of pine wood to be used for preparing biomorphic SiC was studied. In order to make carbon reactive, it was activated by physical activation and the resulted activated carbon was also studied. All the results obtained from wood and carbon are compiled in this chapter. This chapter also includes characterization results of other raw material used, i.e. phenolic resin, etc.

3.2 Thermo gravimetric analysis

3.2.1 Thermo gravimetric analysis of pine wood

Pyrolysis behavior of pine wood sample was studied using Thermo gravimetric analyzer (Mettler TG-50). The samples were subjected to thermo gravimetric analysis in inert atmosphere (nitrogen) at a heating rate of 5°C/min. Fig 3.1 shows thermogram. The weight loss of wood starts below 100°C and reaches maximum at 330°C. It gets almost
completed at 700°C. It indicates that the initial weight loss begins around 100°C, where
the moisture is removed. Further weight loss occur due to decomposition of
hemicellulose at temperature range of 240-350°C followed with release of volatile
products. In slightly higher temperature range of 280-500°C, majority of weight loss
occur due to decomposition of cellulose and lignin leaving behind a carbon preform.
After 500°C, very little weight loss occurred which is due to entrapped volatiles in the
pore. The peaks in the DSC curve indicate that the reaction and gas evolution during
pyrolysis occur in the same temperature range of 200°C to 400°C.

![Fig: 3.1 TGA and DSC of as such pine wood](image)

**Fig: 3.1** TGA and DSC of as such pine wood
3.2.2 Thermo gravimetric analysis of phenolic resin

![TGA of phenolic resin](image)

**Fig.3.2 TGA of phenolic resin**

Fig 3.2 is the TGA curves of phenolic resin. It shows weight loss of phenolic resin as a function of heating temperature. The maxima in decomposition of phenolic resin occur in the temperature range 500-600°C. The carbon generated from phenolic resin is much higher than that from the same weight of wood powder, because phenolic resin has higher carbon yield ratios during carbonization than the other main components such as cellulose and hemicellulose in wood [161]. As shown in the TG curve of phenolic resin, (Fig.3.2) weight loss starts slowly at about 200°C, and gets faster above 450°C, indicating the formation of a great deal of volatiles. Weight loss rate reaches maximum at approximately 550°C and evidently decreases above 600°C, which, hardly varies above 800°C. Yamashita et al. [161] has reported that thermal weight loss below 450°C was
caused by the dehydration reaction of phenolic resin, including thermo curing reaction
between hydroxyl methyl groups and hydrogen groups within aromatic rings and the
condensation reaction between methylene and hydroxyl groups. The condensation
aromatic polynuclear structure began to form above 450\(^0\)C and develop above 500\(^0\)C
\[161\], releasing small molecular substances such as CH\(_4\), H\(_2\), CO, CO\(_2\), etc. Weight loss
at approximately 700\(^0\)C was attributed to further carbonization and dehydrogenation
reactions in phenolic resin.

3.3 Carbonization of pine wood

Pine wood was cut into cube shaped samples, dried at 110\(^0\)C for 5 days. The
dimensions of the samples were measured accurately. Sample were carbonized under
inert nitrogen atmosphere at 750\(^0\)C for 7 hour in an electrically heated furnace with slow
heating rate of 10\(^0\)C/hr up to 350\(^0\)C, 15\(^0\)C/hr up to 550\(^0\)C and at 20\(^0\)C/hr up to 750\(^0\)C.
The cooling was done in nitrogen atmosphere to prepare a carbon template. Slow heating
and cooling were maintained to avoid formation of cracks due to degradation of
cellulosic material. Table 3.1 indicates the results obtained after pyrolysis. Pyrolysis
resulted into weight loss of 70±5%. After pyrolysis, dimensions were taken and
percentage axial, radial and tangential, shrinkages was 28.5\%, 21\%, and 12\% respectively resulting in total volume reduction of about 64%. Before pyrolysis the
density of pine wood was 0.51g/cm\(^3\), and after pyrolysis it got reduced to 0.44 g/cm\(^3\).
Pine wood contains 24.2% carbon and 0.38% of ash.
3.4 Steam activation of Carbon template

Pyrolysed sample of pine wood was activated by steam at 750°C with nitrogen gas as carrier. The hold time was one hour. During activation, steam removes loosely held carbon atoms from the net work and form clogged pores. The rate of flow of steam has profound effect on the activation reaction. Therefore steam activation was studied at different flow rates, of 0.1ml/min, 0.3 ml/min, 0.5ml/min and 0.7ml/min. Table 3.2 indicates physical properties of activated carbon derived from pine wood under different steam rates. Activation temperature (750°C) and time (60 min.) were the same during steam activation.

