CHAPTER 4

PROCESSING OF SOLID CARBON THROUGH SELF SINTERABLE ROUTE
4.1 INTRODUCTION:

On grinding, the semi coke powder gets transformed to sinterable one. This powder, the so called, sinterable carbon was cold pressed at room temperature into cylindrical samples of diameter 5 cm and height about 0.5 to 0.8 cm under a pressure of about 450-1000 kg/cm². These samples were sintered at temperatures from 1000-2700°C without pressure. The sintered samples were evaluated for various physical characteristics. The characteristics of the original coke, the grinding parameters as well as sintering conditions, all have significant influence on the properties of end products. Therefore, systematic studies were made on the effect of processing parameters on the microstructure of the sintered products and their properties. These were also done to understand the sintering mechanism. All these studies have been elaborated in this chapter.

4.2 GREEN COMPACTS FROM SINTERABLE COKES:

4.2.1(A) GREEN COMPACTS FROM RAW PETROLEUM COKES (UH):

Raw Petroleum Coke (UH type) grounded for different times were compacted into solid cylindrical samples.

As discussed in chapter 3, on grinding the coke undergoes tremendous changes. Obviously, these changes will have effect on the development of the products therefrom and their properties. The powders obtained after grinding of coke for less than 30 hrs., on compaction, did not result in a solid compacted sample even at compaction pressure of 1000 kg/cm². On removing the samples from the die, these used to break down. Powders obtained by grinding of RPC(UH) for 50hrs. and above resulted in solid strong samples (green samples). The density of the green samples was found to increase with grinding time. Fig. 4.1 shows the density of green samples obtained for RPC (UH) grounded for different time. As seen from the Figure, the increase in density of the samples is more for mechanical grinding up to 150hrs. Afterwards the increase in density is tapered off. This can be
Fig. 4.1. Effect of grinding time on green density of RPC(UH)
attributed to the change in shape of the powders with grinding time. With grinding time, the grains become more and more spherical in shape. Spheres have possibility of higher packing efficiency and therefore, the density of green samples increase with grinding time of semicokes. With higher grinding times, further increase in density due to packing of grains is reduced.

4.2.1(B) EFFECT OF COMPACTING PRESSURE ON DENSITY OF GREEN SAMPLES:

The compacting pressure will have influence on packing of grains and have on density of the green samples. In order to study this, the sinterable carbon obtained by grinding for 150hrs. were compacted into solid cylindrical shapes under pressure varying from 350 to 1000kg/cm². Figure 4.2 shows the change in density with compacting pressure. As seen from the figure the increase in density is very high for increase in pressure from 350-450 kg/cm². On compacting the samples at higher pressures say 700-900 kg/cm², though, the density is found to increase but it is very small. The increase in density with high compacting pressure is obviously due to decreased interparticle distances. For academic purpose, one can press the samples at such high pressures but for commercial applications such high pressures are not viable especially for large size products.

4.2.1(C) GREEN COMPACTS FROM SINTERABLE COKE CHEMICALLY TREATED WITH QUINOLINE:

In chapter 3, it has been described that raw petroleum coke contain volatile hydrocarbons which exhibit an increase after grinding. In order to ascertain the role of volatile contents of the sinterable carbon on compaction and density of the green samples, the sinterable coke (grounded for 150hrs.) were treated with quinoline. The low molecular weight hydrocarbons get dissolved in quinoline and hence the sinterable carbon, treated with quinoline show low volatile contents. The volatile
contents reduced from 13% to 6%. This carbon powder was compacted under similar conditions. The green samples obtained from treated powder was found to possess almost same density (1.25 g/cc) as those obtained from untreated powder (1.238 g/cc). This shows that the compaction of the grains and increase in density of the green compacts is mainly attributed to the powder compaction phenomenon and depends on the grain shapes, size and surface energetics and not on volatile contents.

4.2.2 GREEN COMPACTS FROM RAW PETROLEUM COKE (IC):

The effect of grinding of second type of raw petroleum coke (IC) on compaction and properties of the green samples was also studied. The experience gained from RPC (UH) was utilized and hence in this case, elaborate studies were not made. The coke was grounded for different times varying from 50 hrs. to 150 hrs. Fig 4.3 shows the density of green compacts made with IC sinterable carbon grounded for different times. It is found that it follows the same pattern as UH carbon though former coke contained higher volatile contents. It further conforms that volatile contents have little role on the compaction and density of green samples.

