

THERMOGRAVIMETRIC STUDIES IN PREDICTION OF COAL BEHAVIOUR DURING COAL LIQUEFACTION

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Different chemical and petrographical methods were earlier proposed for the prediction of coal liquefaction. Thermogravimetric studies (DTG, TG) of coals were now performed and the same coals were liquefied.

A good correlation was found between ΔA_{\max} (the main decomposition area during the maximum rate of decomposition in DTG) and S_k (the degree of conversion of organic substances during coal liquefaction).

ΔA_{\max} measurement may be a good, quick and quite reliable method for the prediction of coal liquefaction, which needs to be standardized.

Keywords: coal liquefaction, degree of conversion, maceral comp., thermogravimetric analysis

Introduction

Chemical methods, such as the H/C and O/C ratios [1, 2], the OH/O ratio [3] and free radical measurements [4], were earlier used to predict coal liquefaction. Low-rank coals are more reactive during coal liquefaction [5-7].

Coals of the same rank can also behave in different manners and show different reactivities. Kinetic measurement of the reactivity of coal is considered to be good method for assessment of the reactivity of coal [8]. The behaviour of coal macerals during coal liquefaction has been studied [9-12].

Various workers found a fair correlation between the conversion and the total concentration of the presumed reactive macerals, i.e. the sum of vitrinites and exinites [6, 7, 13-15]. For the conversion of coal, Tiskarev *et al.* [16] consider that coal should not contain vitrinite (huminite) plus exinite less than 80%.

However, these conventional methods have been found to be inadequate [17]. The association of macerals (microlithotypes) has been shown to play an important role during coal liquefaction [18–20]. According to Abdel-Baset, Yarzab and Given [21] the chemical-petrographic character of a coal influences the coal liquefaction process. The effects of heating rate, temperature and reactor type on coal devolatilization have been demonstrated [22].

Thermogravimetric analyses have been used for the proximate analyses of coals [23]. The correlation of surface area analysis on raw coal samples in a thermoanalyser under a gradual controlled gradient with derivative thermogravimetry (DTG) appeared quite promising. Burning profiles as established by DTG were confirmed as a valuable means of diagnostic differentiation of coals [24].

Mahajan *et al.* used differential scanning calorimetry in hydrogenation studies of coals [25]. The present article for the first time applies thermogravimetric studies (DTG and TG) for prediction of the behaviour of coals during coal liquefaction.

Experimental

Six different inertinite-rich coal samples ($I^{mmf} > 30\%$) from different sedimentary facies of low and medium ranks were chosen. Four coal samples were of low rank, of which two (C-3 and D-4) belong to paralic sedimentary facies and the other two (E-5 and F-6) to limnic sedimentary facies. Of the two samples of medium rank, one (A-1) belongs to a limnic sedimentary facies and the other (B-2) to a paralic sedimentary facies. Maceral group analysis, reflectance measurements of vitrinite in oil, calculation of the mean reflectance of vitrinite in oil (R_m^o) and sulphur content analysis (S_t^d , S_p^d and $S_{SO_2}^d$) were performed according to Polish standards. The results are shown in Table 1. The representative coal samples were crushed to < 0.006 mm and representative samples each of 600 mg were obtained after coning and quartering for thermogravimetric analysis. Thermogravimetric analysis (DTG and TG) of each coal sample with 400 mg alumina (Al_2O_3) was carried out in a derivatograph in an atmosphere of nitrogen [20]. DTG and TG results are shown in Figs 1 and 2, respectively.

The temperature T_1 and T_2 at which the main reaction of disintegration starts and ends with maximum rate during DTG were calculated according to the method suggested earlier [26]. The areas ΔA and ΔA_{max} were measured by planimeter according to the method suggested in [20, 27] and shown in Fig. 3. ΔA is the main decomposition surface area during DTG between temperatures T_p and T_k , whereas ΔA_{max} is the main decomposition surface area during DTG with maximum rate of decomposition between temperatures T_1 and T_2 [27]. The results of DTG and TG analyses are shown in Table 2.

Table 1 Petrographical and technological properties of coals used for coal liquefaction (methods used according to Polish standards)

Coal samples	Maceral comp. mmf. / % Vol			Technological properties / % mass						
	Vitrinite V_t	Exinite L	Inertinite I	Rank R_m^o %	W^a	V^{daf}	A^d	S_t^d	S_p^d	SSO_4^d
A-1	50.28	0.38	49.34	1.21	0.86	22.89	2.73	0.49	0.17	0.09
B-2	54.53	0.00	45.06	1.12	0.75	25.98	5.55	0.55	0.35	0.15
C-3	54.15	7.33	37.47	0.59	6.10	39.58	15.61	1.82	1.11	0.26
D-4	56.61	5.56	37.81	0.55	6.13	42.14	10.24	1.26	0.67	0.19
E-5	62.22	7.33	30.47	0.45	9.96	39.48	11.79	2.64	1.49	0.76
F-6	56.56	10.53	32.90	0.44	9.76	45.91	16.86	3.58	2.08	1.03

Explanations: mmf = mineral matter free basis, W^a = moisture content, R_m^o = mean reflectance of vitrinite in oil,

V^{daf} = volatile matter content (on dry ash free basis), A^d = ash content (on dry basis),

S_t^d , S_p^d and SSO_4^d = total sulphur, pyritic sulphur and sulphatic sulphur (on dry basis) respectively

Table 2 Characteristics of thermogravimetric analyses (DTG, TG) of coal samples and their degree of conversion, S_k during coal liquefaction

Coal samples	Thermogravimetric analyses														Correlation coefficient, (r) between A_{max} and S_k	
	W^{at} / V^{at}	T_p / T_k	$T_k - T_p$	T_1 / T_2	$T_2 - T_1$	$U^{th} \Delta T_{max} / f = \frac{V^{at}}{W^{at} T_{max}}$	$\Delta A / \Delta A_{max}$	σ_1	S_k / σ_2	σ_2	$Wt\%$	units	σ_1	σ_2		
	$Wt\%$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$Wt\%$	units	units	$Wt\%$		
A-1	1.17	21.33	290	660	370	470	520	50	50	7.50	0.36	440	92	48.41		
B-2	1.16	22.50	350	785	335	465	530	65	65	8.00	0.29	378	65	39.11		
C-3	5.67	36.00	250	650	400	390	485	95	95	10.00	0.07	462	80	42.18		
D-4	5.67	36.33	295	544	249	390	450	60	60	10.00	0.11	450	108	55.10		
E-5	8.83	34.17	258	595	337	380	490	90	90	9.92	0.04	282	50	38.68		
F-6	8.67	30.83	315	700	285	400	470	70	70	8.25	0.05	524	85	44.61		

W^{at} = moisture content (analytical state), [2] V^{at} = Volatile matter content (analytical state), [3], T_p = temperature at which main disintegration reaction (under DTG) begins, [4] T_k = temperature at which main disintegration reaction (under DTG) ends

$\Delta T = T_k - T_p$ (difference between T_k and T_p), [6] T_1 = temperature at which main disintegration reaction (under DTG) begins with maximum rate of decomposition, [7] T_2 = temperature at which main disintegration reaction (under DTG) ends with maximum rate of decomposition, [8] $\Delta T_{max} = T_2 - T_1$ (difference between T_2 and T_1), [9] $U^{th} \Delta T_{max}$ = loss in weight during temperatures T_1 and T_2 ,

f = thermogravimetric indicator proposed by Gabzdyl and others, [11] ΔA = main decomposition area (under DTG) during temperatures T_p and T_k , [12] ΔA_{max} = main decomposition area with maximum rate of decomposition during temperatures T_1 and T_2 , [13] σ_1 = standard deviation for ΔA_{max} , [14]

S_k = degree of conversion of organic substances in coal (Wt%), [15] σ_2 = standard deviation for S_k ,

r = correlation coefficient between ΔA_{max} and S_k

The coal samples were crushed to < 0.1 mm. A representative coal sample of 500 g and 1500 g of previously hydrogenated anthracene oil as solvent were mixed in the form of pastes and liquefied without the addition of any catalyst in a 4-litre agitated autoclave (LAM-104 type) in the presence of hydrogen at a pres-

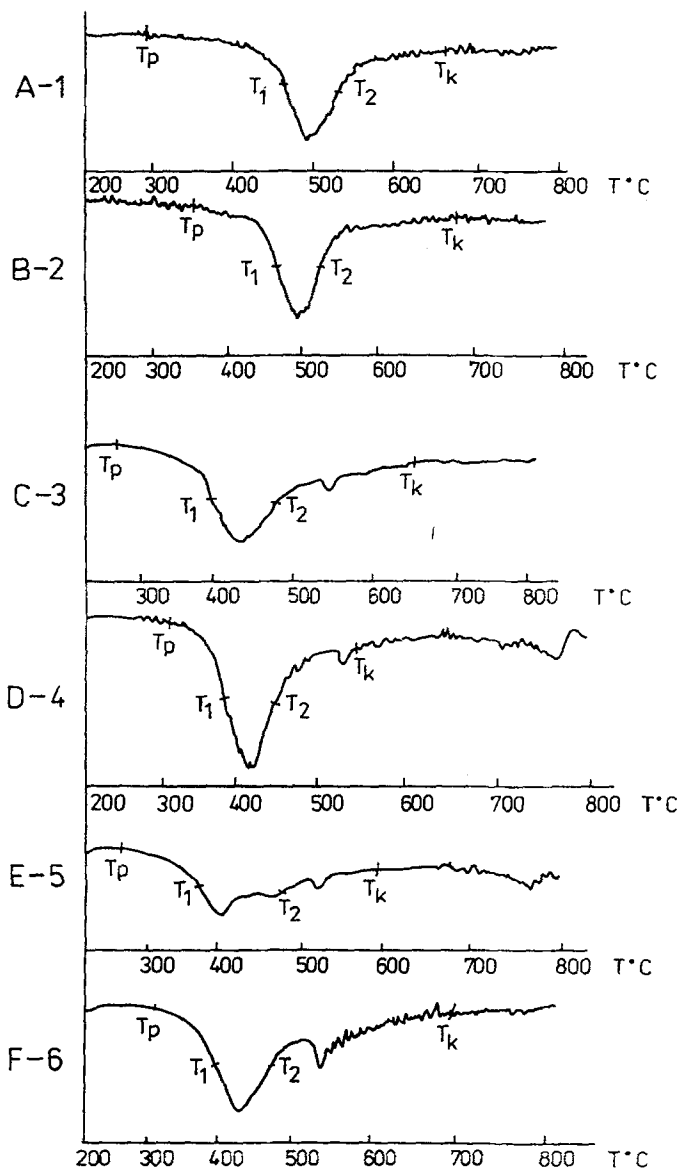


Fig. 1 DTG curves of coal samples for coal liquefaction

sure of 20 MPa. These reactions were carried out for 60 minutes at the controlled temperature of 450°C.

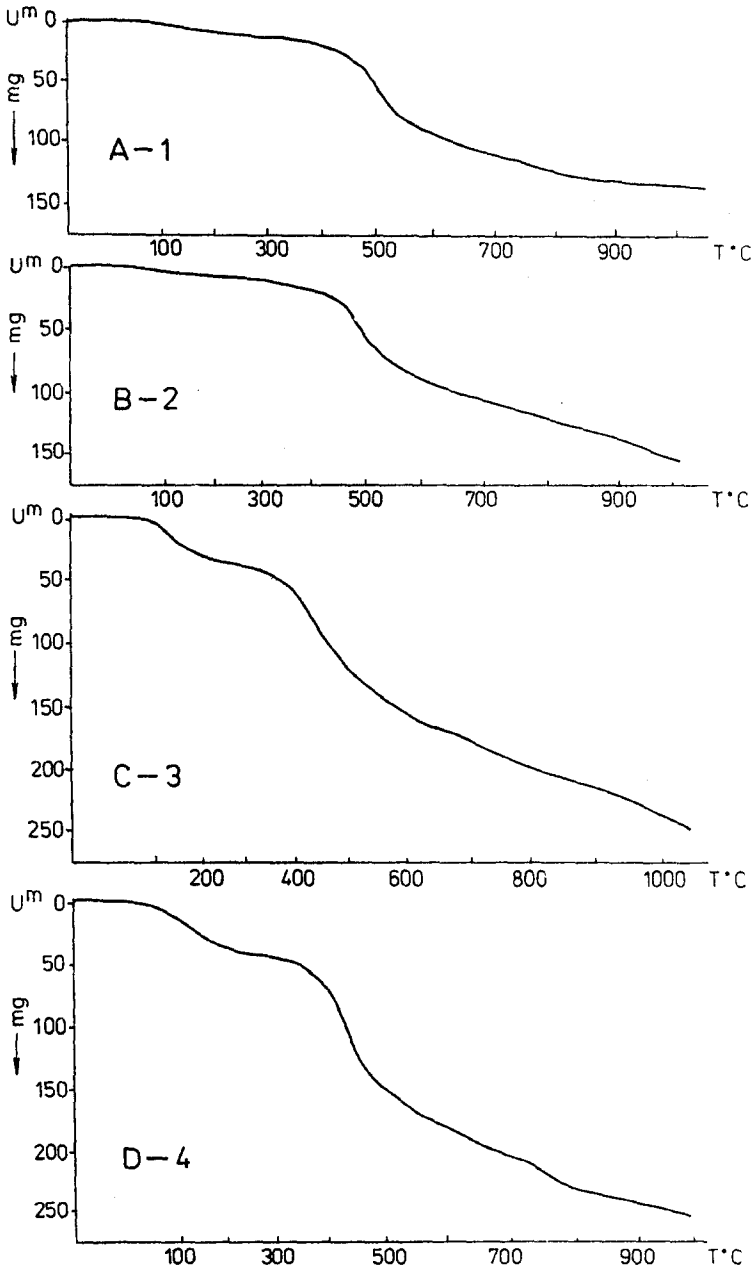


Fig. 2 TG curves of coal samples for coal liquefaction. Explanation U^m = loss of weight (mg)

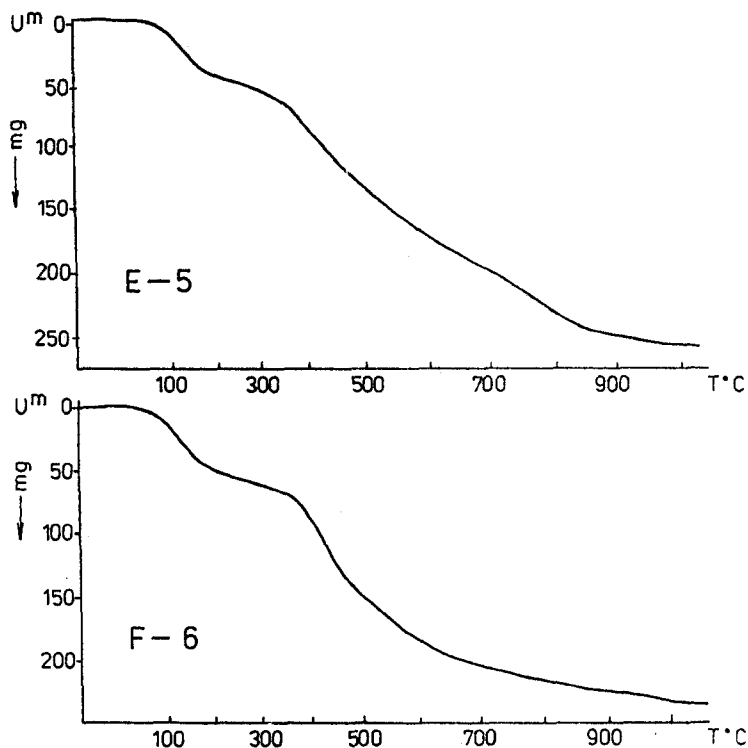


Fig. 2 (Continued) TG curves of coal samples for coal liquefaction. Explanation U^m = loss of weight (mg)

The degree of conversion Sk (% mass) of organic substances during coal liquefaction was calculated according to the following formula:

$$Sk = \frac{M_1 - \left[M_2 - \frac{M_3 \cdot A^d}{100} \right]}{M_1} \times 100$$

where

Sk = degree of conversion of organic substances in coal (wt%),

M_1 = mass of organic substances in the given coal sample, (g),

M_2 = mass of THF (tetrahydrofuran)-insoluble constituents in the given coal sample (g),

M_3 = mass of dry coal (g),

A^d = ash content (on dry basis) in the coal sample (wt%).

The degrees of conversion of the organic substances in the coals are shown in Table 2.

Results and discussion

The proximate analyses (W^{at} , V^{at}) of coals by thermogravimetry nearly agree with the results obtained by proximate analyses according to Polish standards.

The temperature T_p (at which the main disintegration reaction during DTG begins) varies from 250° to 350°C, whereas the temperature T_k (at which the main disintegration reaction during DTG ends) varies from 544° to 785°C. ΔT ($\Delta T = T_k - T_p$) varies from 249 deg to 400 deg, and does not show any correlation with the rank, with the sedimentary facies or with the degree of conversion, Sk . The temperatures T_1 and T_2 at which the main disintegration reaction (during DTG) begins and ends with maximum rate of decomposition, respectively, differ somewhat with the rank of the coals. In the low-rank coals, the main disintegration reaction with maximum rate of decomposition during DTG begins and ends earlier than for the medium-rank coals.

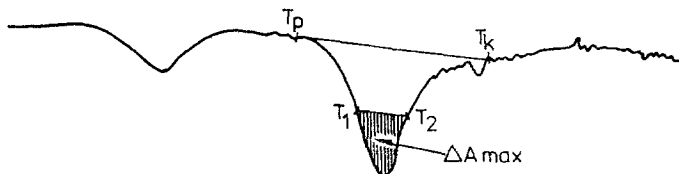


Fig. 3 Method of determination of ΔA_{max} under DTG using planimeter [27]

The loss of weight $U^m \cdot \Delta T_{max}$ between temperatures T_1 and T_2 varies in the range 7.50–10.00%, which again shows no relation with the rank, with the sedimentary facies or with the degree of conversion of the coal, Sk .

The thermogravimetric indicator I^t (proposed by Gabzdyl *et al.*) shows a relation with the rank of the coal. Medium-rank coals have higher thermogravimetric indicators I^t than low-rank coals. ΔA varies in the interval 282–524 units and shows no relation with the rank, with the sedimentary facies or with the degree of conversion, Sk . However, ΔA_{max} , which varies between 50 and 108 units, shows a very good correlation with the degree of conversion of the organic substances in the coal, Sk . Here, the correlation coefficient, r , between ΔA_{max} and Sk is very good ($r = 0.94$) (Fig. 4). Measurements of the parameter ΔA_{max} should be standardized for the prediction of coal liquefaction and for comparison of the results from different laboratories worldwide.

The parameter ΔA_{max} shows a very good correlation (correlation coefficient, $r = 0.96$) with the index of hydrogenation, I_H [20]. I_H depends mainly on the microlithotypes and on the ranks of the coals [20, 27]. The correlation between

ΔA_{\max} and I_H reflects the fact that the decomposition of organic substances in coal during coal liquefaction depends on the microlithotypes (i.e. the association of the macerals) and on the rank of the coal.

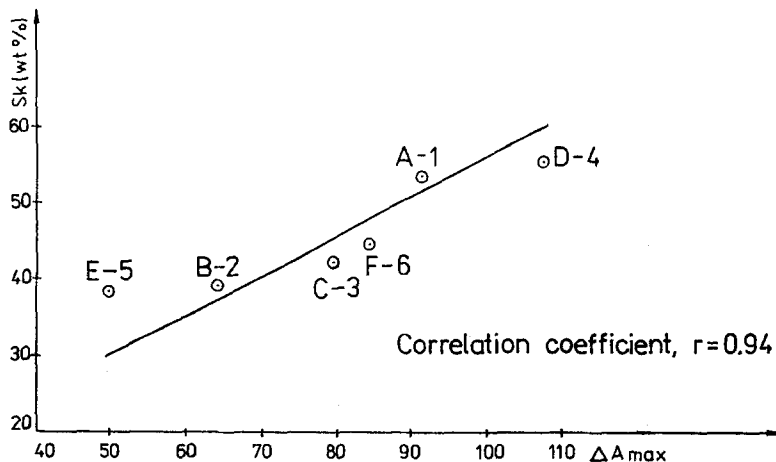


Fig. 4 Relation between ΔA_{\max} and Sk [27]

The puzzling large difference in reactivity for coals of the same rank, with similar elemental compositions and degrees of aromaticity [28], can be explained by ΔA_{\max} , which is correlated with the microlithotypes (i.e. the association of the macerals).

Conclusions

The proposed ΔA_{\max} determination may be a quite satisfactory and quick method for the prediction of coal liquefaction behaviour and the degree of conversion of the organic substances in coal. The measurements of ΔA_{\max} should be standardized so that the results are comparable with those from other laboratories world wide.

The parameter ΔA_{\max} depends on the microlithotypes (i.e. the association of the macerals) and on the rank of the coal.

The association of the macerals may explain the puzzling large difference in reactivity for coals of the same rank with similar elemental compositions and degrees of aromaticity.

Thermogravimetric analyses may indicate the moisture content (W^{st}) and volatile matter content (V^{st}) satisfactorily with certain limits of accuracy with relation to proximate analyses of the coal.

Thermogravimetric indicators differ somewhat with the ranks of coals.

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Zusammenfassung — Zur Prognose der Kohleverflüssigung wurden bereits verschiedene chemische und petrographische Methoden vorgeschlagen. In dieser Arbeit werden thermogravimetrische Untersuchungen (DTG, TG) an Kohlen durchgeführt und dieselben Kohlen verflüssigt.

Zwischen ΔA_{\max} (Fläche der Hauptzersetzung bei der maximalen Zersetzungsgeschwindigkeit in der DTG) und Sk (Konversionsrate organischer Substanzen bei der Kohleverflüssigung) wurde eine gute Korrelation gefunden.

Die Messung von ΔA_{\max} kann eine gute, schnelle und recht zuverlässige Methode zur Prognose von Kohleverflüssigung sein und muß standardisiert werden.