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Feasibility studies of formation of carbon foam from high sulfur Meghalaya coal

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Carbon foams have been produced from a high sulfur sub-bituminous Meghalaya (India) coal with good plasticity properties using a two-stage thermal process under different conditions of pressure and temperature. The first stage consists of a controlled carbonisation under pressure at 450°C, while the carbonisation product is baked at 1100°C in the second stage. The foams show macroporous texture. The mean pore size and the volume of pores have been determined. The increase in pressure reduces the pore size, while the pore volume increases with increasing temperature.

Keywords: Coal, High sulfur coal, Carbon foam, Coal conversion, Value added product

Carbon foams are porous materials. In the recent years, the development of carbon foam from various precursors has attracted attention due to its great potential for use. The carbon foam conceivably can replace balsa wood, intumescent mats, polymer matrices, metallic honeycombs, ceramic fibrous insulation, ceramic tile polystyrene, plastics, fibre-glass, rubber and various metals that currently are in use as basic, conventional materials of construction. Their properties widely vary as a consequence of the precursor and the production methodology used[1]. Carbon foam is characterized by high thermal conductivity, low density, high mechanical strength, low thermal expansion coefficient, good thermal stability, high electrical conductivity, low cost and versatility of manufacture, design and finish[2-5]. It is also an alternative to carbon fibre composite materials due to those properties. Unlike conventional lead acid batteries, carbon foam batteries have deep discharge cycles that can last for up to 1,200 cycles, thrice the life of the former.

Coal can be a good source material to make carbon foam as an advantageous alternative from an economical point of view as reported elsewhere[6]. The structural properties of coal-based carbon foams make them perfectly useful in numerous applications, when very high conductivity is not required[1] and the manufacturing cost can be considerably reduced because coal is easily available and can be used without any previous preparation process.

The north eastern region (NER) of India has a substantial deposit of high sulfur coals[7-8] with a total reserve of about 260 million tonnes with a great potential for energy conversion[9]. These coals are normally called as abnormal coals because of the physico-chemical characteristics present and their behaviour does not commensurate with property adopted for rank classification[10]. The feasibility studies for production of carbon foam from these coals have not been initiated till now, while vast works on other aspects such as desulfurization, demineralisation and trace metals contents have been reported[11-19]. In this communication, the first feasibility studies for production of coal-based carbon foam from the high sulfur Indian coals have been reported.

Experimental Section

Coal samples and physico-chemical characteristics

A sub-bituminous coal from Bapung area of Meghalaya (India) was used as precursor in this study. It was subjected to proximate, forms of sulfur, ultimate, FT-IR spectroscopy, and thermogravimetric analyses (TGA). FT-IR spectra were taken in the spectrometer (Perkin- Elmer 2000). TGA analysis was carried out using TA Instruments (Model: SDT Q600) in inert atmosphere at heating rate of 10°C/min. The Tables 1 and 2 list the chemical data of the precursor coal sample. It possesses high sulfur content (3.45%), of which about 75% is organically bound.

Carbon foam preparation

Carbon foams were prepared from the coal sample by using standard two-stage procedure[1]. Table 3 lists the specific operating conditions used to prepare the carbon foams during the study.

Porosity characterisation of carbon foams

Porosity characterization of the samples involved the determination of true and apparent densities by He and Hg displacement, respectively, and mercury porosimetry. True density and apparent density were measured by using a pycnometer, Accupyc 1330

Table 1 — Physico-chemical of the coal (as received wt %)

Coal	Ash	Moisture	Volatile matter	Fixed carbon	Pyritic sulfur	Sulfur	Organic sulfur	C	H	N	S	O
Bapung	14.1	2.14	38.5	45.3	0.33	0.63	3.27	86.2	5.94	1.0	4.23	2.63

(C: Carbon; H: Hydrogen; N: Nitrogen; S: Sulfur; O: Oxygen)

Table 2 — Ash composition of the coal (wt %)

Coal	SiO_2	Fe_2O_3	MgO	CaO	SO_3	TiO_2	Al_2O_3	Others
Bapung	48.8	22.0	1.5	0.5	1.6	1.7	19.7	4.2

Table 3 — Carbonisation properties

Foam	Coal	Initial load (g)	Foam (g)	%mass loss	Initial T (°C)	Tf (°C); Residence t (min)	P_f (bar)
E_{rc} 132	Bapung	70.3763	59.2383	15.8264	325	430;120	85

Table 4 — Properties of carbon foam at 450 and 1100°C

		Foam 450°C			Foam 1100°C					
Espuma	Coal	Mass (g)	h (cm)	d (cm)	Mass (g)	h (cm)	d (cm)	% mass loss	% h	%d
E_{rc} 132	Bapung	58.3439	9.44	5.03	42.8734	8.2	4.17	26.52	13.14	17.10

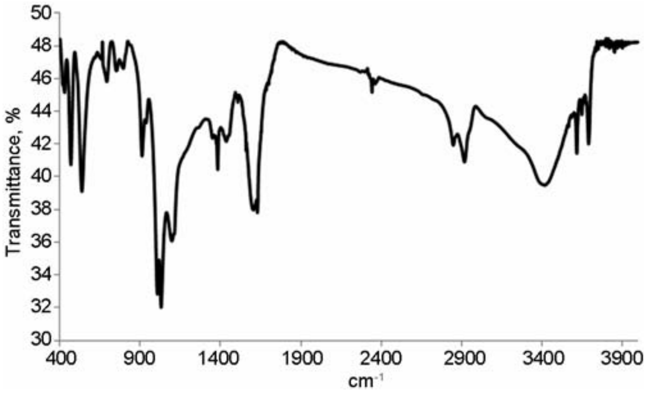

Fig. 1 — FTIR spectra of the raw coal sample

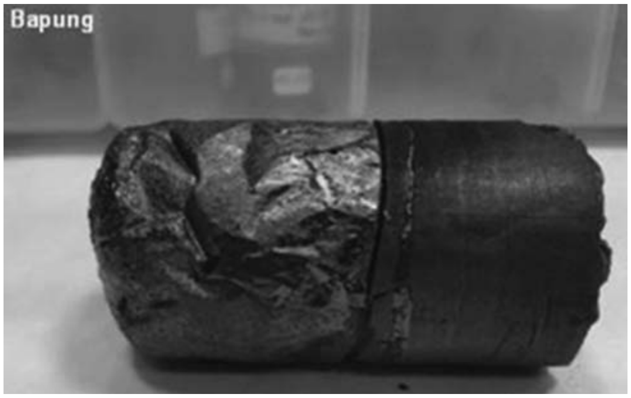

Fig. 2 — Carbon foam from the sub-bituminous coal sample

and AutoPore IV apparatus from Micromeritics as reported[1]. The open porosity was calculated from true and apparent densities.

The total open pore volume, VT, can be obtained from the equation reported elsewhere[20]. The pore volume distributions were evaluated with a mercury porosimeter (AutoPore IV, from Micromeritics).

Results and Discussion

The physico-chemical properties of the raw coal sample reveals that it is sub-bituminous in rank with high contents of sulfur. The FT-IR plot of the coal is provided in Fig. 1. The absorption bands in the region around 550-600 cm^{-1} are assigned to the stretching vibration of S-S bonds of sulfides and C-S bonds in primary and secondary thiols. The bands in the region of 1415-1380 cm^{-1} and 1200-1185 cm^{-1} are observed due to the presence of organic sulfonates. The stretching frequencies in the range of 1070-1030 cm^{-1} are generally due to the presence of sulfoxide, and bands near 1050-1020 cm^{-1} are due to the symmetrical stretching of S=O. The FTIR study reveals the presence of organically bound sulfur in the coal. The thermogravimetric profiles (TGA-DTA-DSC) indicate that the pyrolysis of the coal sample proceeds through different temperature regions. After loss of moisture at 50-110°C, desorption of gases started at about 250°C. Initial loss of lighter molecules is associated physically with carbonaceous matrices (i.e. macerals) of the coal samples. At about 400-600°C, the rate of thermal decomposition reached maximum. At higher temperatures, the thermal decomposition of coal occurs by breaking of bonds and formation of tar and hydrocarbons takes place. The pyrolysis was also predominantly characterized by the formation of hydrogen[14,15].

The coal renders good foam as shown in Fig. 2 and Table 4. The coal foam carbonised at

1100°C displays average textural properties, comparable to those obtained from other coals[1]. However, the coal foam does not perform too well in graphitisation, at least in terms of structural parameters (Table 5). This is presumably due to the presence of high sulfur concentrations in the raw coal. The coal sample was chosen to study the influence of several carbonisation variables (temperature, heating rate, pressure, residence time) on the characteristics of the resultant carbon foams.

Table 5 — Mass loss during carbonization

		% Mass loss		
Foam	Coal	1st Carbonization	2nd Carbonization	Total
E_{rc} 132	Bapung	18.67	26.52	45.19

Pore size distributions were determined by mercury intrusion up to 227 MPa (Table 6). Figure 3 shows the differential pore volume of the foam studied. The sample seems to present a broader pore size distribution. According to the results observed, mechanical strength seems to be diminished with increase in temperature of the carbonization process. Thus, the porous structure developed in the foam degraded its mechanical properties. In order to improve the thermal properties of the foam, the total pore volume must increase, which could be achieved by increasing the carbonization temperature. On the other hand, increase in carbonization temperature will decrease the pore size leading to improvement in its electrical properties[3]. However, a subsequent graphitisation stage will be necessary in order to improve thermal and/or electric properties.

Table 6 — Porosity determination of the foam

	Sample	
	Erc 132 Bapung (1100°C)	Erc 132 Bapung (1100°C)
True Density (g cm^{-3}) (ρ_{He})	1.8616	1.8444
Apparent Density (g cm^{-3}) (ρ_{Hg}) (a 0.05 atm)	0.6191	0.6217
Open porosity $\varepsilon = 1-(\rho_{Hg}/\rho_{He})$ 100 (%) (ρ_{Hg} a 0.05 atm)	66.7	66.3
Total Pore Volume $V_T = (1/\rho_{Hg})-(1/\rho_{He})$ (cm^3 g^{-1}) (ρ_{Hg} a 0.05 atm)	1.08	1.07
Porosity (a 0.05atm) (%)	60.52	62.42
Total Intrusion Volume (mL/g)	0.9775	1.0040
Total Pore Area (m^2/g)	2.893	1.871
Median Pore Diameter (Volume) (nm)	72320.9	88547.7
Median Pore Diameter (Area) (nm)	0.0125	0.0146
Average Pore Diameter (4V/A) (nm)	2.0897	1.3884
Pore diam max curve (µm)	73	100

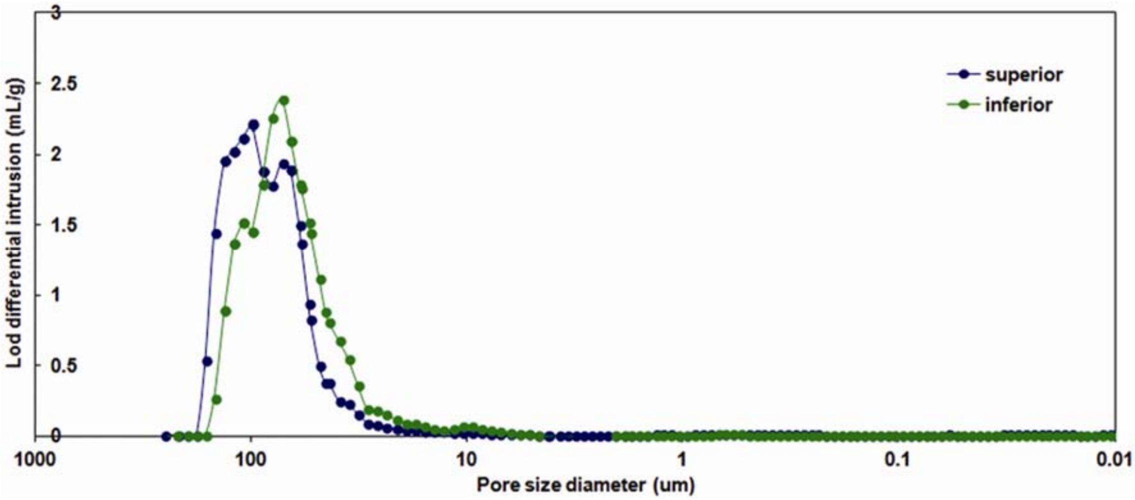

Fig. 3 — Differential pore volume of the foam sample

Conclusion

In summary, the preparation of high plasticity carbon foam with macroporous texture is feasible from high sulfur Meghalaya (India) coal. The narrow distribution of pore volume and sizes were found in the foams obtained. However, further studies are warranted for optimization of the process.

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