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INDUCING MESOPHASE IN LIGNITE

by

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INTRODUCTION

Lignite, which is non-coking and non-agglomerating, does not produce mesophase during carbonization because it contains a considerable amount of hydroxyl and carboxyl functional groups as well as aliphatic groups. Previous work indicated formation of mesophase from low-rank coals (1, 2) by treating either with hydrogen or carbon monoxide and water at certain pressures and temperatures. Liquefaction of lignite by hydrogen alone produces oil of high oxygen content as well as a large quantity of unreacted residual char which is mostly isotropic and non-agglomerating (3). Some agglomerating products along with mesophase could be obtained by treating Chinese lignite with hydrogen and carbon monoxide (4) possibly due to the removal of oxygen functional groups.

The objective of the present work was to investigate the effect of hydrogenation of Spanish lignite slurried with heavy oil or bitumen on the size of mesophase. The formation of larger mesophase will eventually produce a flow-type structure, which on further pyrolysis, produces strong coke. Hydrogenation of lignite with heavy oil or bitumen offers potential as a new route for improving the reactor residue for coke making as well as the production of fuel oil.

EXPERIMENTAL

Materials: Spanish coal-lignite from Meirana and La Coruna, heavy oil obtained from Western Canada, or tetralin. **Catalyst:** Zinc and Iron salts (12%) impregnated on lignite. The characteristics of these materials are shown in Table 1.

A schematic diagram of the experimental set up used in the reaction of lignite and heavy oil is shown in Fig. 7. The reactor is an inconel autoclave having a capacity of 0.5L. The contents of the autoclave were stirred by a magnetically operated impeller rotating at 500-1000 rpm. The autoclave was heated by an external salt bath and the temperature inside the reactor and the salt bath was measured by means of thermocouples.

In a typical experiment 65 g of dry lignite (-200 mesh), and 130 g heavy oil and catalyst were mixed in the autoclave. The autoclave was purged and pressurized with the designated gas to 13.8 MPa (2000 psi) pressure at room temperature and heated to the desired temperature. Upon completion of the reaction,

TABLE 1
CHARACTERISTICS OF MATERIALS USED

HEAVY OIL				
Elemental analysis				
C	H	N	(O-S)dif	H/C
%				
86.36	10.42	0.69	2.53	1.45
Solubility fractions				
Pentane solubles	Asphaltenes	Toluene insolubles		
82.4%	17.6%	0		
LIGNITE				
Proximate analysis (as received)	wt%	Elemental analysis		
Moisture	40.1	C	35.6	
Ash	9.9	H	2.5	
Volatiles	26.5	S	9.4	
Fixed carbon	23.5	N	0.3	
		H/C	0.8	

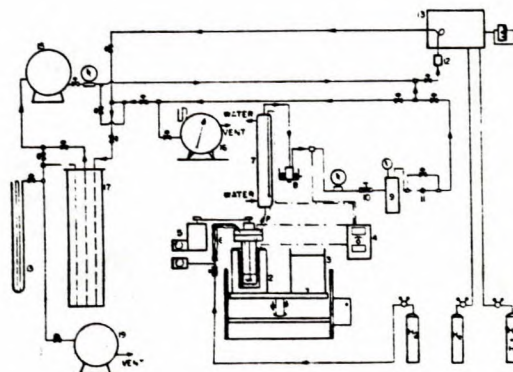


Fig. 7 Experimental Set-up

the autoclave was cooled rapidly to room temperature by means of a water bath. After depressurizing, the toluene insoluble material was separated and dried. These materials were embedded in epoxy resin, polished and examined microscopically to study the formation of mesophase.

MICROSCOPICAL EXAMINATION

The residue obtained from the hydrogenation of lignite does not show any mesophase (Fig. 1). The hydrogenated residue from the heavy oil alone shows both spherical and flow type mesophase (Fig. 2). The formation of dense mesophase along with flow type structure has been observed in the hydrogenated residue from lignite and heavy oil (Fig. 3). On addition of catalysts such as iron and zinc to the lignite-heavy oil slurry, a decrease in mesophase formation was noted for the residue with iron catalyst (Fig. 4) and the residue with zinc catalyst (Fig. 5) possibly owing to efficient hydrogen transfer which favours more conversion to oil products. Tetralin is a very good hydrogen donor solvent and very little mesophase formation was observed in the hydrogenated residue (Fig. 6).

RESULTS AND DISCUSSION

Table 2 gives the operating conditions and product distribution. Experiments were carried out at 13.8 MPa and 55 min residence time. The

residue obtained from the blank experiment with experiments were carried out at 2000 psi and, 55 min residence time. The residue obtained from the blank experiment with heavy oil alone was 23.9%. The weight of the residue decreases on hydrogenating lignite with heavy oil in the presence of a catalyst, iron and zinc compared with the amount of residue obtained from hydrogenating without catalyst (39.3%). Possibly these catalysts help to transfer hydrogen more efficiently. Run #5 shows that tetralin is an excellent hydrogen donor as indicated by the low percentage of residue.

CONCLUSION

Usually lignite does not produce anisotropic coke, but rather an isotropic char. By treating lignite with heavy oil under suitable conditions, formation of dense mesophase along with flow-type structure has been observed. This indicates that coke having desirable metallurgical properties may be produced by blending processed lignite with coking coal thereby demonstrating an alternate use of the world's vast lignite resources.

TABLE 2 OPERATING CONDITIONS AND PRODUCT DISTRIBUTION

Run	Catalyst	Temp °C	Maltenes	Asphaltenes %	Residue
1	Heavy oil (HO)	450	55.26	10.99	23.9
2	Lignite + HO	450	44.34	5.75	39.3
3	Lignite + HO Fe	433	44.61	8.84	24.1
4	Lignite + HO Zn	450	43.8	10.01	24.9
5	Lignite + Tet	450	79.6	5.85	6.7

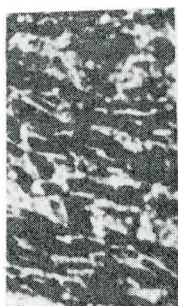


Figure 1
Lignite



Figure 2
Heavy Oil



Figure 3
Lignite and
Heavy Oil

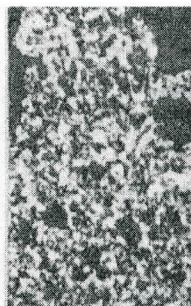


Figure 4
Lignite
Heavy Oil
and Fe

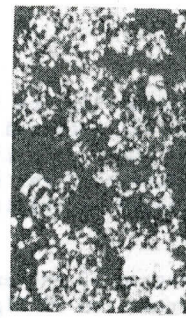


Figure 5
Lignite
Heavy Oil
and Zn

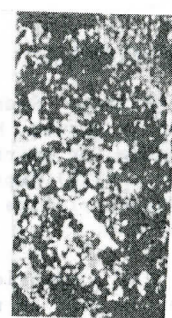


Figure 6
Lignite
Tetralin

Micrographs of Hydrogenated Residues (X600, in oil)

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