DETERMINATION OF COAL RANK BY THERMOGRAVIMETRIC ANALYSIS

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INTRODUCTION

The thermogravimetric analysis patterns of coals and their residues reveal subtle differences between coals and changes which occur during the processing. It is the purpose of this paper to call attention to some of the various processes occurring during the TG analysis, and to show how these patterns can be interpreted in terms of changes or differences in coal structure. It is also our purpose to show how manipulation of the various TGA parameters, i.e., heating rate program, purge gas type, and the way in which the TG data are treated, can be used to reveal important aspects of the coal structure. Finally, the use of TGA as an objective criterion for determining coal rank is discussed.

EXPERIMENTAL

Apparatus. A horizontal thermogravimetric analyzer (TGA), TA Instruments model 51 (New Castle, Delaware), was employed. An approximately 30 mg sample of the coal or coal residue was loaded in a quartz pan and mounted in the instrument. The program of manipulation of the TG variables were determined by the objectives of the particular experiment.

RESULTS AND DISCUSSION

A representative TG scan on Illinois #6 coal from the Argonne Premium Coal Sample program dried in a vacuum oven with a nitrogen purge at 105 °C for 48 hours is shown in Figure 1. The weight loss resulting from heating at a ramp rate of 10 °C/min to 950 °C in nitrogen at 100 cm^3/min defines the amount of Volatile Matter (VM) in the coal. Further weight loss occurred at 950 °C after the introduction of oxygen, which was caused by the combustion of the organic material remaining. This defines the Fixed Carbon content (FC). The residue represents the ash content, which is in agreement with ash content determined by ASTM D3174.

The differential of the weight loss (DTG) curve highlights the various TG processes more clearly. The DTG curve for Illinois #6 shows a pattern which is more complex than the other Argonne coals. This becomes even more distinct and complex if the heating rate is slowed down to about 1 °C/min. The curve shown in Figure 2 has been smoothed by a rigorous mathematical treatment (1) of the numerous data points obtained in the analysis. There is a low temperature peak representing the loss of residual moisture below 200 °C. The main Volatile Matter peak starts at 350-400 °C and actually consists of three or perhaps four individual weight loss processes. The large peak is broad and probably consists of a number of pyrolysis processes. The well defined peak at 571 °C is tentatively identified as due to pyrite decomposition to pyrrhotite and sulfur because this peak is absent in coals containing little or no pyrite. Also, the decomposition temperature corresponds closely to that reported for pyrite (2). Two other small peaks are not yet identified but are fairly broad. They disappear gradually during coal liquefaction.

The DTG curves of the Illinois #6 coal in nitrogen and in hydrogen given in Figure 3 show similar patterns. However, all three peak temperatures in hydrogen, especially the highest temperature peak, are shifted to lower temperatures than those run in nitrogen. This might be due to the quenching by hydrogen of free radicals generated in the pyrolysis process to form more volatile products. The difference in the effect of the different gases is particularly apparent when the Volatile Matter produced is compared. Figure 4 shows the Volatile Matter produced in hydrogen and in nitrogen over a wide range of heating rates. The Volatile Matter yields are consistently higher, and therefore the Fixed Carbon yields are lower, in hydrogen than in nitrogen.

The heating rate also has a strong effect on the yields of Volatile Matter in either hydrogen or nitrogen (Figures 4a, 4b, and 4c). In hydrogen, the Volatile Matter yields decrease somewhat as the heating rate increases. This may be because, at the higher heating rates, the pyrolysis times are shorter, providing less time for reaction with the molecular hydrogen to form more volatile products. However, in nitrogen, the Volatile Matter yields increase with heating rate. At the low heating rates, the unquenched free radicals react to form more retrograde products (fixed carbon). This is in agreement with the well known observation of the increase in yield of flash pyrolysis products compared with that of slow pyrolysis. This is shown by experiments on three coals of differing rank.

TGA of Coal Liquefaction Residues. When the Illinois #6 coal is reacted in tetralin (8:1 tetralin to coal by weight) at 400 °C, the fine structure of the DTG profile of the partially reacted coal residue gradually disappears. This is shown in Figure 5, which suggests that liquefaction promotes the removal of the materials producing the fine structure peaks.

It is interesting that the changes in Volatile Matter of the residue during liquefaction are insensitive to whether the liquefaction is run in nitrogen or hydrogen, or in the presence of catalyst and hydrogen (Figure 6). This is not true, however, for the formation of Fixed Carbon. In general, more Fixed Carbon is formed as the liquefaction proceeds. However, the amount formed is greatly diminished when the liquefaction is carried out in the presence of hydrogen and a hydrogenation catalyst (Figure 7).

TGA of Coals of Various Ranks. DTG curves for all eight Argonne Premium Coals, dried at 105 °C for 48 hours and run at 10 °C/min with a nitrogen gas purge rate of 100 cm^3/min, are shown in Figure 8. This clearly shows the gradual shift of peak temperature as the coal rank increases from Lignite to low volatile bituminous coal. At the same time, the peak height increases to a maximum and then decreases again as the rank increases. This trend is more clearly evident in the plot of peak temperature vs carbon content (in wt%) shown in Figure 9. If peak height is plotted against carbon content, a volcano type curve is obtained. This is shown in Figure 10. While there are a number of measures of coal rank (3 - 12), this provides an independent and objective measure of coal rank which can be useful particularly in borderline cases.

SUMMARY AND CONCLUSIONS

1). Thermogravimetric Analysis (TGA) provides sensitive, rapid and reproducible results concerning the various weight loss processes that can be a reflection of the physical and chemical structure of coals. Additional information can be obtained by variation of TG variables, such as heating rate and purge gas type.

2). TGA also reveals changes in the physical and chemical structure of coal as it undergoes coal liquefaction. This technique also is capable of revealing the onset and rate of the retrograde reactions occurring during the liquefaction process.

3). TGA provides an independent measure of coal rank.

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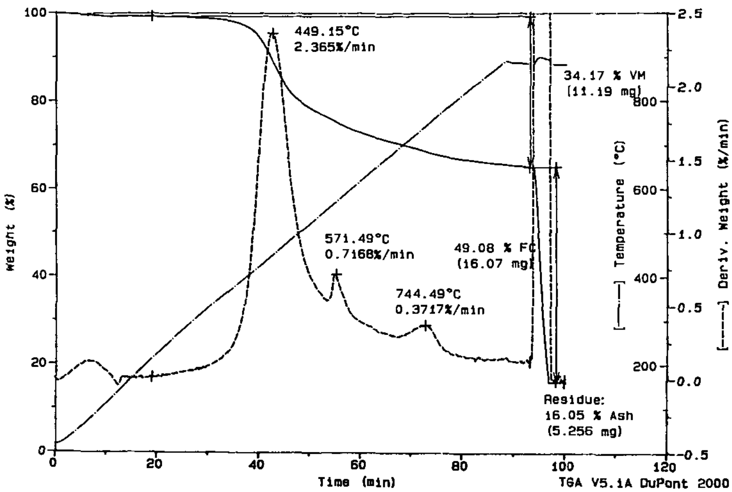

Figure 1 A TG scan on the Illinois #6 coal at 10 °C/min

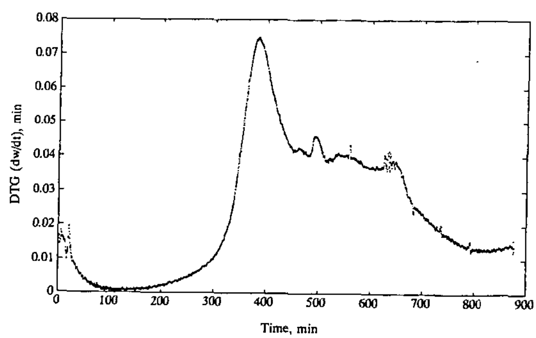

Figure 2 A TG scan on the Illinois #6 coal at 1 °C/min

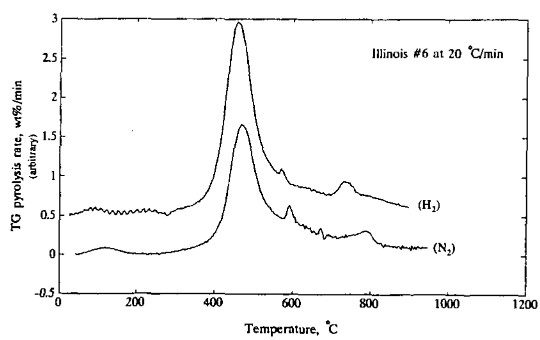

Figure 3 - Effect of gas atmospher on DTG of the Illinois #6 coal pyrolysis

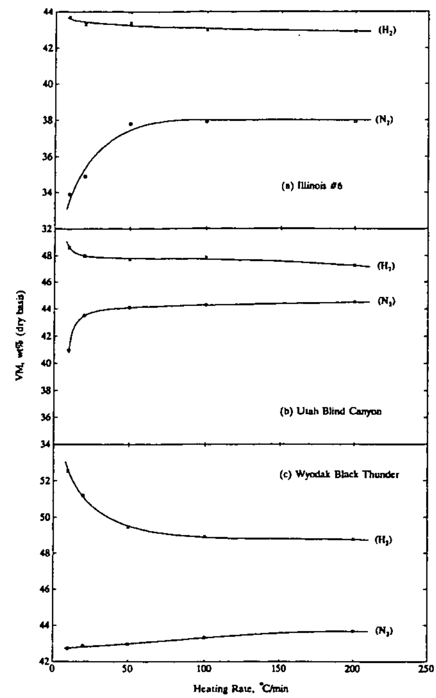

Figure 4 Effect of heating rate on the VM yields determined by TG pyrolysis in N_2 and H_2 of a). Illinois #6, b). Utah Blind Canyon, and c). Wyodak Black Thunder

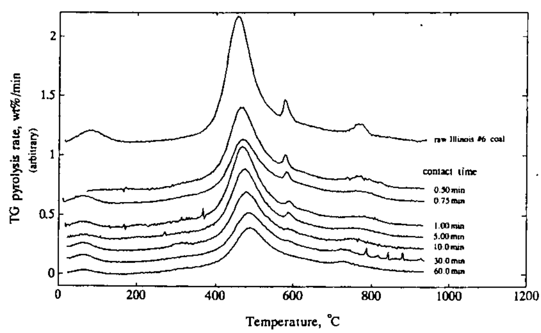

Figure 5 DTG profiles for residues of the Illinois #6 coal after liquefaction in tetralin at the selected contact times (TG scan at 10 °C/min; Liquefaction run at 390 °C under 1000 psig N_2)

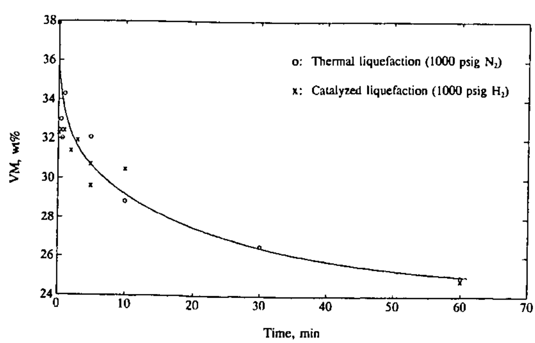

Figure 6 VM (volatile matter) in the liquefaction residues determined by TGA

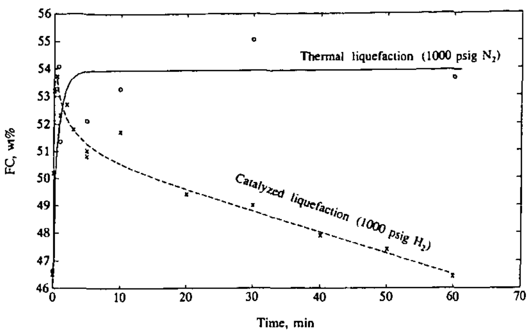

Figure 7 FC (fixed carbon) in the liquefaction residues determined by TGA (Liquefaction run: T:C = 8:1; 390 °C; TG scan: 100 cm^3(STP)/min N_2; 100 °C/min)

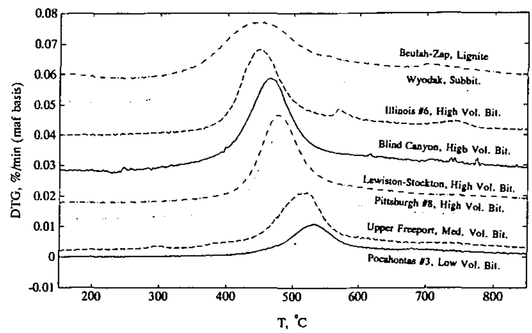

Figure 8 Pyrolysis DTG profiles of the Argonne Premium Coal samples

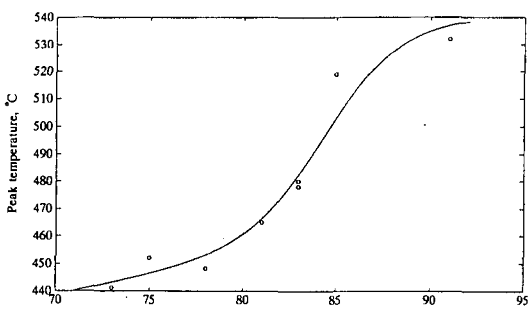

Figure 9 Peak temperature vs. carbon content of the Argonne Premium Coal samples

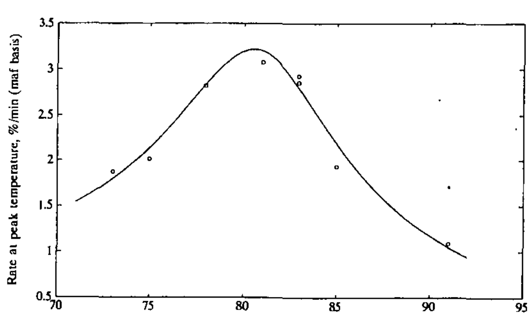

Figure 10 Rate at peak temperature vs. carbon content of the Argonne Premium Coal samples