Table 3.1 Physical characteristics of pyrolysed wood

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density of wood (g/cm³)</th>
<th>Density after pyrolysis (g/cm³)</th>
<th>Char, %</th>
<th>axial shrinkage, %</th>
<th>radial shrinkage, %</th>
<th>volume shrinkage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine Wood</td>
<td>0.51</td>
<td>0.44</td>
<td>24.2</td>
<td>28.5</td>
<td>21</td>
<td>64</td>
</tr>
</tbody>
</table>
Table 3.2 Physical properties of activated carbon derived from pine wood under different steam rate

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Input steam rate (ml/min)</th>
<th>Activation temperature (°C)</th>
<th>Activation time (min)</th>
<th>Surface area (m²/gm)</th>
<th>micro pore, %</th>
<th>Average Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>750</td>
<td>60</td>
<td>497.697</td>
<td>90.56</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>750</td>
<td>60</td>
<td>654.73</td>
<td>87.17</td>
<td>1.76</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>750</td>
<td>60</td>
<td>710.45</td>
<td>86.50</td>
<td>1.78</td>
</tr>
<tr>
<td>4</td>
<td>0.7</td>
<td>750</td>
<td>60</td>
<td>721.28</td>
<td>79.87</td>
<td>1.92</td>
</tr>
</tbody>
</table>

After activation kerosene porosity of activated carbon increases by 15%. Table 3.3 shows the changes in density and porosity of activated carbon.

Table 3.3 Kerosene porosity of carbonized and activated carbon

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Density before steam activation (g/cm³)</th>
<th>Density after steam activation (g/cm³)</th>
<th>Kerosene porosity before activation</th>
<th>Kerosene porosity after activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.44</td>
<td>0.32</td>
<td>71.34%</td>
<td>86.21%</td>
</tr>
</tbody>
</table>
3.5 Characterization of carbon template

3.5.1 FT-IR analysis of pyrolysed and activated pine wood

FT-IR spectra of pyrolysed wood and activated carbon are shown in figure 3.3. FT-IR spectra of as such pyrolysed wood (Fig. 3.3a) shows absence of surface oxygen complexes. On activation, an increase in surface oxygen complexes like carbonyl and carboxylic groups is observed. These groups increase reactivity of carbon with silica.

Fig. 3.3 FTIR spectra of (a) pyrolysed pine wood and (b) steam activated pine wood
Table 3.4 indicates all FT-IR bands present in pyrolysed and activated carbon. The peak at 1657-1658 cm\(^{-1}\) which confirms the presence of conjugated carbonyl C=O groups present in the pyrolysed pine wood (fig4.3a). The region between 700-900 cm\(^{-1}\) contains various bands related to aromatic, out of plane C-H bending with different degrees of substitution (Fig.3.3a). The C-H stretching and bending vibrations of methylene (CH\(_2\)) of aliphatic hydrocarbons were assigned to band at 2881 cm\(^{-1}\) in pyrolysed pine wood. The band at 1774 cm\(^{-1}\) was assigned to carbonyl stretching (C=O) in aldehyde, ketons, ester and carboxyl groups.

While in case of activated pine wood the band present at 3222 cm\(^{-1}\) confirms the presence of phenolic methylol hydroxyl (OH) vibration, the bands at 2889 cm\(^{-1}\) (C-H aliphatic stretching) and 1465 cm\(^{-1}\) (C-H aliphatic bending) are more intense in activated carbon. The peaks at 1535-1570 cm\(^{-1}\), 1676 cm\(^{-1}\), 1693 and 1774 cm\(^{-1}\) are attributed to carboxylic acid, amide C=O and keton C=O indicates the presence of oxygen on the surface of activated carbon. Also peaks at 1085 cm\(^{-1}\) and 1153 cm\(^{-1}\) shows strong and medium band of secondary and tertiary alcohol respectively.
### Table 3.4 IR data of pyrolysed and activated carbon

