PETROLOGICAL STUDIES OF LOW TEMPERATURE OXIDATION OF LIGNITES

K. MARKOVA[1], Y. STEFANOVA[1], M. BONEVA[2]

A b s t r a c t . The low temperature oxidation processes which has taken place in lignites and their lithotypes (xylain, humovitrain, semifusain, fusain and liptain) from the East Maritza basin have been studied. The changes occurring in the coals/lithotypes composition and structure during their oxidation have been followed by examining reflectance, microhardness, proximate, ultimate, functional, and increment analyses. The main kinetic parameters such as duration of the induction period, maximum and stationary rates and the apparent activation energies were evaluated. The complex investigation provides a detailed information for the behaviour of low rank coals and their lithotypes towards the action of atmospheric oxygen. Thus some suggestions concerning the mechanisms of their oxidation reactions can be made. The individual way of the genesis of each one of the lithotypes and the resulting physicochemical structure predetermine the basic mechanism of these reactions. However, it has been found that in spite of the similar genesis the lithotypes differ in the mechanism of their oxidation. For xylain the oxidation takes place mainly via aryl radicals yielding tertiary peroxide and carbonyl groups. The oxidation of humovitrain is characterised by the dominant participation of aroxyl radicals resulting in accumulation of primary hydroperoxide and phenol groups. The oxidation of semifusain leads mainly to the formation of molecular products. The oxidation of fusain is found to be essentially different from that of other lithotypes. It is characterised by the formation of carbonyl groups attached to biphenyl aromatic structures. The peculiar petrographic composition and structure of liptain account for the occurrence of oxidation processes accompanied by destruction reactions at relatively lower temperatures. It has been established that the intensity of the oxidation processes varies from one lithotype to an other. Xylain and humovitrain oxidise most intensively. The intensity drops off from the first towards the second member of the corresponding genetic series, i.e. from xylain to humovitrain and from semifusain to fusain.

K e y   w o r d s : lignites, lithotypes, oxidation, East Maritza Iztok basin.

INTRODUCTION

There has been considerable interest in evaluating the effect of autooxidation processes during coal processing, transportation and storage (Van Krevelen, 1961; Kucher *et al.*, 1978, 1980; Volborth, 1979; Saranchuk, 1982; Saranchuk *et al.*, 1994; Markova, Rustschev, 1991, 1994; Wagner, 1995). The research in this field could contribute to the solution of a wide range of problems related to purely geological and petrological goals and also for evaluating coals as raw material for industrial purposes. On the other hand, these processes are closely connected with coal selfignition thus being of great ecological interest. However, the different opinions on the character and mechanisms of autooxidation processes occurring in low rank coals, the limited range of study from petrological standpoint as well as the lack of similar concepts and studies on the separate lithotypes of lignite coals impose the performance of a complex and expanded in petrological aspect investigation. Thus, following the structural changes in lignite coals and their lithotypes, it is possible to supplement and clarify some obscure steps in the mechanisms of the autooxidation processes in lignite coals and propose an appropriate mechanism pathways for these processes in low rank coal lithotypes.

