CHAPTER-1

INTRODUCTION

1.0 About Lignite.

Lignite and brown coal are the common names given to young coals which have undergone less coalification than bituminous coal and anthracite. Lignites (as mined) have a moisture content between 35 to 60% by weight and a low heat value from about 6 to 16 MJ/kg and a higher oxygen content than bituminous coals. The coalification process sequence involves the deposition and humification of plants and the initial formation of peat. The degree of coalification is indicated by the changes in chemical and physical structures of coal.\textsuperscript{1,2} For example, an increase in the rank of coal is marked by a decrease in porosity and an increase in optical anisotropy parallel to the bedding planes. These changes are further related to the rise of overburden pressure with depth. Considering the brown coal stage, increasing rank within this stage is characterized by a decrease in the total moisture content (Schürmann's rule)\textsuperscript{3} as shown below:

<table>
<thead>
<tr>
<th>Brown coal-coalification stages (As per German usage)</th>
<th>Decrease in moisture content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft brown coal stage (lignite)</td>
<td>4% per 100 m depth</td>
</tr>
<tr>
<td>Dull brown coal stage (lignite to subbituminous C)</td>
<td>1% per 100 m depth</td>
</tr>
<tr>
<td>Bright brown coal stage (Subbituminous B-A)</td>
<td>1% per 100-200 m depth</td>
</tr>
</tbody>
</table>
Thus the variability in moisture contents of lignite is evident. Cellulose-rich parts of plants (leaves and stems) and also certain woods, e.g. the wood of angiosperms in tertiary brown coals, largely decompose to humic detritus of cell wall remains. In part, they become further decomposed and transformed into colloidal humic solutions which infiltrate into the peat. On drying, they are precipitated as finely divided gel particles between the detritus. Thus humic detrital matter intimately mixed with amorphous gel particles form the main constituent of brown coals formed from the treeless swamps. Indian lignites especially Neyveli lignites which are mainly of drift origin invariably contain humic detritus. Humic acids form with varying molecular weights and solubilities due to slow oxidation of peat surface. These acids can exist in the presence of appropriate cations as humates (especially $\text{Na}^+$, $\text{Ca}^+$, $\text{Mg}^+$, $\text{Fe}^{2+}$, and $\text{Al}^{3+}$ humates). For the conversion of lignin to humic acid, oxygen is necessary. Lignin is first attacked by wood destroying fungi and then by aerobic bacteria, and in the end, the humic substances form. As early as 1962, artificial coalification experiments were conducted using autoclaves in the presence of water by Kreulen. Experiments revealed that up to 20% humic acids were produced from cellulose, but only a few percent from lignin. Similar experiments by Davis and Spackman indicated the
development of vitrinite purely through chemical reactions from cellulose at 200° and from lignin at 300°. The above experiments were done on the wood of taxodium distichum under pressure and in the presence of water. Since oxidation is the basic reaction for the formation of humic substances in lignites, the generally accepted structural picture for lignite is a complex system of condensed aromatic rings to which various oxygen containing (carboxyl, hydroxyl, methoxyl, ether, and carbonyl) functional groups are found attached. Thus lignites contain more oxygen than higher rank coals, normally over 20% on a daf basis. The distribution of oxygen among the functional groups of Rhenish brown coal, Texas lignite and Wyoming subbituminous coal (U.S.A) was studied by Wolfram and Chung et al. The above studies showed that the proportion of carboxyl groups in Rhenish brown coal was highly variable. Higher proportion of the ether and hydroxyl groups were found in Texas lignite compared to Wyoming subbituminous coal. During the hydrothermal treatment of lignites (discussed in the forthcoming chapters) mild pyrolysis at temperatures up to 320° causes the decomposition of carboxyl groups, and results in CO₂ formation which can expel water from the pore structure and leave a product with enhanced calorific value.
Depending on the temperature reached during the hydrothermal treatment, these functional groups, notably the carboxyl groups, are reduced. The above process results in removal of moisture which can be regarded as a further process of coalification resulting in changes of surface properties and chemical structure.

The degree of conversion of plant matter into colloidal substances, notably humic acids and humates, affects the behavior of particles during hydrothermal drying. These substances shrink in volume when dried, giving rise to the changes in the porosity, apparent density and plasticity and particle size distribution.\textsuperscript{10}

Lignites are organogels traversed by pores and capillaries of varying diameters, some of which retain a certain amount of water (about 15 to 30%, depending on the nature and the extent of the inner surface) even after air drying.