<table>
<thead>
<tr>
<th>Pyrolysed carbon</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR peaks (cm⁻¹)</td>
<td>FTIR peaks (cm⁻¹)</td>
</tr>
<tr>
<td>432 cm⁻¹</td>
<td>756 cm⁻¹, 808 cm⁻¹, 893 cm⁻¹</td>
</tr>
<tr>
<td>516 cm⁻¹</td>
<td>1085 cm⁻¹</td>
</tr>
<tr>
<td>671 cm⁻¹</td>
<td>1153 cm⁻¹</td>
</tr>
<tr>
<td>846 cm⁻¹</td>
<td>1427 cm⁻¹</td>
</tr>
<tr>
<td>1141 cm⁻¹</td>
<td>1485 cm⁻¹, 1500 cm⁻¹, 1517 cm⁻¹, 1583 cm⁻¹</td>
</tr>
<tr>
<td>1242 cm⁻¹</td>
<td>1535 cm⁻¹, 1554 cm⁻¹, 1570 cm⁻¹</td>
</tr>
<tr>
<td>1288 cm⁻¹</td>
<td>1676 cm⁻¹</td>
</tr>
<tr>
<td>1685 cm⁻¹</td>
<td>1693 cm⁻¹, 1747 cm⁻¹</td>
</tr>
<tr>
<td>1774 cm⁻¹</td>
<td>2364 cm⁻¹</td>
</tr>
<tr>
<td>2362 cm⁻¹</td>
<td>2889 cm⁻¹</td>
</tr>
<tr>
<td>2416 cm⁻¹</td>
<td>3222 cm⁻¹</td>
</tr>
<tr>
<td>2881 cm⁻¹, 3016 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>3652 cm⁻¹</td>
<td></td>
</tr>
</tbody>
</table>
3.5.2 Surface characteristics

Pyrolysed pine wood at 750°C was analysed for surface characteristic by BET instrument. Nitrogen adsorption was carried out at liquid nitrogen temperature. Process of adsorption was continued for more than 20hrs but there was no adsorption of nitrogen on pyrolysed pine wood. The pores present in the pyrolysed pine wood appeared to be not interconnected and therefore nitrogen could not pass through. Surface morphological structure of pyrolysed pine wood in figure 3.9 also showed presence of macropores filled with highly decomposed cellulosic materials. Thus no adsorption was observed.

Figure 3.4 shows nitrogen adsorption of steam activated carbon. The isotherm belong to type – I Isotherm, showing presence of microporosity with a wider micropores size distribution and the linear branch is reached gradually. Therefore, steam activated carbon has narrow microporous but wider micropore size distribution.

![Fig.3.4](image)

Fig.3.4  (a) Adsorption isotherm of steam activated carbon (b) Pore size distribution of activated carbon by BJH method
Nitrogen adsorption-desorption isotherms of activated carbon powder samples are with different steam rates as shown in Figure 3.5. These isotherms show highly microporous nature showing maximum adsorption of nitrogen gas at low relative pressure. The volume of nitrogen adsorbed is increasing with increase in steam flow rate. It is clearly observed that the sample activated by 0.7ml/min shows the maximum adsorption and minimum for sample activated by steam at flow rate of 0.1 ml/min. The comparison of surface characteristics of activated carbons is included in table 3.2. As observed from the table, the surface area shows an increase with increasing flow rate of steam, while percentage micro porosity decreases with increasing the flow rate of steam during activation process. Hence the micro porosity and surface area can be controlled by controlling the flow rate of steam during activation process.

**Fig.3.5** Nitrogen adsorption isotherm of activated carbon
Fig. 3.6 shows the variation of micro porosity and pore diameter of the activated carbons produced by changing the flow rate of steam. Though, micro porosity shows an increase with increasing flow rate of the steam up to 0.3ml/min, further increase in the flow rate decreases the micro porosity as higher rate results in high rate of oxidation of carbon to carbon dioxide leading to fall of pore walls and widening of pores. Any further increase up to 0.7ml/min, decrease the micro porosity while the surface area is found to increase. High rate of oxidation beyond 0.7ml/min leads to fracture of the materials and entire structure collapse. However, the average pore diameters in all samples were found to be less than two nanometer showing micro porous sample. Also, the sample activated with steam at flow rate 0.1ml/min has smaller pore volume than sample activated with steam at flow rate of 0.7ml/min. Though with higher flow rate of steam higher surface area can be achieved but by controlling flow rate of steam pores of specific size for specific adsorption can be generated.

![Graph showing the correlation of effect of steam rate versus percentage micro pore and average pore diameter](image)

**Fig. 3.6** Correlation of effect of steam rate versus percentage micro pore
3.5.3 Raman analysis

A number of Raman studies on carbonaceous materials have been reported in the literature. Tuinstra and Koenig [162] studied the Raman spectra of several kinds of graphite. Moreover several authors applied both XRD and Raman spectroscopy as complementary method for characterization of carbon. Raman spectroscopy has become an important technique for characterizing materials such as diamond-like carbon because most of the Raman spectra of these materials exhibit two prominent and several other bands in the spectral region 1000–1800 cm\(^{-1}\). Although the assignments of Raman bands appearing in this region are still controversial, two characteristic bands, usually classified as the D-band and the G-band by wave number, have been regarded as a source of information on the molecular structure and chemical bonding of carbon atoms in carbonaceous materials. The D- and G-bands usually appear near 1340 and 1580 cm\(^{-1}\), respectively. Both bands are generally attributed to graphitic sp\(^2\)- bonded carbon [163]. D-band is thought to arise from a fairly disordered or distorted structure at the edge of the micro crystallite. In most of the Raman spectroscopic studies, the properties of carbonaceous materials have been discussed according to this attribution. Despite the wide use of the Raman technique for carbonaceous materials, there have been only a few Raman studies on the thermal degradation or carbonization of wood [163, 164]. This is probably because, with conventional Raman analysis, fluorescence arising from visible laser irradiation of raw or low-temperature-treated lignocellulose frequently prevents one from obtaining a satisfactory spectrum. These investigations cover a wide range of carbon and silicon carbide materials with different structures, properties and applications [165–174].
Fig. 3.7 Raman spectra of pyrolyzed pine wood

Fig. 3.8 Raman spectra of activated pine wood
The pyrolysed and activated pine wood were analyzed by Raman spectroscopy. Fig. 3.7 indicate the Raman spectra of pyrolysed pine wood. As observed from the fig 3.7, Raman spectra of pyrolysed wood shows only two broad peaks at 1338.64 cm\(^{-1}\) and 1595.74 cm\(^{-1}\) mainly known as D and G band confirming presence of disorder carbon. The ID/IG ratio was found to be 1.61 for pyrolysed pine wood. Raman spectrum of activated carbon is shown in fig.3.8. It also exhibits peaks at 1332 and 1600 cm\(^{-1}\) resembling those of disordered carbons. ID/IG ratio for activated carbon was found to be 1.44. ID/IG ratio of both pyrolysed and activated carbons were measured from the area of peaks not form the intensity of peaks.

As seen from these studies, though ID/IG ratio for both the samples is higher than one confirms the characteristic of disordered carbons. The ratio decreases after activation, which clearly reveals that the loose carbons removed on activation were highly disordered or amorphous in nature.
3.5.4 SEM analysis of Pyrolysed and Activated carbon.

Surface morphological studies of as wood and carbonized pine wood samples were studied using HITACHI S-3000N Scanning Electron Microscope. Fig 3.9 is SEM of pine wood as such. As observed in fig 3.9, pine wood consists of cellular structure of a porous network but the pores are not fully clear. These contain hemicelluloses as well as cellulose and lignin. Fig 3.10 shows SEM micrograph of carbonized sample. Fig 3.9 and fig. 3.10 are the SEM of the sample in axial direction. As seen from the figure 3.9, the charred material retains the cellular structure. However the pores get cleared on pyrolysis. Therefore, on pyrolysis the cellulose and lignin and other filled materials get decomposed while walls of the struts retained their morphology. The filled mass gets highly decomposed resulting in clear pore structure. It also shows slit like structure exhibiting channel like continuous structure (Fig.3.11). Pyrolysed pine wood, exhibit pores having average pore diameter between 22~37 μm.
Fig. 3.9 SEM micrograph of as such pine wood [In axial direction]

Fig. 3.10 SEM micrograph of carbonized pine wood at 750$^0$C [In axial direction]
Fig. 3.11 SEM micrograph of carbonized pine wood at 750°C [In radial direction]

Fig 3.12 (b & c) is the SEM micrograph of activated carbon with flow rate of 0.1 and 0.7ml/min of steam. These figures also indicate that pore morphology is retained. With increasing flow rate, not only the original voids get enhanced but the carbon constituting the walls of the pores also get removed slightly resulting in new pores. Though the surface area of all samples increases on increasing the flow rate of steam, but due to higher flow rate, diffusion is faster resulting in collapsing of pore walls, hence the micro pores get widened [Fig.3.12 (c)] and average pore diameter increase from 1.65nm to 1.92 nm. Micro porosity also falls from 90 % to 79%.

These results show that on activation with steam with increasing flow rate, not only the original voids get enhanced but the walls constituting the pore in carbon get burnt to carbon dioxide leaving behind bigger pores as shown in fig 3.12 (c).
Fig. 3.12 Scanning electron micrograph of (a) carbonized pine wood (b) steam activated carbonized pine wood having steam rate 0.1ml/min & (C) steam activated carbonized pine wood having steam rate 0.7ml/min