[1] Sofia University "St. Kl. Ohridski", 15 Tzar Osvoboditel Blvd., 1000 Sofia, Bulgaria
[2] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev Street, Bl. 9, 1113 Sofia, Bulgaria
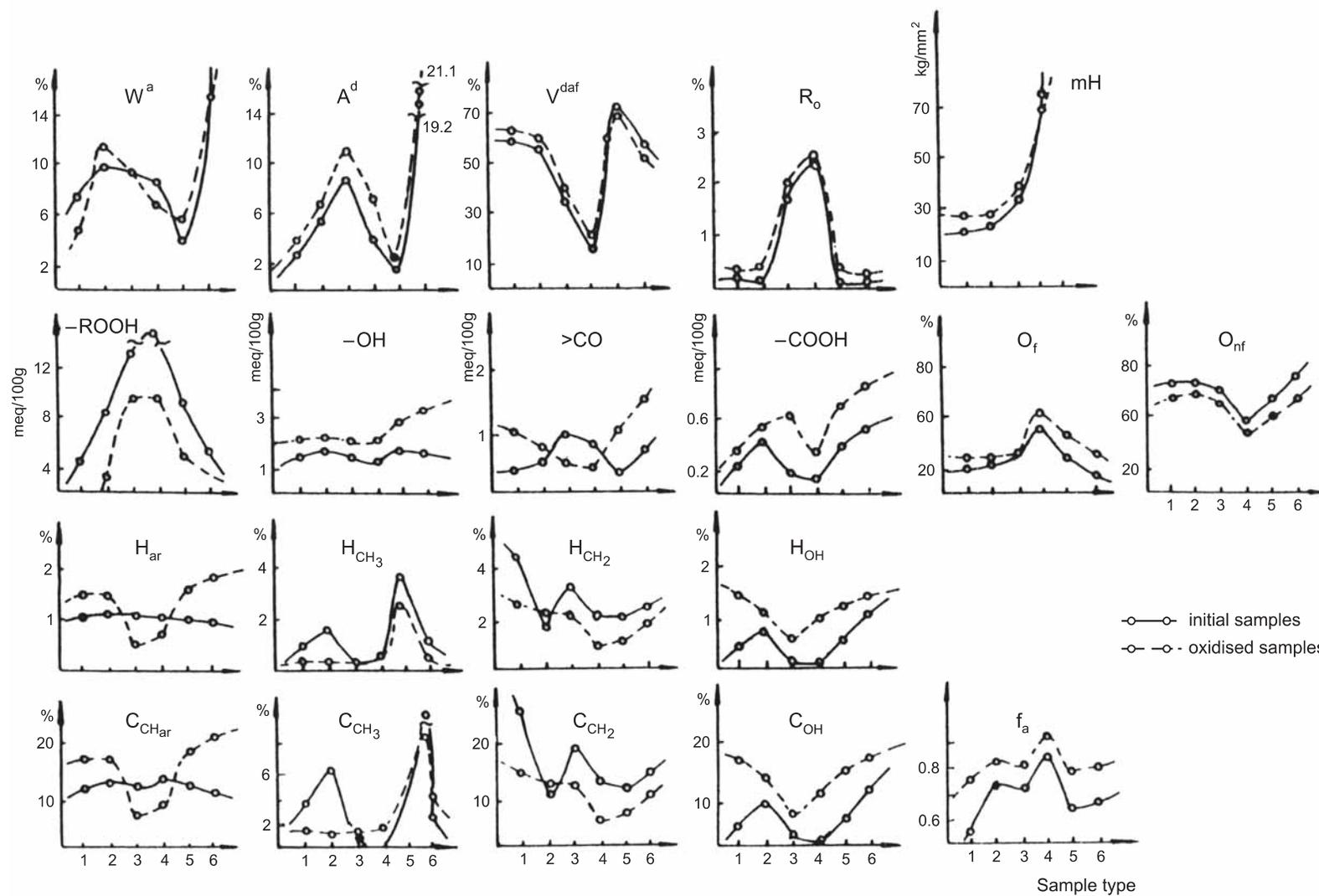
K. Markova, Y. Stefanova, M. Boneva