4.3 SINTERING OF GREEN COMPACTS MADE FROM SELF SINTERABLE COKE:

Sinterable carbon pressed in a cylindrical mold at room temperature were then sintered to 1000°C in electrically heated furnace under nitrogen atmosphere with heating rate varying from 1 to 18°C/min., under normal pressure. These compacts were then further heat treated to temperature between 2000°C and 2700°C.

During sintering solid-solid reaction takes place between grains of sinterable carbons. This results in various physical changes in the samples such as shrinkage,
Fig. 4.3. Effect of grinding time on green density of RPC(IC)
Fig. 4.5. Effect of compacting pressure on density and linear shrinkage during sintering at 1000 °C
Similarly, the amount of shrinkage has been found to be affected by the volatile contents. The shrinkage during sintering is found to increase with increase in volatile contents. This is shown in Fig 4.6. This shows that the volatile contents influence the sintering mechanism.

4.3.2 CHANGE IN DENSITY WITH SINTERING TEMPERATURE:

As seen in the Fig. 4.4 and described in section 4.3.1, there are appreciable changes in dimensions and weight during sintering of carbon products. Since the density is dependent on weight of the samples and its dimensions, it will also vary with sintering. Figure 4.7 shows variation in density of solid carbon products during sintering to 1000°C. As described earlier the density is a function of ultimate shrinkage and weight loss, the shrinkage of the sample should be high to get good dense solid samples. The initial expansion of the sample has to be minimize, so that the sample can shrink more. In the above figure the initial expansion is 5.72%. Because the coke is pre heat treated to around 550°C, it shows minor weight loss up to 550°C. Therefore, the density of the sample will decrease in this range. Beyond 550°C, the sample shows remarkable shrinkage and small weight loss. Therefore, the density shows increase with temperature in the range 550-1000°C. In this temperature range solid-solid reaction is also taking place stage. All these phenomena lead to increase in density of the samples.

4.3.3 DENSITY AND POROSITY OF THE SINTERED SAMPLES MADE UNDER DIFFERENT CONDITIONS:

Density and porosity in the carbon samples are very complex properties, particularly when carbon is made from binder less pressure less method. In this case two parameters are responsible for the formation of the pores. First is the particle size and the second is heating rate during sintering. The porosity seems to be affected by compacting pressure also.
Fig. 4.7. Effect on density with sintering temperature of solid carbon sample
Figure 4.8 shows the effect of grinding time on density and porosity of the sintered samples. It shows that with increase in grinding time, the porosity decreases and density increase, i.e. with decrease in particle size the density increases and porosity decreases.

There are many definitions of sintering, but the widely perceived model involves reduction of interparticle porosity by mass transport. Carbon materials shows significantly different characteristics, it does not sinter in the conventional sense and the densification and shrinkage arise from the substitutional changes in the solid structure from polyaromatic molecular solid to carbon and ultimately to graphite with the associated increase in true solid density. Carbons of high bulk density only result when the individual grains are strongly bonded to each other such that the total shrinkage of the sample matches to the individual grain. In this case the particle size distribution is significant in a number of ways. During sintering the small and spherical particles will provide greater driving force and enhanced sinterability. The decrease in particle size and change of shape from irregular to spherical one decreases interparticle distance which ultimately results in higher compaction. With heating to 1000°C and cooling, the bigger particle may develop shrinkage cracks. This is because of the differential shrinkage of the different particles which are not uniform in size. This differential shrinkage leads to greater stresses at the boundaries of larger particles and cracks develop at the interphase. This also contribute to the porosity of samples[45].

Effect of forming pressure on density and porosity of the solid carbon products:

As discussed in section 4.2.1(b) forming pressure has effect on the green
sintered compacts as shown in the figure 4.9. However, the percentage in increase (density of sintered samples over density of green samples) is found to exhibit remarkable increase at higher compaction pressure of more than 700 kg/cm². It shows that the decrease in interparticle particle distance has profound effect on sintering carbon materials [47].

