EVALUATION OF GASIFICATION REACTIVITIES OF COALS BY DIFFERENTIAL THERMAL ANALYSIS[a]

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Introduction

Thermal analysis of coals is inherently difficult because of the heterogeneity of the material, the complexity of the chemical reactions and the physical changes which occur during coal pyrolysis. However it has been shown that with careful experimentation D.T.A. can be useful both in differentiating between coals of differing rank and in characterizing some of the processes taking place throughout pyrolysis and carbonization [1]. D.T.A. has not been used significantly for assessing the reactivities of various coals towards gasification, even though most of the technologically important gasification reactions are either strongly exothermic or endothermic. We report here the results of some preliminary D.T.A. experiments made on several Western Canadian coals in an attempt to use the technique to assess their gasification reactivities.

Experimental

D.T.A. experiments were carried out using a DuPont-900 instrument in the normal manner except that a one-way (upward) gas flow was maintained in the combustion tube. Thermograms were recorded in dry air, N_2, CO, CO_2 and H_2 and steam atmospheres at various heating and gas flow rates. T.G.A. tests were run under similar conditions in air and N_2 to aid interpretation of the thermograms. Coals ranging in rank from semi-anthracite to lignite were tested.

Results and Discussions

Highly reproducible thermograms were obtained for all coals tested once optimum heating and gas-flow rates, sample packing and base-line compensation conditions etc. were established. In nitrogen atmosphere, D.T.A. thermograms reveal information about the internal processes occurring as coals are heated. Three distinct activities are present: (1) Dehydration of moisture at low temperatures (endothermic); (2) distillation and polymerization of volatiles in the range 300°C-500°C (exothermic) and (3) carbonization which continues to high temperatures (endothermic). D.T.A. in carbon dioxide does not differ from that in N_2 up to 800°C, but above this a strong endothermic peak occurs, due to reduction of CO_2. The inflection temperature of the endothermic peak, T_m, occurs in the range 900°C-1400°C depending on sample reactivity and heating rate. Typical thermograms for a lignite sample are shown in figure 1.

In CO atmosphere, there is no evidence for major additional activity, thermograms resembling closely those in nitrogen, although some methanation could have occurred (exothermic). In H_2 environment D.T.A. thermograms are even less informative, due primarily to high thermal conductivity of H_2 gas, which lowers the sensitivity of the system.

Reactivity towards the water gas reaction is found to vary not only with the heating rate, but also the 'soak period' of the coal in the steam prior to reduction of H_2O. The following have been observed: (1) a strong endothermic peak, at 950°C-1050°C depending on heating rate, which is due to the reduction of H_2O to CO and H_2; (2) broad exothermic peaks in the range 700°-800°C appear if steam is introduced at this stage or earlier, and the intensity increases with "soak period"; (3) a fast heating rate results in complete reduction to ash, while the slower the heating rate, the lower the extent of reaction at the same temperature. These observations confirm the fact that steam has an activating effect on coal towards hydrogenation and methanation, especially prior to the plastic zone. However the coal cannot be reactivated if it has undergone substantial carbonization.

Kinetic parameters can be obtained from the variation of endothermic peak inflection temperatures with heating rate [2,3]. Figure 2 shows plots of $\ln [(T_m^2)/\alpha]$ versus $1/T_m$ (α = heating rate) for present results and approximate activation energy and frequency factor values obtained from slopes and intercepts of these plots are listed in table 1. We note that deviation from linearity of such plots, as in the lignite (Hat Creek) coal, is frequently observed in diffusion-controlled processes [4].

The use of non-isothermal kinetic methods (eg. D.T.A.) to study reactivities of coal has many advantages over isothermal methods (e.g. T.G.A.), although the kinetic analysis is more complex since reaction rates are changing with temperature [5]. The reactivity of coal towards a gasification reaction at a certain temperature has meaning only if the detailed history of prior thermal treatment is included. Fortunately the use of the D.T.A. method monitors all changes taking place up to the temperature where reaction occurs. In the case of an isothermal method such as study of weight loss with time at a fixed temperature this important information is not obtained.

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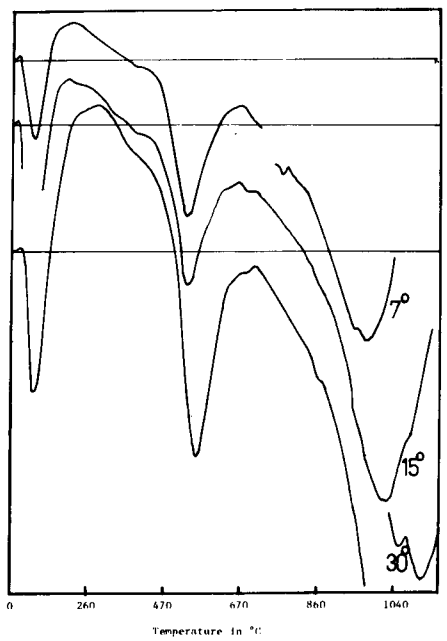

Fig.I. DTA endotherms of a Hat Creek coal(lignite) in I atmosphere of N_2 at 3 heating rates.

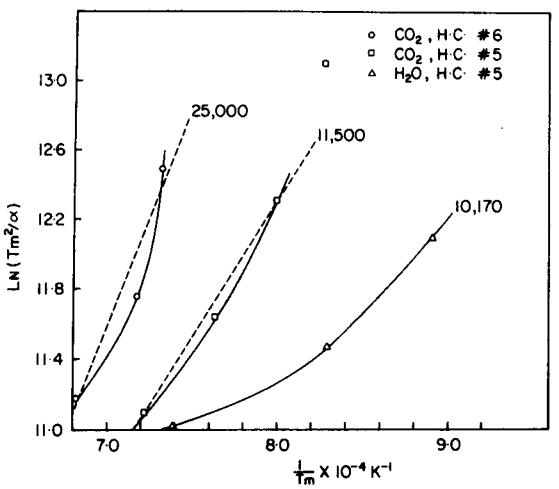

Fig. 2. Kinetic plots for Hat Creek coals in CO_2 and steam reactions.

Sample	E/R(K°)	K_o (Min^{-1})
HC#5 (CO_2)	11500	2.5 x 10^5
HC#6 (CO_2)	25000	50 "
Kaiser(Washed)	26315	207 "
HC#5 (H_2O)	10170	2.37 x 10^5

Table I. Kinetic parameters for gasification reactions with reacting gases given in parenthesis.

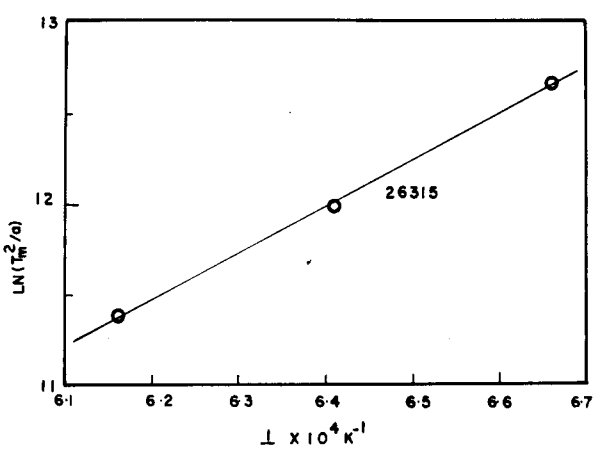

Fig.3. Similar plot for a Kaiser coal(semi-anthracite) where good linearity is observed,due to the absence of diffusion process.