Fig. 1. Main parameters of lignite coals and their lithotypes

Sample type: *1* — xylain, *2* — humovitrain, *3* — semifusain, *4* — fusain, *5* — liptain, *6* — lignite coal
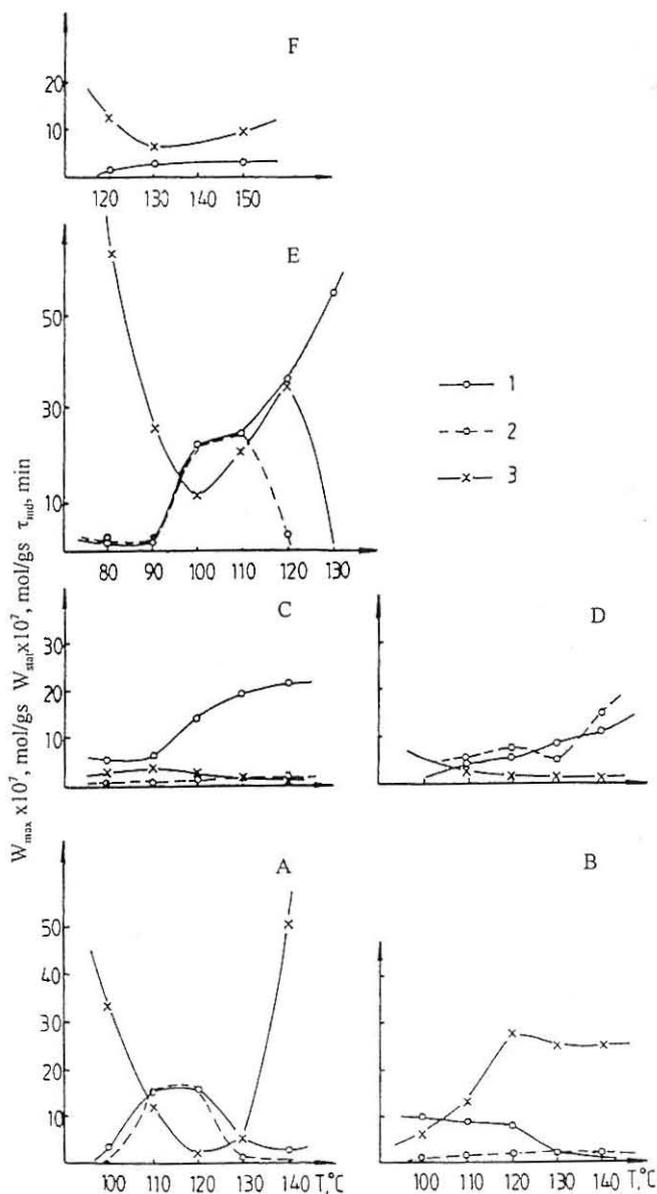
Fig. 2. Temperature dependence of the kinetic parameters of lignite coals and their lithotypes

A — xylain; B — humovitrain; C — semifusain; D — fusain; E — liptain; F — lignite coal; *1* — maximum rate W.[(mol/g s)x10], *2* — stationary rate, W. [(mol/g s)x10], *3* — induction period, τ. [min]

100°C. Contrary to it, at this temperature the stationary rate attains its minimum value. The induction period for humovitrain oxidation is the shortest at 100°C.

The temperature increase in case of semifusain autooxidation leads to rise of the maximum and stationary rates, and decrease of the induction period. The increase of the maximum rate of oxidation is more significant than that found for the stationary rate.

Up to 100°C fusain does not undergo oxidation. Only after 110°C its maximum rate increases gradually. The stationary rate begins to rise after 140°C. Simultaneously, the induction period decreases gradually.

Liptain autooxidation is characterised by an increase both of maximum and stationary rate with temperature, particularly above 90°C. The latter oxidation has the longest induction period.

With the autooxidation of the mean lignite coal sample, the rise in the maximum rate is more intensive below 130°C than at higher temperatures. The duration of the induction period decreases with temperature rise and at 130°C it has a minimum value.

The kinetic parameters and the apparent activation energy of the autooxidation process reveal that xylain is more susceptible to oxidation that humovitrain. It should be also noted the intensive oxidation of semifusain. The higher activation energy for fusain suggests that this lithotype is more stable against oxidation and confirms the proceeding of the oxidation reaction in the kinetic region. The value of the activation energy for liptain suggests a high activation barrier for the initiation step of the overall process. The low activation energy, found for lignite coal similar to that of peat (Rouschev *et al.*, 1978), demonstrates the similar character of the mechanisms of these autooxidation process and the participation of similar easily oxidizable and dominating structures.

