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PYROLYSIS AND TG ANALYSIS OF SHIVEE OVOO COAL FROM MONGOLIA

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Abstract

The coal sample of the Shivee Ovoo deposits has been non-isothermally pyrolysed in a thermogravimetric analyser to determine the influence of temperature, heating rate and purge gas employed on the thermal degradation of the sample. The heating rates investigated in the TG were 10–50 K min^{-1} to final temperature of 1000°C. N_2 or CO_2 were employed as well as type of purge gas on the process of thermal degradation of the coal sample. The coal was also investigated in a fixed bed reactor to determine the influence of temperature and heating rate of the pyrolysis on the yield of products and composition of the gases evolved. The main gases produced were H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 and also minor concentrations of other gases.

Keywords: coal, heating rate, pyrolysis, TG

Introduction

Pyrolysis is the initial step in most coal conversion processes, such as combustion, gasification and liquefaction, and has a significant influence on the subsequent stages. Accurate descriptions of coal pyrolysis are helpful in the effective utilization of coal and also important in the development of new pollution control strategies [1]. The heterogeneous nature of coal and the complexity of the process have made it very difficult to perform unambiguous experiments on pyrolysis [2]. Thermogravimetric analysis (TG) is widely used to determine the rate of composition reaction occuring in solid fuels under the action of heat [3]. Most of the works in the field of coal study,

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which have been used TG, related to the kinetics of the thermal decomposition and effects of pressure on conversion of coal [1–5].

In literature, also pyrolysis of various coal using different kind of apparatus and with different heating rate have been investigated and various suggestions have been reported [6–11]. But for the energy potential of any solid fuels to be maximised the conversion process of the fuels to oil should be undertaken under optimal process conditions. These parameters include pyrolysis temperature, heating rate, pyrolysis atmosphere, particle grain size, etc. Recent papers, which related to these were investigated on other fuels particularly on oil shale [12–13]. The chemical investigation of the coal from Shivee Ovoo deposits has received much less attention.

The present investigation is an experimental study using a TG apparatus (under non-isothermal conditions) to determine the influence of temperature, heating rate and purge gas employed on the thermal degradation of the sample. The sample also was pyrolysed in a fixed bed reactor to determine the influence on tar and gas yield and gas composition in relation to heating rate and final pyrolysis temperature.

Experimental

Shivee Ovoo coal deposit has been analysed geologically for exploitation purposes. The deposit is located south of Sumber in the province of Dornogovi aimag. The estimated resources reach 2.7 billion tons of coal. The main characteristics of Shivee Ovoo coal are shown in Table 1.

Table 1 The main characteristics of Shivee Ovoo coal (mass%)

Characteristics	Mass%
Moisture	26.4
Ash	10.2
Volatile matter	30.6
DAF volatile matter	48.3
Sulphur	0.73
Chlorine	0.02
Phosphorus	0.012
Carbon	46.0
Hydrogen	2.58
Nitrogen	0.7
Oxygen (diff.)	13.36
H/C	0.67
Calorific value, (kcal kg^{-1})	5306

Thermogravimetric analyses

Thermogravimetric analysis of the coal sample was investigated using a DMT Hochdruck Thermowaage TG analyser and a more detailed description of its design and operation is given elsewhere [3, 14]. In this work a ~0.5 g sample was heated to 1000°C at 10, 20, 30, 40 and 50 K min $^{-1}$ heating rate using nitrogen and carbon dioxide as the purge gas. The total volatile yield was calculated from the mass loss in TG. The main characteristics of TG are summerized in Table 2.

Pyrolysis reactor

A fixed bed gas purged pyrolytic reactor was used to pyrolyse the coal in relation to final temperature and heating rate. The influence of these process conditions was determined with respect to product yield. The reactor had a volume of 50 cm^3 and externally heated by an electric ring furnace. The reactor was heated at reaction temperature for 1 h. The furnace and reactor were controlled by a programmable temperature controller. For the sample investigated in relation to final temperature, the heating rate was fixed at 20 K min^{-1}, to final temperatures of 450, 500, 550 and 600°C, the sample investigated in relation to heating rate, the final temperature was 550°C and heating rate was 20, 30, 40 and 50 K min^{-1}. The liquid tar phase was trapped in a cold trap. Figure 1 shows a schematic diagram of the fixed bed reactor. The amount of tar and char were measured by weighing.