Theories of adhesion have been put forward involving pore and / or colloidal structure to account for the different ways in which the water is held in the moist coals.\textsuperscript{11}

Using the relationship between water content and its heat of desorption, Allardice\textsuperscript{12} has shown for Australian brown coal that about 20% of water is bound more strongly to lignite than the water molecules are to each other. For 80% of the water, the heat of desorption is the latent heat of evaporation. It is assumed that the water molecules are held
strongly by the lignite surfaces by hydrogen bonding. Evans\textsuperscript{13} has shown that this tends to happen within the fine pore structure. In the course of hydrothermal drying, the varying strength of the water bond will produce different evaporation behaviour. Lignite differs significantly from bituminous coal where most of the moisture is present on the surface in that. In lignite a high proportion of the water is held in the pores. According to Jüntgen\textsuperscript{14}, the coalification process in the younger coals (lignite and brown coals) has not advanced so far, and a substantial amount of water is present in the pore structure. The overall porosity of lignites is much the same as for bituminous coals, (about 0.1 ml/g - pore volume). But, in the case of lignites, there are more larger pores of over 30 \(\mu\)m diameter.\textsuperscript{15} A large proportion of the porosity of lignites is accounted for by the larger diameter pores, and in turn these hold a large fraction of the total moisture content. This property varies considerably in different lignites and brown coals. The macropore system in coals is strongly influenced by overburden pressure. Klein et al.\textsuperscript{16} have shown that the macropore structure depends on the chemical make-up of the coal and is largely independent of the confining stress. Additionally, some water is chemically combined as the water of hydration of some of the minerals present such as calcium
sulphates and clays. According to Butcher, the equilibrium moisture level of the coals increases with decreasing rank. This agrees well with the observations of Rashid et al. with respect to Canadian coals during their study on the drying rates at 100° in a Brabender drier. In the above experiments longer period taken for drying the coal with higher equilibrium moisture has become evident. According to Sears et al., evaporative drying of lignites using hot gases tends to cause decrepitation of the coal particles due to shrinkage and loss of elasticity. The dried product is dusty and liable to spontaneous combustion. Further, when lignite is dried by evaporation it can subsequently readsorb moisture. Willson et al. observe that when lignites are thermally treated at temperatures over 230° under pressure, the pore structure tends to change and water readsorption is reduced. The extent of the change depends on the extent of the thermal treatment.

A number of generically similar processes based on the use of pressure and either hot water or saturated steam have been investigated. They result in a product with lower equilibrium moisture content and higher calorific value. The above mentioned work of researchers involving thermal treatment of lignites under pressure in presence of water,
formed the basis of the current investigations with respect to Indian lignites.

1.1 Variability of Lignite Characteristics

Eventhough lignites are available near the surface, with relatively simple geology, the properties of lignite vary widely from deposit to deposit and often within a deposit.\textsuperscript{23} This inherent variability can occur vertically and horizontally within a seam or seams. Attempts have been made to correlate calorific value of lignites (as mined) with corresponding moisture and ash contents for the brown coal and lignite deposits of the Balkans and Turkey.\textsuperscript{24,25} Eventhough acceptable relations could be made between calorific value and moisture content, no clear correlation between calorific value and ash content could be achieved due to large variation in the results.

The same is the case with Indian and other lignites worldwide.\textsuperscript{26} The variability in the ash composition of several lignites was studied by several agencies.\textsuperscript{27-30} The origin of the lignite deposits decides the ash composition. Indian lignites, German and Spanish lignites and some of the Texas lignites (USA) are found to have high proportion of $\text{SiO}_2$ in their ashes. Australian brown coal ash contains a high proportion of $\text{Al}_2\text{O}_3$. North Dakota lignite ash, Kutch (India) lignite ash and some lignite ashes in
Germany (West) are high in Na$_2$O. Lignite ash from Germany (East), Yugoslavia, are found to have higher proportion of CaO. The tar contents of the lignites vary depending on the origin and geological background. The surface chemistry dependent variations among the lignite deposits result in different levels of hydrophilicity.

Hydrothermal treatment is dependent on the properties like pore characteristics, moisture content and distribution, oxygen content and ash chemistry of the lignite feedstock. These properties of lignites are fixed at the stage of lignite’s natural availability itself. The inherent variations in the above properties of lignite, affect the hydrothermal treatment process parameters like temperature and pressure and reflect in the product characteristics as well.

Considering the vast differences in origins, in the degree of coalification as evidenced by proportion of petrographic constituents, in the surface characteristics, and in the mineral constituents, it is very essential to evaluate individual lignites with respect to their behaviour during hydrothermal treatment and to characterize the corresponding products.
1.2 Indian Lignite Scenario

Lignite reserves in India have been estimated at 19,455 million tonnes. Of this, 92.37% are accounted for by Tamil Nadu alone. The lignite availability in India is given below:

**State-Wise Distribution of Lignite Reserves**

(As on January, 1993)

<table>
<thead>
<tr>
<th>State</th>
<th>Million tonnes</th>
<th>% to total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tamil Nadu</td>
<td>17,970</td>
<td>92.37</td>
</tr>
<tr>
<td>Rajasthan</td>
<td>1,033</td>
<td>5.31</td>
</tr>
<tr>
<td>Gujarat</td>
<td>324</td>
<td>1.67</td>
</tr>
<tr>
<td>Jammu &amp; Kashmir</td>
<td>28</td>
<td>0.14</td>
</tr>
<tr>
<td>Kerala</td>
<td>100</td>
<td>0.51</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>19,455</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>

The Neyveli fields in South Arcot district of Tamil Nadu have vast potential of 3300 million tonnes spread over 480 sq.km. Out of this, about 2000 million tonnes are mineable under the present mining technology. Recently, in Tiruchirapalli district of Tamil Nadu, geological reserves of about 1150 million tonnes of lignite have been found. In Mannargudi and East Veeranam, geological reserves of about 11,000 and 1255 million tonnes of lignite respectively have been estimated. The geological reserves of lignite in Tamil Nadu and Pondicherry are given below:
<table>
<thead>
<tr>
<th>State</th>
<th>Place</th>
<th>Geological reserve (MT)</th>
<th>Moisture %</th>
<th>Ash %</th>
<th>Calorific value (kcals/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tamil Nadu</td>
<td>Neyveli</td>
<td>3300</td>
<td>45-55</td>
<td>2-9</td>
<td>2500-2800</td>
</tr>
<tr>
<td></td>
<td>Jayamkonda Cholapuram</td>
<td>1150</td>
<td>40-50</td>
<td>5-12</td>
<td>2200-2800</td>
</tr>
<tr>
<td></td>
<td>Mannargudi</td>
<td>11700</td>
<td>40-50</td>
<td>4-12</td>
<td>2200-3200</td>
</tr>
<tr>
<td></td>
<td>East of Veeranam</td>
<td>1235</td>
<td>40-50</td>
<td>5-12</td>
<td>2500-2800</td>
</tr>
<tr>
<td>Pondicherry</td>
<td>Bahur (mostly in Pondicherry and partly in Tamil Nadu)</td>
<td>585</td>
<td>45-55</td>
<td>3-9</td>
<td>2500-2800</td>
</tr>
</tbody>
</table>

Only exploratory drillings have been carried out at Jalipa and Giral in Barmer district and at Bithnok in Bikaner district in Rajasthan. Mining at Palana in Bikaner district is under progress. In Gujarat, Kutch district has got a geological reserve of 204 million tonnes out of which 94 million tonnes are estimated at Panandhro, 45 million tonnes at Akrimota and 34 million tonnes at Madanamodh. Rest of the 120 million tonnes of lignite are estimated to be available at the districts of Bharuch, Bhavnagar, and Surat. At Neyveli (Tamil Nadu), lignite reserves are exploited by Neyveli Lignite Corporation (NLC). The NLC has an integrated complex at Neyveli consisting of two lignite mines, two linked
thermal power stations, a fertilizer plant based on fuel oil, and briquetting and carbonization plant.

NLC has done exploratory work in Jammu and Kashmir in the Nichahom sector in Baramulla district. The current lignite reserves in the state have been estimated at 28 million tonnes. Exploratory investigations in Kerala showed lignite deposits at the coastal districts near Azhikode in Cannanore district and Warkalai in Trivandrum district, the total geological reserves being about 100 million tonnes.

For the above lignites, the diversities in petrological constituents are evident due to differences in their geological background. The Neyveli lignite deposit is of tertiary age (Miocene, Bararkar stage). The Neyveli lignite may have been formed in the lagoons formed by rivers near coastal areas where there was not much vegetation, but into which drifted large quantities of vegetation that fringed the pool. The occurrence of mainly decay resistant attritus and macerated woody tissues suggests rapid decay which might have been promoted by periodic renewal of fresh water by floods during heavy rains. Geological studies of the subsurface of the area do not reveal any major structural features such as folds or faults, but the coal seam is situated between high pressure artesian aquifers.

The Kutch lignite (Panandhro) is of Eocene age. The marine
tertiary rocks of Kutch extends from Lakhpat to Ramania showing close resemblance with the strata of the present coast line of Kutch district. Within the tertiary basins of Kutch, lignite occurs in isolated small depressions. The lignite is found to be salty and have high total sulphur content. The Rajasthan lignite is of Palaeocene age (Upper Cretaceous). The desert sand of Rajasthan conceal all the outcrops of lignite and the associated rock formations. These lignites are of the ash content 10-20% and found to have high total sulphur content (2-5%).

1.3 Lignite Utilization in India

About 90% of lignite produced annually in India are used for power generation. According to the survey made at the World Energy Conference in 1986, most of the countries producing lignites are using the same mostly for power generation other than using it for industry, upgrading and domestic purposes. It is to be noted that in India, lignite is used mainly for mine-mouth power generation. It is generally regarded as uneconomic to transport lignite over long distances because of high moisture content and hence low specific energy content. Further, precautions must be taken to prevent spontaneous combustion from partially dried lignite. A recent case study was made at New Zealand which has
extensive lignite deposits. The deposits are available at the south end of the South Island, while the major energy use is over 1000 km away in North Island. A study has been undertaken to compare the costs of various methods of providing 1250 MWe for use in North Island. Various possibilities of transporting the lignite were examined. The outcome of the study was that with current technology and costs the use of the South Island lignite is not competitive. If the lignite were to be used, the cost effective option would be the mine-mouth power generation with the energy transported by power line. However, it was recognized that technologies that would produce dried material which can be used to prepare energy rich lignite-water slurry fuels, should be evaluated further.

Due to various difficulties in transporting bituminous coal from eastern side of India, future power generation in southern and western regions would depend mainly on lignite. Considering the above factors, it will be an additional benefit to the power sector if lignite can be upgraded into a form of energy which is economically transportable other than by power line. Hence there is a basic need for the investigations regarding hydrothermal upgradation of lignites.
1.4 Hydrothermal Treatment - Competitive Among Other Thermal Upgradation Processes for Lignites - Status World-Wide.

The high inherent moisture level of lignite results in poor loading of lignite in lignite-water slurries, with much lower calorific value compared to run-of-mine lignite. Thermal upgradation of lignite will result in a product, with which a water slurry of increased solids loading is possible. Several processes for thermal upgradation of lignites are at present available, which are capable of reducing the inherent moisture level. These include Fleissner process (batch and continuous), and Evans-Siemon process which use steam for heating the low rank coal. Koppelman process uses the technique of drying and partial pyrolysis at high pressures and temperatures up to 430° for upgrading lignites. Processes like WECO and Mitsubishi adopt fluidised bed drying techniques. Other processes involving partial carbonization are also known. Some processes involving the use of high pressure steam (DK process, Kawasaki Industries) and Thermocoal Process which uses step-by-step high speed heating of lignite by a gaseous heat carrier are only at testing stage.

Hydrothermal treatment of coals was first studied by Fischer and Schrader. Hydrothermal treatment features high temperature and pressure, non-evaporative drying, and
results in the production of lignite-water slurries with higher solids loading. Willson\textsuperscript{52} reports that substantial amounts of carbon dioxide are released, further increasing the calorific value of the remaining solids. It is a permanent moisture reduction process, through induced coalification, with reuse of the water removed, to make the slurry of the treated fuel. Most of the developmental work have been carried out at the University of North Dakota Energy and Minerals Research Centre\textsuperscript{53}. The available data found in published literature on hydrothermal treatment of lignites worldwide, are compared with the results of the studies made on Indian lignites. Based on the principle of hydrothermal treatment, other processes\textsuperscript{54-56} like Bechtel, SPC (Saskatchewan Power Corporation), IGT exist and only little information is available in published literature. Recently, several other organizations have focussed on non-evaporative high pressure, hydrothermal drying. These are summarized in a number of patents in United States, India and in other countries by Texaco,\textsuperscript{57,58} Shell,\textsuperscript{59} Bharat Heavy Electricals Ltd\textsuperscript{60}, and others\textsuperscript{61-63}. 
1.5 Need for The Present Investigations.

Eventhough much work has been done to characterize the products obtained from foreign lignites through hydrothermal treatment, no such experimental work has been done on Indian lignites so far. Data obtained for Indian lignites through such investigations will be useful to optimize parameters of hydrothermal process and even for scaling up. Technology exists today to utilize lignites for power generation as evidenced by installations at Neyveli in Tamil Nadu and at Panandhro in Gujarat. However, the use of lignites as substitute for fuel oil has not been possible in India. The present investigations are aimed at filling this need.

At present small cement industries transport lignite from Neyveli mines either in the form of as mined lignite or in the form of briquetted ones. Similarly, in Gujarat some textile industries use lignites as fuel for boilers. The need for massive transportation has not been felt so far. Most of the small industries use furnace oil in their oil fired boilers due to the non-emergence of newer technologies for drying lignites enabling economic transportation. Lignite-water slurry is an apt substitute for the furnace oil which can be used with minimal retrofitting and derating of the boiler, the benefit being the reduction in the cost of fuel and the cost of handling.
Ultimately a single large LWS facility located at a lignite mine and connected to the end user by the most economical transport (combination of barge, pipeline, tanker, or rail) could make clean low cost energy available without any of the problems normally associated with handling and transporting raw lignite.

The following deficiencies are identified during an elaborate review of the literature.

➤ The literature directly pertaining to hydrothermal drying of low rank coals are only dealing with details which are oriented towards the view point of users.

➤ Not much of experimental data linked with the process or the product characteristics are dealt in literature.

➤ The main characteristics of lignites before and after hydrothermal treatment (like surface area, particle size distribution, rheological and thixotropic characteristics of the slurries, variation in the content of carboxyl groups and minerals) are only partially dealt in the available literature.

➤ Further, the informations available in the literature do not fully consider the variability of the lignite characteristics.

➤ Detailed informations on carboxyl group content, pore volume distribution, and IR spectral studies indicating functional groups are not found in literature with respect to hydrothermally treated Indian lignites.
Adequate informations are not available regarding petrological studies, thermogravimetric studies, and tar content to evaluate the amenability of the Indian lignites towards HTT.

Sufficient informations are not found in the literature regarding rheological characteristics and thixotropic behaviour of the hydrothermally treated lignite-water slurries.

The present investigations are aimed at meeting the needs created by the above deficiencies found in the literature.

**Scope and objectives of the Present Work.**

The lignites belonging to major reserves in India are selected for the investigations.

The lignites from different geological regions having differences in their petrological constituents are chosen.

**Investigations are done on the following lignites.**

1. Neyveli (Mine I)
2. Neyveli (Mine II)
3. Kutch (Panandhro)
4. South Gujarat (Rajpardi mines)

The lignites selected belong to mines which are currently operating on a large scale.

A bituminous coal (Singareni mines) is also used to compare the rheological characteristics of the untreated lignites and to use as a gauge for ranking since the rank of lignites is found to apparently increase during hydrothermal treatment depending on the temperature of the treatment.
The objectives are given as below:

1.6.1 Raw and Hydrothermally Treated Lignite Analyses
To determine the fundamental characteristics of lignites before and after hydrothermal treatment in an attempt to ascertain the extent of both physical and chemical changes.

1.6.2 Response of Lignites to Hydrothermal Treatment Process
To determine the amenability of lignites for hydrothermal treatment which results in upgradation.

1.6.3 Slurriability of Lignites.
To determine slurriability for both raw and hydrothermally treated lignites. The lignites are treated at different temperature and pressure conditions using an autoclave. This is done in order to link the lignite characteristics with slurriability and to evaluate the trend with increasing temperature of treatment and finally to achieve a highly concentrated LWS after HTT.

To determine solids volume fraction at maximum packing for various raw and hydrothermally treated LWSs.

1.6.4 Rheological Characterization.
To evaluate the extent of variation of rheological characteristics of treated LWSs with different process parameters like temperature and pressure.
To determine rheological constants like flow consistency number and flow behaviour index.

To evaluate effect of time of shear on the shear stress/viscosity of hydrothermally treated LWSs at different temperatures.

The above studies are meant for establishing a link between the rheological characteristics of treated lignites with hydrothermal treatment conditions like temperature and pressure and also with fundamental characteristics of treated lignites.

1.6.5 Studies on Thixotropy

To determine the quantity of thixotropy of raw LWS and treated LWS which will help to understand the difference in intensity of hydrogen bonding before and after hydrothermal treatment.

1.6.6 Studies on Stability of Lignite-Water Slurries.

To evaluate the static stability of raw and hydrothermally treated LWSs.