Effect of heating rate on density and porosity of the solid carbon products:

Sintering of solid product is interaction between solid particles. Sintering is the reaction between individual solid particles of the substance to give hard, less porous high density product.

In solid carbon through self-sinterable carbon, sintering takes place due to the evolution of low volatile components, sintering and heating causes crosslinking of the low or short range order molecules to the long range order molecules. Since during sintering many chemical transformations, as stated above takes place accompanied with many physical transformations such as solid-solid grain to grain linking and dimensional changes, the rate of heating during sintering may effect the extent of sintering, density and properties of the end products.

Therefore, in the present study four different heating rates were tried. Table 4.1 shows effect of heating rate on shrinkage during sintering as well as on the density of the end products. As seen from the table the linear sintering shrinkage of the samples increase with increase in heating rate. Percentage increase in density is also found to increase with heating rates.

With increased heating rates, the volatile contents within the body of the samples do not get sufficient time to escape but gets carbonized within the samples. It helps in sintering. However, at very high heating rates, the increase in density slows down. Moreover, at high heating rates thermal expansion of coke grains induce stress inside the compact. Due to this reason the compact gets cracked. Therefore, though high heating rates can be chosen in the present process the rate of
Fig. 4.9. Effect of compacting pressure on density and porosity of carbon sample
heating has to be optimized to obtain the highest density and uncracked products. So it is clear from the above analysis that grinding time (particle size), compacting pressure and heating rates are all important parameters. The porosity of the samples can be controlled by the competing shrinkage processes, i.e. intraparticle shrinkage (as the crystal structure develops) and bulk shrinkage (determined by the mutual shrinkage of the grain assembly). Stresses developed between shrinking grains can open up voids during the carbonization process and also differential thermal contraction opens voids on cooling.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Heating rate (°C/min)</th>
<th>Green Density (gm/cc)</th>
<th>Sintered Density (gm/cc)</th>
<th>Shrinkage (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>1</td>
<td>1.15</td>
<td>1.29</td>
<td>19.12</td>
<td>22.52</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>1.20</td>
<td>1.43</td>
<td>26.21</td>
<td>19.32</td>
</tr>
<tr>
<td>41</td>
<td>5</td>
<td>1.20</td>
<td>1.47</td>
<td>27.5 ?</td>
<td>15.72</td>
</tr>
<tr>
<td>31</td>
<td>18</td>
<td>1.15</td>
<td>1.4 ?</td>
<td>27.3 ?</td>
<td>17.38</td>
</tr>
</tbody>
</table>

Table : 4.1 Effect of heating rate on density and porosity of the solid carbon samples.

4.4 HIGH TEMPERATURE TREATMENT OF CARBON PRODUCTS MADE THROUGH SELF SINTERABLE TECHNIQUE:

The carbon compacts after sintered to 1000°C were heat treated at higher temperature (2000-2700°C) under argon atmosphere. These solid carbon bodies were then characterized for physical changes, density, porosity and microstructure properties. These were also characterized for mechanical, electrical and thermal properties.

The sinterability of the carbon product could be easily understood by using optical microscopy and SEM.
4.4.1 PHYSICAL CHANGES TAKING PLACE DUE TO HIGH TEMPERATURE TREATMENT:

Figure 4.10 shows volume shrinkage of the solid carbon products during sintering to high temperatures in the range 1000-2700°C. As seen from the figure, the shrinkage increases with HTT. However, the maximum shrinkage is observed up to a temperature of 1000°C. In this temperature range the shrinkage is about 25-30%. In the temperature range 1000-2000°C, the shrinkage is about 7-8% and in the temperature range 2000-2700°C, it is between 2-3%. Since the shrinkage has been attributed to the sintering takes place up to 1000°C followed by in the temperature 1000-2000°C. This is further supplemented by the weight loss of the product in that temperature range.

Figure 4.11 shows weight loss of the sample during heating to 2700°C. Weight loss is also maximum in the temperature up to 1000°C. In the temperature range 1000-2000°C, the weight loss is much less and least in the temperature range 2000 to 2400°C. In the temperature range 2000-2700°C ordering of the carbon structure takes place. The ordering is maximum in the temperature range 2500-2700°C. As seen from the figure the initial density of the green compact has influence on the shrinkage of the product during high temperature treatment. If the initial density is high, the subsequent shrinkage in the temperature range 1000-2000°C and above is also high. This is mainly because the products having high green density have lower inter grain distance than the other. This helps in further sintering of the products and hence result in higher shrinkage.

4.4.2 CHANGE IN DENSITY OF SOLID CARBON PRODUCTS WITH HIGH TEMPERATURE HEAT TREATMENT:

The enhanced sintering of carbon products in the temperature range 1000-2000°C and ordering of carbon structure to a well packed graphitic structure should result in change in density of the products. This is evident from figure 4.12. Figure
Fig. 4.10. Volume shrinkage of the solid carbon products during sintering to high temperature
Fig. 4.11. Weight loss of solid carbon samples during sintering to different temperatures
Figure 4.12 shows increase in density of the product with heat treatment temperature. As seen from the Figure 4.12a, the increase in density is maximum with the temperature up to 1000°C due to sintering of green compacts. In the temperature range 1000-2000°C, the rate of increase in density is found to be reduced. This is since most of the sintering has taken place up to the heat treatment temperature of 1000°C. There is little scope of sintering in the temperature range 1000-2000°C. However, after 2000°C further increase in density is observed when the samples are heat treated to 2700°C. The rate of increase of density is quite appreciable. This increase in density of the products (in the temperature range 2000-2700°C) is due to ordering of the carbon structure from disordered to ordered graphitic structure.

The initial density of the green samples is found to have effect on the ultimate density and porosity at 1000°C and 2700°C. This is also evident from Figure 4.12b where the densities and porosity of the two products at different heat treatment temperature having different green densities have been compared. Though both the products show similar trends in increase in densities and decrease in porosity with heat treatment temperatures, the ultimate densities and porosity are quite different. The densities of the green samples differ by about 4%. This difference in densities increases to about 10% at 1000°C and about 14% at 2700°C. This suggests that the samples having greater compactness in the green stage show better sinterability and crystalline ordering during high temperature heat treatment.

4.5 STRUCTURE OF SOLID CARBON SINTERED AT DIFFERENT TEMPERATURES:

The development of solid carbon is based on compacting sinterable carbon powder and their sintering at high temperature treatment during which many physical transformations take place. Therefore, these will also affect the macrostructure as well as microstructure of the products. In order to correlate the
Fig. 4.12a. Effect of grinding time on density and porosity of the sintered carbon samples
Fig. 4.12b. Change in porosity with sintering temperatures
structure with the processing of the products, the macro as well as microstructure of various samples at different processing stages were studied using optical microscope, SEM & XRD.

4.5.1 OPTICAL AND SEM MICROSCOPY OF SOLID CARBON SAMPLES:

Optical microscopy:

Polished samples were viewed under normal as well as polarized incident light using Leitz optical microscope.

Figure 4.13 shows optical micrograph of green samples made with coke grounded for 60 hrs. It shows coke particles with very large variation in size. Fig. 4.14 shows optical micrograph of sintered samples heat treated at 1000°C made from sinterable coke grounded for 60 hrs. It shows that the individual particles retain optical activity (anisotropic character). Also the small particles exhibit good sintering (Area A), whereas the large particles do not show any sintering characteristic (Area B). Figure 4.15 shows optical micrograph of sintered composites sintered at 1000°C made from same coke grounded for 150 hrs. It shows that the particles lose optical activity, shows more or less isotropic character and excellent sintering to each other. The sintering is found to be markedly improved on heat treatment to 2700°C. This is shown in optical micrograph (Figure 4.16).

The observation made by optical microscopy are further confirmed by Scanning Electron Microscopy (Figure 4.17).

4.5.2 XRD STUDIES OF HEAT TREATED SOLID CARBON MATERIALS:

The graphitizing of heat treated solid carbon was studied by XRD using Rigaku X-Ray Diffractometer. Fig. 4.18 shows XRD of solid carbon heat treated at 2700°C. This shows a prominent sharp peak at $2\theta = 26.5^\circ$ with $d=0.3357$ nm.
Fig. 4.13: Optical micrograph of green sample made with coke grounded for 60hrs.
Fig. 4.14: Optical micrograph of sintered sample heat treated to 1000°C made from sinterable coke grounded for 60hrs.
Fig. 4.16: Optical micrograph of solid carbon sample heat treated to 2700°C.
Fig. 4.17: SEM micrograph of solid carbon sample heat treated to a) $1000^\circ$C and b) $2700^\circ$C.
Fig. 4.18: X-ray Diffraction pattern of solid carbon heat treated to 2700°C
corresponding to (002) line of graphite crystal. It also shows sharp peak at \( \theta = 42.36^\circ \) with \( d = 0.213 \) nm corresponding to (100) line; at \( \theta = 44.5^\circ \) with \( d = 0.203 \) nm corresponding to (101) line; at \( \theta = 54.47^\circ \) with \( d = 0.1683 \) nm corresponding to (004) line; at \( \theta = 77.45^\circ \) with \( d = 0.123 \) nm corresponding to (110) line. Presence of all these peaks show that the material is highly graphitic even at the lower temp.

4.6.1: EFFECT OF HEAT TREATMENT TEMPERATURE ON ELECTRICAL RESISTIVITY OF SOLID CARBON SAMPLES:

Figure 4.19 shows the electrical resistivity of two different samples having different densities. The resistivity is measured after each stage of heat treatment. As shown from the figure, the resistivity in two directions (perpendicular and parallel to the compacting pressure) are different. Sample having higher density show lower value of the resistivity then that of poor density sample. And the value of resistivity reaches almost same in both the directions with higher temperature treatment (2400°C). This attributed to the structural changes from carbon to graphite. From the figure 4.19 it is also seen that the values in both the directions are same i.e. isotropic nature. Therefore, it can be concluded that the ultimate product is combination of order and disorder structure.

4.6.2: MECHANICAL PROPERTIES OF CARBON SOLIDS SINTERED AT DIFFERENT TEMPERATURES:

Solid carbon samples made from highly sinterable coke and heat treated to different temperatures from 1000°C to 2700°C were tested for compressive strength. Fig. 4.20 shows the compressive strength of two types of samples having different initial densities. Sample (A) made of coke after 50 hrs. grinding have density at 1000°C of 1.48 g/cc. Sample (B) made with coke for 150 hrs grinding have density at 1000°C of 1.59 g/cc. As seen from the figure 4.20 compressive
Fig. 4.19a. Effect of heat treatment temperatures on electrical resistivity of solid carbon samples
Fig. 4.19b. Effect of heat treatment temperatures on electrical resistivity of solid carbon samples
strength of the sample increases with heat treatment temperature up to 2200°C. After that the strength decreases. Both the samples show sintering behavior with heat treatment temperature.

However, the strength of the sample (B) is higher than that of the sample (A) during sintering to different temperatures. This is because of the reason that during prolonged grinding the compactness of particles will be improved and the green sample will obtain higher density. This sample shows good sintering mechanism, when they are heat treated to different temperatures. Therefore, the porosity of such sample will also reduce with sintering to high temperatures. This attributes to the higher compressive strength of this sample. However, the strength is decreasing with high temperature heat treatment. With high temperature treatment to 2700°C, the strength of both the samples will decrease. This is attributed to the transformation of the structure from polyaromatic carbon to graphitic carbon. And graphite is poor under compression.

4.6.3 THERMAL PROPERTY OF CARBON PRODUCT HEAT TREATED AT DIFFERENT TEMPERATURES:

The TGA weight loss was studied by using Mettler Thermal Analysis system, TA 4000. Figure 4.21 shows the oxidation behavior of the solid carbon samples treated at different temperatures. As seen from the figure, the sample treated at 1000°C shows 100% weight loss when treated at 1000°C in air. After heat treatment to higher temperature to 2700°C, the weight loss reduces remarkably. But still the weight loss is quite high. The decrease in weight loss is attributed to the change in structure of the solid carbon during high temperature heat treatment. The XRD studies and microscopic observation conforms that the structure of the solid carbon sample is combination of order and disorder in nature i.e. it is a combination of graphitic and non graphitic structure. Therefore, the weight loss in the solid carbon sample heated to higher temperature (2700°C) gets reduced.
Fig. 4.21. Oxidation behaviour of carbon sample treated at different temperatures.