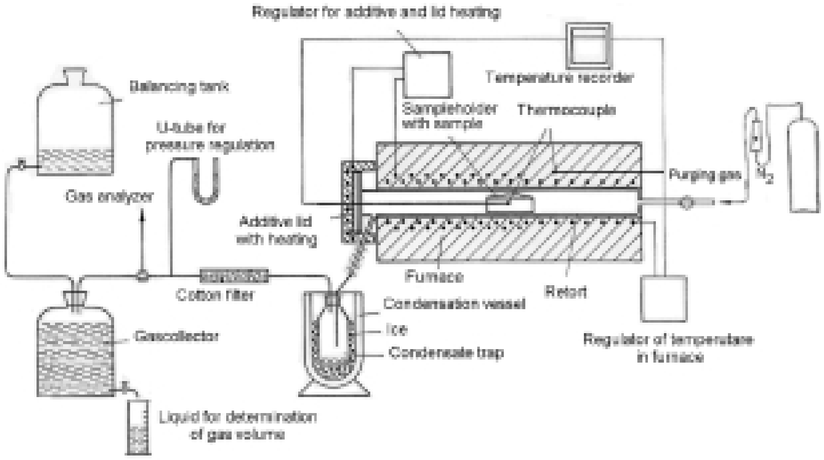

Fig. 1 A schematic diagram of the fixed bed reactor

Gas analysis

The evolved pyrolytic gases were analysed off-line by packed column gas chromatography. The gases were analysed for H_2, CH_4 and CO using a molecular sieve 5 Å column with argon as a carrier gas and a thermal conductivity detector. H_2S, COS and

CO_2 were determined using a Pora Plot U column, for the gaseous hydrocarbons up to C_4 an aluminium column was used. In both cases, helium was the carrier gas with a thermal conductivity detector.

Results and discussion

The coal sample of Shivee Ovoo deposits has been pyrolysed in the thermogravimetric analyser and in the fixed bed reactor. Coal pyrolysis is a very complex process which depends on many factors such as coal rank, particle size, pressure, heating rate, peak temperature and residence time.

Thermogravimetric analysis

A typical variation of the percentage conversion and differential mass loss (i.e. TG and DTG curves) in nitrogen with temperature is shown in Fig. 2, while Fig. 3 shows curves in carbon dioxide for Shivee Ovoo coal.

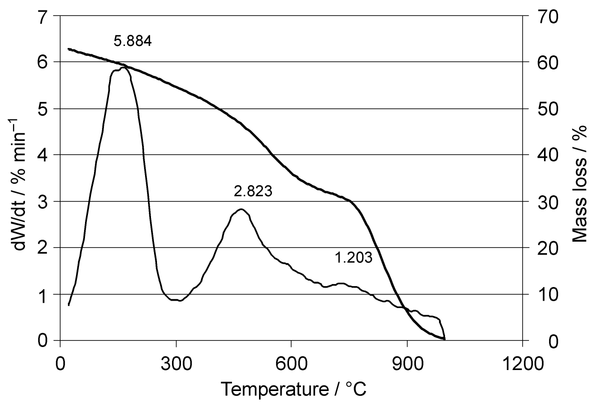

Fig. 2 TG profiles of Shivee Ovoo coal (in N_2, heating rate 30 K min^{-1}) with respect to pyrolysis temperature

Figure 2 indicates that the samples completely lose their moisture water below 200°C. The essential mass loss occurs mainly in the range of 250–550°C. The loss between 250–300°C may be attributed to the loss of a small amount of pyrolysis water as a result of the decomposition of the phenolic structures, the carbonyl groups or the peroxy radicals. The rapid devolatilization after 300°C is associated with primary carbonisation. At temperatures above 650°C, a mass loss is related to secondary pyrolysis [3].

Mass losses during the pyrolysis and gasification of coal sample with regard to heating rate and the temperature at which the maximum rate of decomposition occurred, are presented in Table 2.

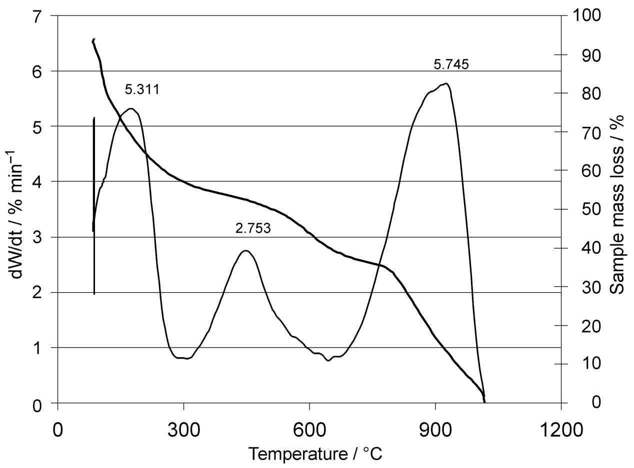

Fig. 3 TG profiles of Shivee Ovoo coal (in CO_2, heating rate 30 K min^{-1}) with respect to pyrolysis temperature