The overall results from the study of the autooxidation processes of lignite coals and their lithotypes at 150°C allow us to assume a probable mechanism for these processes from the standpoint of the chain-radical theory of liquid phase oxidation of hydrocarbons (Semenov, 1934; Emanuel', Knorre, 1962; Denisov *et al.*, 1975). The observed generation of paramagnetic particles (Markova *et al.*, 1993) during the oxidation of these lithotypes supports the proceeding of the following reaction:

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \tag{1}$$
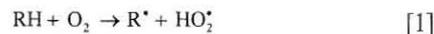
The generation of free radicals in coal induces their oxidation and formation of peroxide radicals:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{2}$$

The latter react further with other radicals or groups leading to the formation of peroxides and regeneration of alkyl radicals — $R^{\bullet}$, which propagate the chain:

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{3}$$
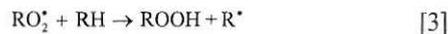
The kinetics of peroxides change during coal autooxidation at 150°C reveals the probable formation of two types of peroxides. The first one — hydroperoxides, decompose readily at this oxidation temperature, and the second type which are thermally more stable, includes polymer or endocyclic type peroxides (Windaus, Brauken 1928; Kucher *et al.*, 1980). Probably the oxidation of xylain yields tertiary hydroperoxides that is also confirmed by the reduced percentage of –CH$_3$ and –CH$_2$ groups (Fig. 1):
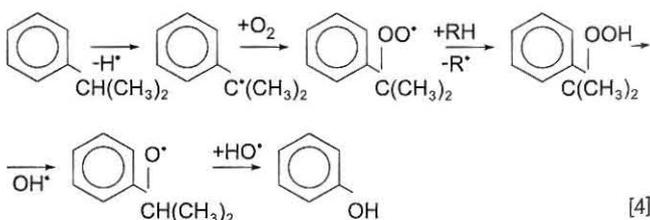
The decrease of the $-CH_3$ amount and the rise of $-CH_2$, the analytical moisture and $-OH$ groups registered for humovitrain suggests the formation of primary hydroperoxides:

[5]
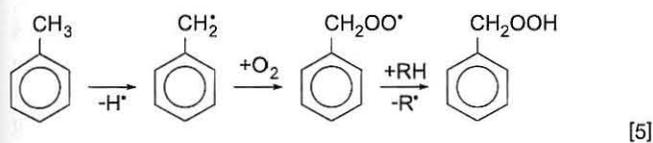
The decomposition of the thermally (at this temperature) unstable hydroperoxides could be accomplished via monomolecular or bimolecular reaction pathway:

$$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH \qquad [6]$$

$$ROOH + ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O \qquad [7]$$
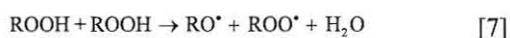
The proceeding of the above processes is also confirmed by the termination of the kinetic chain through deactivation of the free radical in the system — $R^{\cdot}$, $RO^{\cdot}$, $RO_E^{\cdot}$, ${}^{\cdot}OH$ at the addition of an inhibitor — phenol and aniline (Rustchev, Jetscheva-Markova, 1969; Rouschev et al., 1975; Markova, 1976).

The results from the IR and functional analysis together with the data obtained in our earlier investigations (Rouschev et al., 1975; Markova, 1976, 1989; Markova, Petrova, 1984; Saranchuk et al., 1994) indicate that peroxides play the role of intermediates in the process of further molecular products formation:

$$ROOH \rightarrow R'COR'' \qquad [8]$$

$$ROOH + RH \rightarrow 2ROH \qquad [9]$$

Simultaneously, the phenol and carbonyl groups, present in the coal macromolecule, are further oxidized as shown below:

$$ROH + O_2 \rightarrow R'COR'' + H_2O \qquad [10]$$

$$R'COR'' \rightarrow acidis \qquad [11]$$
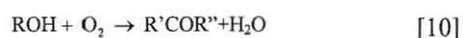
The data from the ultimate analysis (Fig. 1) combined with the kinetics of the oxygencontaining functional groups alterations as well as some of the ESR results, i.e. the PMC concentration and the ESR signal linewidth (Markova et al., 1993), point out that reactions [8] and [10] are dominating for xylain and lead to higher concentrations of >CO groups. Simultaneously, the amount of $-OH$ increases, too. For humovitrain in addition to the two reactions typical for xylain, proceeding to a lesser extent, the reactions yielding acids [11] take place with a higher rate. The change of the content of oxygen-containing groups suggests that the humovitrain autooxidation concerns mainly the phenol groups which are further converted into carboxyl ones. The reduced content of $-CH_3$ groups for this lithotype suggests the formation of oxygencontaining cyclic structures of phthalate type:

[12]
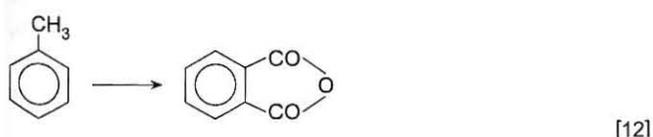
The increase in the PMC during humovitrain oxidation (Markova et al., 1993), the higher amount of $-OH$, >CO and $-CH_2$ functional groups in its macromolecules, as well as the reduced $-CH_3$ amount and the increased aromaticity confirm the proceeding of rearrangement processes of aroxyl radicals into benzyl one. The latter undergo dimerization and oxidation giving quinones:

[13]
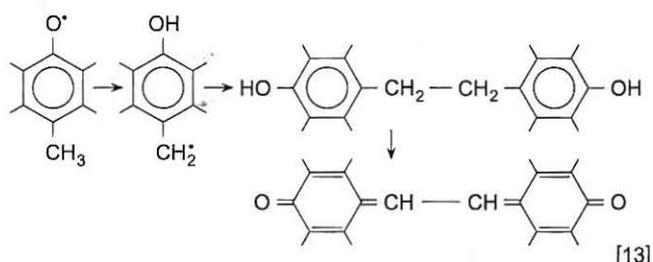
Thus, it may be concluded that the first product of the microbial-oxidative destruction of the lignin-cellulose tissues, i.e. xylain, composed mainly of textinite (Table 2) with preserved lignite matrix partially filled with resinite (Šiškov, 1988), is oxidised predominantly to >CO containing products. The increased content of $-OH$ groups may be related to the formation of tertiary hydroperoxides which precursors are the tertiary carbon atoms of textinite.

The rearrangement of the aroxyl radicals into benzyl ones followed by dimerization and oxidation to quinones after reaction [13] is also relatively intensive. The xylain oxidation leads to the formation of relatively unstable structures which is also confirmed by the lower value of the activation energy.

The final product of the microbial-oxidative destruction of the lignin-cellulose tissues, i.e. humovitrain, is oxidised less intensively than xylain. Its autooxidation is characterised by the formation of primary hydroperoxides, hydroxyl (phenol) and carboxylic groups. The rearrangement of the aroxyl radicals into benzyl ones with their consecutive dimerization and oxidation is also registered. The autooxidation process, similarly to that of xylain, occurs with a high intensity which is probably related to destructive reactions resulting in water liberation (Kasatochkin, Larina, 1975).

The first member of the second genetic series, semifusain — fusain, resulting from the thermooxidative processes, consists of partially preserved lignin-cellulose tissues and resinite and a higher content of oxygencontaining functional groups. At 150°C, its carbonyl groups are predominantly oxidized to carboxyl ones via reaction [11]. These oxidation steps are accompanied by the occurrence of destructive reactions which comprise a part of the non-functional oxygen. This assumption is supported by the reduced percentage of aromatic hydrogen and carbon, and the $-CH_3$ groups formation (Fig. 1) (Hofmann, 1963; Saranchuk et al., 1994).

The end member of this genetic series — fusain, differs by its mechanism of oxidation from the other lithotypes. Its peculiar biphenyl structure (Markova et al., 1993; Markova, Budinova, 1996) and the higher content of carbonyl groups in the oxidized samples (Fig. 1) point that the oxidation takes place through the following reaction: