

Heat Treatment of Maceral Groups Obtained From Turkish Bituminous Coals

Elif Sultan VAYISOĞLU* & Nevin Gaye ERBATUR

*Çukurova University, Chemistry Department,
01330 Adana-TURKEY*

Received 01.02.1995

The dilatation properties of parent coals and their maceral fractions were examined. In all the coal samples, the main petrographic constituent was the vitrinite maceral. Reflectance of the vitrinite and inertinite macerals increased after carbonization, while the liptinite maceral disappeared and caused large pores in the vitrinite macerals. All of the coals developed anisotropic coke.

Introduction

The most important area of research in the thermal upgrading of coal and, similarly, of applied coal petrography, is the production of a blast furnace coke which satisfies high standards of strength and constant quality. The possibility of producing a good coke from a given coal depends on its coking power, and several modification techniques have been proposed for achieving better cokes with low-rank coals¹⁻³. The changes brought about by heat-treatment over temperatures ranging from 25 to 3000°C are as follows⁴:

- 1) 25 - 1000°C, carbonization
- 2) 1000 - 1400°C, semi-graphitization
- 3) 1400 - 2300°C, graphitization
- 4) > 2300°C, crystallization

Laboratory heating experiments and pilot coke oven experiments have been used extensively in the past to give petrographers a basis for understanding the nature of the reactions of different macerals in the coking process⁴⁻¹¹. Interaction between coal macerals during carbonization has been widely studied^{12,13}. The development of optical anisotropy during carbonization of bituminous coals from coking-steam coals with a volatile material of greater than 15% dmmf to highly volatile medium coking-coals is well established. Coals of higher rank show only intensification of the reflectance of coal vitrain anisotropy, and coals of lower rank tend to remain isotropic as viewed under the optical microscope.

In the present study, the behavior of a number of Turkish coals and their maceral concentrates against heat treatment was studied. The development of anisotropic cokes from whole coal and maceral concentrates was also studied.

* Present Address: Chemistry Department, Mersin University. Mersin 33080, Turkey

Experimental

Three coal sample of bituminous roal rank were selected from the western Black Sea region of Turkey. The samples were obtained from different seams. They are listed in Table 1 with some analytical data.

Table 1. Analytical data for coals*

Coal	C%	H%	N%	O+S% ^a	V.M	Moisture%
ZB	77.3	4.5	0.8	17.4	25.5	0.4
ZP	82.0	5.4	1.3	11.3	35.0	1.3
ZC	73.4	4.8	1.9	19.9	31.3	0.5

^a : By difference

* : daf

Since the aim of this project was to assess the degree of reactivity of maceral groups towards dilatation, coal samples were separated into density fractions by a float and sink technique using ZnCl₂ solutions with different densities, as described in the literature¹⁴. In Table 2, the results of maceral separation are given. The numbers 1, 2 and 3 indicate the lightest, the middle and heaviest maceral fractions, respectively. Tests were carried out with a Ruhrkohle Dilatometer (according to DIN 31739). The heating rate was 3°C/min. All samples were prepared as relief-free polished particulate blocks. A Leitz MPV-2 orthoplan microscope was used for the reflectance measurements in oil ($n_{oil} = 1.516$ at 24°C). Bireflectance in oil was taken to be the average of the highest 10 measurements from 50 separate reflectance measurements on each carbonized maceral.

Table 2. Maceral composition of separated fractions

Sample	V% ^a	V+L% ^a	I% ^a	%R _v
ZB	90	5	5	1.0
ZB-1	75	15	10	1.03
ZB-2	90	3	7	1.11
ZB-3	70	5	25	1.00
ZP	85	5	10	0.80
ZP-1	70	10	20	0.86
ZP-2	87	5	8	0.86
ZP-3	75	5	20	0.88
ZC	80	5	15	0.90
ZC-1	65	15	15	0.83
ZC-2	82	8	10	0.87
ZC-3	75	5	20	0.90

^a : v/v

Results and Discussion

As seen in Table 2, raw coals contain vitrodetrinite, which is present in higher amounts than liptinite. Because of the petrographical composition, vitrinite is the major maceral group in all separated fractions. In the lightest fraction, Group 1, it was difficult to separate liptinite macerals because liptinites generally lose their identity with increasing rank, making their isolation and identification extremely difficult. When

we examined the heat treatment behaviour of whole coals and the corresponding maceral concentrates, it was interesting to note that medium density fractions of ZB and ZC coals had greater dilatation than whole coal and the other two fractions (Figure 1).

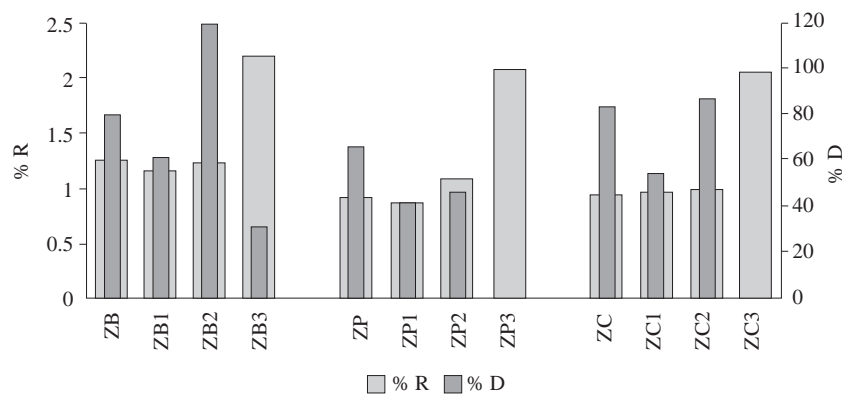


Figure 1. Variation in dilatation distribution and reflectance of whole coals and maceral concentrates.

The results of the dilatation test of whole coals and maceral fractions of these coals are summarized in Table 3, where it is seen that they are good coking coals with a characterized coking power of between G5 and G8¹⁵. All the separated fractions of ZP coal yielded some contraction, while in ZB and ZC coals, only the heaviest maceral fractions yielded contraction. In ZB and ZC coal samples, the percentage of contraction increased with an increasing density of maceral groups; hence, the heaviest fractions gave the highest contraction, greater than that of whole coals and fractions 1 and 2; in spite of this, however, the heaviest fractions did not yield dilatation. Although vitrinite is the major maceral, the amount of inertinite is higher in the heaviest fractions. Hence, even a small amount of inertinite may cause low dilatation since inertinite macerals are characterised by strong cross linkages between aromatics which are difficult to break thermally¹⁶. However, the performance of coal in some industrial processes suggests that not all macerals of the inertinite group are in fact inert but that some contribute to coking and liquefaction¹⁷.

Table 3. Heat treatment results of coal and maceral concentrates

Sample	Softening Temp. (°C)	Maximum contraction (%)	Temp.of max. contraction (°C)	Maximum dilatation (%)	Temp. of max. dilatation (°C)
ZB	375	26	417	80	458
ZB-1	N.O.	N.O.	N.O.	60	465
ZB-2	N.O.	N.O.	N.O.	119	465
ZB-3	389	28	437	30	460
ZP	368	29	410	65	437
ZP-1	400	24	400	40	441
ZP-2	398	25	399	45	436
ZP-3	398	21	428	N.O.	N.O.
ZP	367	30	418	82	450
ZC-1	N.O.	N.O.	N.O.	52	440
ZC-2	380	20	404	85	440
ZC-3	378	26	420	N.O.	N.O.

N.O.: Not observed

Data in the literature indicate that the relationship between reflectance and coking power depends on the maceral composition of the coal¹⁵. Liptinite macerals are known to cause dilatation. More dilatation was achieved from separated fraction 2, which has higher vitrinite concentrate and vitrinite reflectance; therefore, the synergetic effects between macerals of raw coal may be assumed to be responsible for this behaviour.

The increase in the reflectance of the vitrinite cokes can be interpreted in terms of a progressive molecular ordering and increasing molecular size. Measurements taken in polarised light before and after dilatation tests demonstrate that the maximum reflectances increased from 0.86% to 1.25-2.75% in oil after heat treatment. Generally, lower and medium density fractions showed some change in reflectance when heated up to 450°C while small changes were observed for heavier density fractions (Figure 2). The bireflectance measurements also showed that vitrinite macerals of the coals developed flow-type anisotropic coke. The maximum and minimum reflections of the semi-cokes having anisotropic structures were 1.77%-1.35%, 1.55%,1.24% and 1.15%-0.82% for ZB, ZP and ZC, respectively. Anisotropic development is related to the rank of the coals. Coals of higher rank show only intensification of the reflectance of the coal vitrain anisotropy, and coals of lower rank tend to remain isotropic as viewed under optical microscope. The development of optical anisotropy requires not only planar molecules of appropriate size but also conditions that provide the mobility/fluidity necessary for the ordering of the lamellae. When these two conditions are met, optically anisotropic species develop. The type of species and the extent of their growth depends on the chemical nature of the molecular species present at the onset of anisotropic development and in the maintenance of the appropriate conditions within the carbonising mass¹⁸. In this study all coal samples were from the same region, but of different seams. These results indicate how important the selection of the coals in coke industry is.

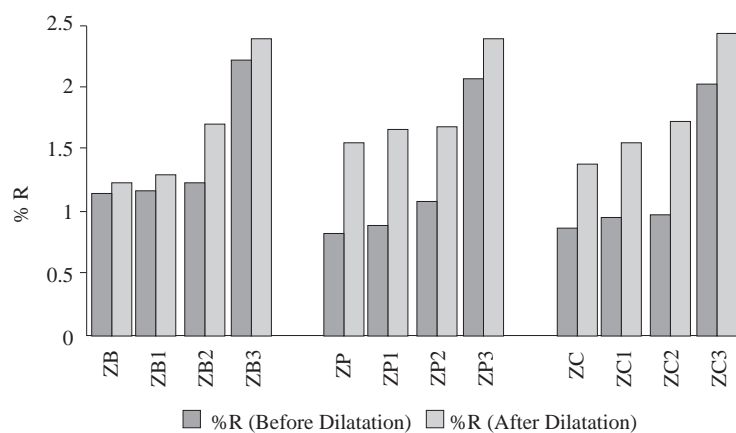


Figure 2. Alteration in reflectance of vitrinites with heat treatment.

The behaviour of sporinite and cutinite depends on their association with other macerals¹⁵. In our samples, liptinite macerals were found together with vitrinites and probably acted as softeners, causing large pores because of fusibility. The transition through a plastic stage is responsible not only for the formation of the pore structures of the coke, but also for its optical character. Microscopic examinations showed that liptinite macerals disappeared, leaving large pores on vitrinites after heat treatment. Vitrinites had higher reflectance, but no differences on inertinite macerals were observed; however, their reflectance was higher than that of untreated material. It is known that inertinite macerals behave as an inert constituent, at least up to 600°C; hence, our results are in accordance with this observation¹⁵. Because of their densities, ash content is higher in the heaviest fractions, and it may also have an effect on thermoplastic properties.

Conclusion

The following conclusions can be drawn from the present study;

1. The reflectance of coke obtained from vitrinite-rich groups is higher than that of raw materials.
2. The heaviest groups gave only contraction while lower and medium density fractions gave only dilatation.
3. The maximum dilatation of vitrinite-rich groups is higher than that of whole coal and the corresponding maceral groups.
4. During heat treatment, liptinite macerals disappeared, leaving large pores on vitrinite macerals, and all coals developed anisotropic coke.

References

1. J. Gibson, 'Coal and Modern Coal Processing' (Pitt, G.J. and Millward, G.R., Eds.) **Academic Press** (1979).
2. Y.J. Sunami, **Fuel Soc. Japan** **58**, 958 (1979).
3. H.J. Kimura, **Japan Petrol. Inst.** (1973).
4. F. Goodarzi, **Fuel** **63**, 820 (1984).
5. F. Goodarzi, **Fuel** **63**, 827 (1984).
6. F. Goodarzi and D.G. Murchison, **Fuel** **51**, 322 (1972).
7. F. Goodarzi and D.G. Murchison, **Fuel** **57**, 273 (1978).
8. M.-Th Mackowsky, '4th Int. Conf. on Coal Science' paper G1, Le Touquet, France (1961).
9. F. Goodarzi and D.G. Murchison, **Fuel** **56**, 89 (1977).
10. F. Goodarzi and D.G. Murchison, **Fuel** **55**, 141 (1976).
11. A. Davis and W. Spackman, **Fuel** **43**, 215 (1964).
12. D.W. Van Krevelen, H.N.W. Dormans and F.J. Huntjens, **Fuel** **38**, 165 (1959).
13. H.R. Brown, A.C. Cook and G.H. Taylor, **Fuel** **43**, 111 (1964).
14. R. Doğru and S.I. Gökçen, **Fuel** **59**, 355 (1980).
15. E. Stach, M.-Th. Mackowsky, M. Teichmüller, G.H. Taylor, D. Chadra, R. Teichmüller, "Stach's textbook of Coal Petrology" Stuttgart (1975).
16. C.F.K. Diessel, **Fuel** **62**, 883 (1983).
17. M. Shibaoka and S. Ueda, **Fuel** **57**, 667 (1978).
18. J.W. Patrick and A. Walker, **Fuel** **70**, 465 (1991).