Table 2 Mass losses of Shivee Ovoo coal for different heating rates

Conditions	Heating rate/ K min^{-1}	Loss of coal mass/%				Temp. of decomp. max./°C
		30–200°C	200–550°C	550–950°C	total	
N_2	10	19.058	16.283	28.530	63.871	452
	20	21.812	16.336	20.950	59.098	466
	30	24.974	22.220	15.742	62.936	473
	40	21.313	20.875	15.972	58.160	467
	50	18.487	28.752	13.424	60.663	474
CO_2	10	27.646	19.437	47.849	94.932	430
	20	25.721	21.735	46.967	94.423	450
	30	29.810	20.972	43.211	93.993	444
	40	19.584	25.419	49.987	94.990	458
	50	17.911	27.970	48.696	94.577	460

In general, within the experimental error, a slightly greater mass loss occurred from the coal sample as a result of using CO_2 instead of N_2 to purge the TG system. This is because CO_2 is more reactive than N_2 due to the presence of alkali metals, which are very effective in CO_2 and/or H_2O reactions with carbon [13]. No significant differences in total volatiles detected between the different kind of heating rates. In the range of 200–550°C, the mass loss is increasing, but in the range of 550–950°C was decreasing with increasing the heating rates. Table 2 shows that mass losses between 30–200 and 200–550°C in the condition of N_2 and CO_2 for Shivee Ovoo coal were almost same, but in the range of 550–950°C the mass loss was quiet different in two different conditions. So we can tell that CO_2 has an effect on the reaction above 550°C. Increasing the heating rate, the temperature of maxim decomposition is slightly increasing from 452–474°C in condition of N_2 and 430–460°C for CO_2.

Fixed bed reactor

Influence of the final temperature

Table 3 shows the yield of tar, gases, water and char from the pyrolysis of Shivee Ovoo coal in relation to temperature from 450 to 600°C to a heating rate of 20 K min^{-1} in the fixed bed reactor.

Table 3 Results of the pyrolysis of coal in relation to pyrolysis temperature

Temperature/°C	Tar/%	Water/%	Gas/%	Char/%
450	3.47	39.89	8.21	47.83
500	5.03	38.92	11.45	44.60
550	5.93	35.91	13.84	44.31
600	5.64	37.60	14.29	42.47

At the lowest pyrolysis temperature examined of 450°C, the tar yield was low at 3.47%, these data reflect incomplete pyrolysis. As the temperature was increased, the tar yield increased until it reached a maximum at 550, after which there was a decrease in tar yield at 600°C. Decreasing is related to the second decomposition of the volatile matter. The gas yield was increased progressively throughout as the temperature of pyrolysis increased from 450 to 600°C, while there was a progressive decrease in water yield and derived char.

Detailed analysis of the gases derived from the pyrolysis of Shivee Ovoo coal in relation to temperature of the pyrolysis is shown in Table 4. In almost all cases as the temperature of pyrolysis was increased the mass percentage of the gases increased. Also Table 4 shows that the alkene/alkane gas ratios increased with an increase in the temperature of pyrolysis. The increased alkene/alkane ratios shows that increased secondary gas phase reactions were occurring as the pyrolysis temperature was increased.

Influence of the heating rate

Table 5 shows the yield of tar, gases, water and char from the pyrolysis of Shivee Ovoo coal in relation to heating rate from 10 to 50 K min^{-1} to a final pyrolysis temperature of 550°C. There was an increase in oil from 20 to 40 K min^{-1} after which the yield of oil decreased as the heating rate was increased 50 K min^{-1}. The yield of gases decreased progressively throughout as the heating rate increased from 20 to 50 K min^{-1}, while there was a corresponding increase of derived char and the yield of water is almost not changed.

Table 4 Yield of gases from the pyrolysis of coal in relation to pyrolysis temperature (mass%)

Components	Temperature/°C			
	450	500	550	600
Non-hydrocarbon gases				
H_2	0.34	1.04	1.97	3.03
CO	1.42	2.02	2.05	2.49
CO_2	4.75	5.49	6.62	5.53
H_2S	0.03	0.05	0.06	0.07
COS	0.002	0.002	0.001	0.001
Total	6.542	8.562	10.701	11.121
Hydrocarbon gases				
CH_4	1.19	2.26	2.49	2.56
C_2H_6	0.23	0.28	0.24	0.21
C_2H_4	0.08	0.11	0.14	0.18
C_3H_8	0.066	0.067	0.054	0.043
C_3H_6	0.071	0.088	0.101	0.122
i-Butan	0.003	0.003	0.003	0.001
Hydrocarbon gases				
n-Butan	0.014	0.013	0.011	0.007
Propine				0.023
Etene/etane	0.35	0.39	0.58	0.86
Propene/propane	1.07	1.31	1.87	2.84
Total alkane	1.503	2.623	2.798	2.821
Total alkene	0.151	0.198	0.241	0.302

Table 5 Influence of heating rate on the product yield from the pyrolysis of Shivee Ovoo coal, mass%

Heating rate/K min^{-1}	Tar/%	Water/%	Gas/%	Char/%
20	5.93	35.91	13.84	44.32
30	6.51	36.02	13.07	44.40
40	6.85	35.80	12.67	44.67
50	6.30	35.50	12.51	46.50

Table 6 shows that there are increased concentrations of hydrocarbons and hydrogen as the heating rate was increased indicating that secondary reactions may be occurring. It particular, the cracking of oil vapour led to the formation of increased hydrocarbons and decreased oil yield. Table 6 shows the ethene/ethane, propene/propane and total alkene/alkane ratios, too. The ratio of alkene to alkane gases in the evolved pyrolysis gases have been used to determine reactions mechanism and indicating pyrolysis conditions [12].

Table 6 Yield of gases from the pyrolysis of coal in relation to heating rate (mass%)

Components	Heating rate/K min^{-1}			
	20	30	40	50
Non-hydrocarbon gases				
H_2	1.97	2.09	2.05	2.71
CO	2.05	1.86	1.80	2.53
CO_2	6.62	6.21	5.99	3.44
H_2S	0.06	0.067	0.068	0.034
COS	0.001	0.001	0.001	0.001
Total	10.701	10.218	9.909	8.715
Hydrocarbon gases				
CH_4	2.49	2.32	2.25	3.12
C_2H_6	0.24	0.22	0.22	0.30
C_2H_4	0.14	0.14	0.13	0.17
C_3H_8	0.051	0.05	0.05	0.07
C_3H_6	0.101	0.097	0.095	0.121
i-Butan	0.003	0.003	0.003	0.004
n-Butan	0.011	0.009	0.009	0.012
Etene/etane	0.58	0.64	0.59	0.56
Propene/propane	1.87	1.94	1.90	1.73
Total alkane	2.798	2.602	2.532	3.506
Total alkene	0.241	0.237	0.225	0.291
Alkene/alkane	0.086	0.091	0.089	0.083

Conclusions

Thermogravimetric analysis of Shivee Ovoo coal in relation to heating rate and final pyrolysis temperature was examined. No significant differences in total volatiles detected between the different kind of heating rates.

Pyrolysis of Shivee Ovoo coalin a fixed bed reactor in relation to heating rate and final temperature has been carried out and oil yield was related to both heating rate and final temperature. The yield of gases was increased with increasing the final temperature and decreased progressively as the heating rate increased.

Analysis of the gases derived from the pyrolysis showed that hydrocarbon, carbon monoxide, carbon dioxide and hydrocarbons were produced which increase in concentration as both the heating rate and final temperature of pyrolysis were increased.

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References

1 C. L. Sun, Y. Q. Xiong, Q. X. Liu and M. Y. Zhang, Fuel, 76 (1997) 639.
2 P. R. Solomon, T. H. Fletcher and R. J. Pugmire, Fuel, 72 (1993) 587.
3 V. Seebauer, J. Petek and G. Staudinger, Fuel, 76 (1997) 1277.
4 F. Garcia-Labiano, E. Hampartsoumian and A. Williams, Fuel, 74 (1995) 1072.
5 A. Mianowski and T. Radko, Fuel, 72 (1993) 1537.
6 Y. Zhuo, R. Messenbock, A. G. Gollot, A. Megaritis, N. Paterson, D. R. Dugwell and R. Kandiyoti, Fuel, 79 (2000) 793.
7 R. Cypres and S. Furfari, Fuel, 60 (1981) 768.
8 J. H. Edwards and I. W. Smith, Fuel, 59 (1980) 674.
9 M. Takeuchi and N. Berkowitz, Fuel, 68 (1989) 1311.
10 P. Arent and K. H. van Heak, Fuel, 60 (1981) 779.
11 G. H. Ko, W. A. Peters and J. B. Howard, Fuel, 66 (1987) 1118.
12 P. T. Williams and N. Ahmad, Fuel, 78 (1999) 653.
13 J. O. Jaber and S. D. Probert, Fuel Processing Technology, 63 (2000) 57.
14 H. J. Muhlen and A. Sulimma, Thermochim. Acta, 103 (1986) 163.