

REMOVAL OF POLLUTANTS FROM POOR QUALITY COALS BY PYROLYSIS

by

**George E. SKODRAS, Panagiotis NATAS, Panagiotis BASINAS, and
George P. SAKELLAROPOULOS**

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Combustion of poor quality coals and wastes is used today worldwide for energy production. However, this entails significant environmental risks due to the presence of polluting compounds in them, i. e. S, N, Hg, and Cl. In the complex environment of combustion these substances are forming conventional (i. e. SO_x, NO_x) and toxic (PCDD/Fs) pollutants, while, the highly toxic Hg is volatilised in the gas phase mainly as elemental mercury. Aiming to meet the recently adopted strict environmental standards, and the need of affordable in cost clean power production, a preventive fuels pre-treatment technique, based on low temperature carbonization, has been tested. Clean coals were produced from two poor quality Greek coals (Ptolemais and Megalopolis) and an Australian coal sample, in a lab-scale fixed bed reactor under helium atmosphere and ambient pressure. The effect of carbonization temperature (200-900 °C) and residence time (5-120 minutes) on the properties of the chars, obtained after pyrolysis, was investigated. Special attention was paid to the removal of pollutants such as S, N, Hg, and Cl. To account for possible mineral matter effects, mainly on sulphur removal, tests were also performed with demineralized coal. Reactivity variation of produced clean coals was evaluated by performing non-isothermal combustion tests in a TA Q600 thermogravimetric analyser. Results showed that the low temperature carbonization technique might contribute to clean coal production by effectively removing the major part of the existing polluting compounds contained in coal. Therefore, depending on coal type, nitrogen, mercury, and chlorine abatement continuously increases with temperature, while sulphur removal seems to reach a plateau above 500-600 °C. Moreover, the prolongation of carbonization time above 20 minutes does not affect the elemental conversion of the pollutants and carbonization at 500-600 °C for ~20 minutes may be considered sufficient for clean coal production from poor quality coals. Clean coal production at higher pyrolysis temperatures results in observed higher initial combustion temperature, mainly due to lower volatile content in produced chars.

Key words: coal, carbonization, clean coal, pollutants removal, reactivity

Introduction

Coal combustion is used today worldwide for energy production, but it results in significant releases of polluting compounds in the atmosphere. Elements such as S, N, Cl,

and Hg, inherent in coals, are responsible for the formation and release of pollutants (*i. e.* NO_x, SO_x, Hg⁰, PCB, PCDD/F *etc.*) during coal combustion and due to equipment corrosion. Therefore, efficient technologies are necessary to control emissions from coal-based power plants and, thus, to meet stringent environmental regulations. However, end-of-pipe technologies are costly and not as efficient as required. The preventive removal of polluting elements, inherent in coals, could be a viable alternative route for cleaner coal production and through that energy generation of lower emissions.

Sulphur in coals is found in inorganic and organic form, while nitrogen is mainly bounded in heterocyclic compounds [1]. Under mild pyrolysis conditions (below 550 °C) the pyritic sulphur is released mainly in the form of H₂S, while fuel-nitrogen as HCN, NH₃, tar-N *etc.* [2]. Due to its low boiling point (356 °C) mercury could be removed in the same conditions, while the removal of chlorine depends on its form and the nature of coal [3]. The literature shows that chlorine is mainly released as hydrogen chloride during heat-treatment of coal in an inert atmosphere or under combustion conditions [4]. Coal pyrolysis is a key step in various coal conversion processes. Coal pyrolysis has recently received attention not only as an important intermediate stage in coal gasification, combustion and liquefaction, but also as a simple and effective method for the production of coal free, at least partly, of its inherent polluting elements [5]. Additionally, clean coals are characterized of improved quality due to moisture removal during pyrolysis stage.

Char reactivity has an important effect on the degree of carbon burnout, which is of major importance from an environmental and economic point of view [6]. Reactivity is defined as the rate at which coal reacts in an oxidizing atmosphere, subsequent to devolatilisation. The coal rank exerts a major constraint on char reactivity, with low rank chars being typically more reactive than those prepared from high rank coals [7].

In this work, pyrolysis efficiency in removing polluting elements (*i. e.* S, N, Hg, and Cl) from three coals samples was investigated. The effects of raw material type, temperature, residence time, and mineral matter were considered. The effect of pyrolysis temperature and residence time on char reactivity was investigated, too.

Experimental

Two poor quality Greek coals from Ptolemais and Megalopolis reserves and an Australian coal were used as raw materials. To account for the possible effects of the inorganic matter on sulphur removal tests were also performed with demineralized Ptolemais lignite. A three-staged acid treatment procedure [8] was employed. Prior to use samples were dried at 105 °C in a N₂ atmosphere for 24 hours, while the desired size range (150-250 μm) was obtained by grinding and sieving. Proximate and ultimate analysis of the raw samples is given in tab. 1, along with their mercury and chlorine content.

Pyrolysis experiments were performed in a lab fixed bed reactor at ambient pressure, under helium flow at temperatures between 200 and 900 °C and 5 to 120 minutes residence time. The pyrolysis procedure and equipment is described in details elsewhere [9]. The obtained chars were characterized by standard methods. Proximate analysis was carried out according to ASTM standard method D 3172-89. A ThermoFinnigan CHNS

Table 1. Proximate and ultimate analysis of the raw samples

Samples	Proximate analysis [wt.% dry basis]				Ultimate analysis [wt.% dry basis]				Cl [μg/g]	Hg [μg/g]
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S		
Ptolemais lignite	56.82	44.84	35.17	19.99	48.55	4.17	1.48	0.72	129.2	0.185
Megalopolis lignite	61.2	34.5	25.6	39.9	29.53	2.80	1.17	2.61	216.3	0.175
Austalian coal	2.47	40.63	47.69	11.68	71.66	5.42	1.57	2.86	179.5	0.37
Demineralized Ptolemais lignite	4.0	51.35	47.59	1.06	60.02	4.36	1.86	1.05	2979.5	0.18

EA1112 elemental analyzer was used to obtain the elemental composition (C, N, H, and S) of the chars. ASTM D 4208-88 and EPA 7471A standard methods determined chlorine and mercury contents of the chars, respectively. The increased chlorine content of demineralized Ptolemais lignite is attributed to the acid treatment that includes the use of 12M HCl acid. The elemental removal of S, N, Hg, and Cl, during coal pyrolysis, was calculated according to the following equation [10]:

$$ER\% = \frac{E_{t\text{ coal}} - E_{t\text{ char}}}{E_{t\text{ coal}}} \frac{(\text{Char conversion})\%}{100} \quad (1)$$

where: $ER\%$ is the elemental removal of N, S, Hg, and Cl; $E_{t\text{ coal}}$ – the total N, S, Hg, and Cl of raw coal; $E_{t\text{ char}}$ – the total N, S, Hg, and Cl of char. Pyrolysis conversion was calculated with the following equation:

$$\%(\text{Char conversion}) = \frac{W_0 - W_1}{W_0} 100 \quad (2)$$

where: W_0 is the weight of the coal (dry basis) at the beginning, and W_1 is the weight of the residue after pyrolysis.

For the thermogravimetric (TG) tests, a TA Instruments thermogravimetric analyser (TGA) simultaneous differential scanning (DSC) thermobalance (SDT Q600) was used. To avoid any interference in measurements accuracy, 20 μg of each char were loaded in an alumina crucible and placed on the thermobalance beam. Respal air with 20% oxygen content was applied for all the combustion tests. All samples were heated at the constant rate of 20 °C/min. from ambient temperature to 1000 °C with the constant airflow rate of 100 ml/min.

Results and discussion

Elemental conversion

During pyrolysis, coal is converted into solid product char. Figure 1 shows the effect of temperature on conversion of the chars. For all samples pyrolysis temperature increase results in higher conversion. For Ptolemais (raw and demineralized) and Megalopolis coals an almost linear increase of conversion with temperature is observed, while for Australian coal a sigmoid shape is observed at low temperatures (<450 °C), whereas char conversion reaches a plateau for higher temperatures.

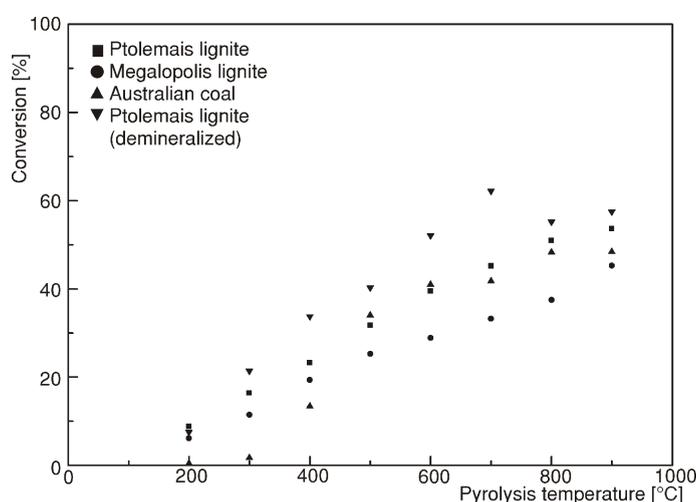


Figure 1. Effect of pyrolysis temperature on the conversion of the chars

The proximate analysis (dry basis) of chars pyrolyzed at different temperatures for a residence time of 20 minutes is given in figs. 2 and 3. Commenting on the behaviour of coal conversion, the volatile content of Ptolemais (raw and demineralized) and Megalopolis coals decline almost linearly with pyrolysis temperature, while the fixed carbon content increases the same way. For Australian coal volatile and fixed carbon contents seem to reach a plateau above 600 °C.

Figure 4 shows that elemental carbon conversion during pyrolysis of the various fuels follows the behaviour of char conversion (fig.1). At low temperatures elemental carbon conversion is quite low reflecting the limited char conversion observed. In the temperature region from 500 to 600 °C elemental carbon conversion varies from 20% to 35% w/w. At higher temperatures it is enhanced and reaches up to ~50% w/w, depending

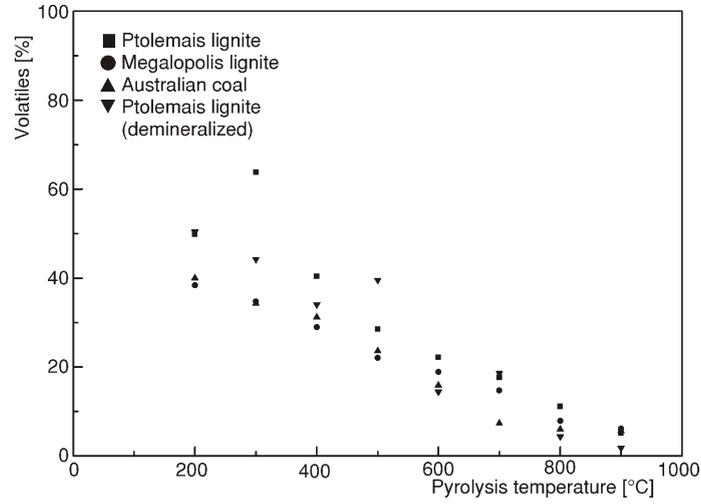


Figure 2. Effect of pyrolysis temperature on the volatiles of the chars

on the carbon content and the chemical structure (*i. e.* volatiles, fixed carbon) of the parent material. Thus sufficient carbon remains in the clean coal fuel produced.

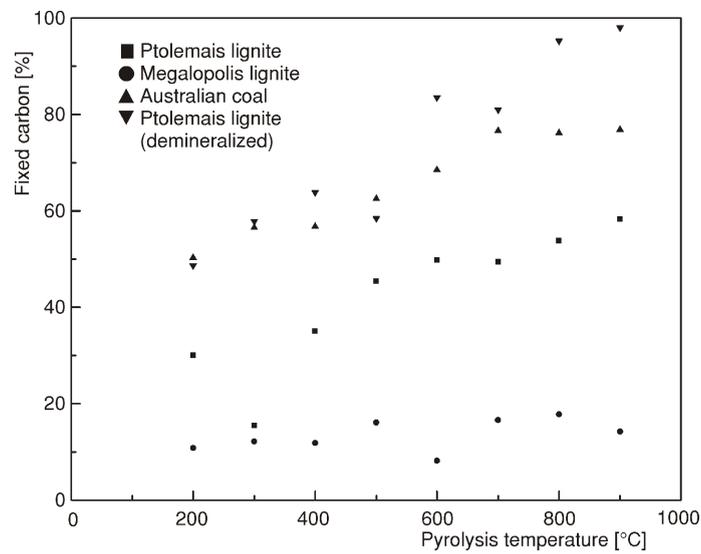


Figure 3. Effect of pyrolysis temperature on the fixed carbon of the chars

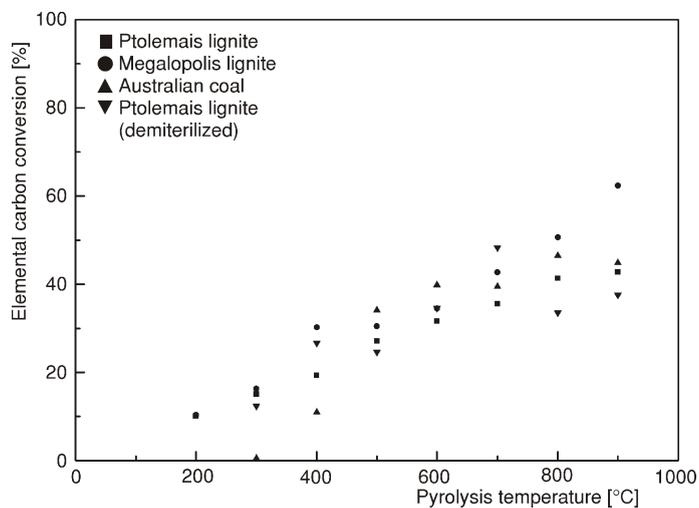


Figure 4. Effect of pyrolysis temperature on elemental carbon conversion of the chars

The elemental hydrogen conversion during pyrolysis is indicatively given in fig. 5. At low temperatures is quite low, but it increases significantly with temperature and reaches quite high values. In all cases it is almost double the conversion of elemental car-

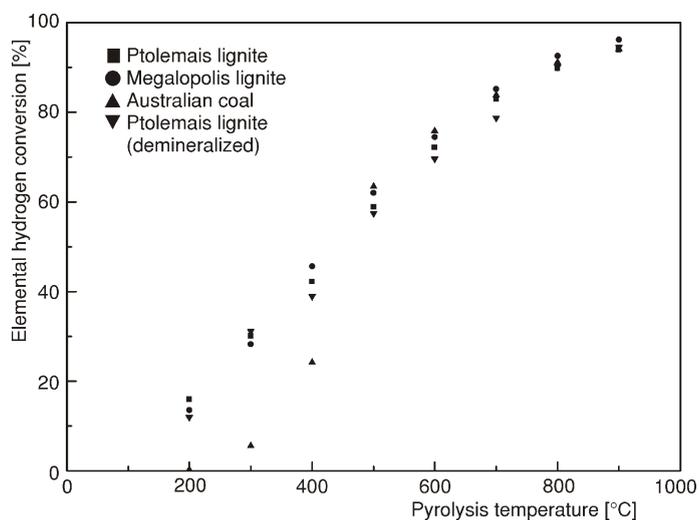


Figure 5. Effect of pyrolysis temperature on elemental hydrogen conversion of the chars

bon. This indicates that char rich in carbon is obtained, while the C/H ratio increases significantly.

Elemental nitrogen conversion during pyrolysis is also concerned. Indicative results are given in fig. 6. As far as elemental carbon conversion, at low temperatures nitrogen conversion is low (less than 10%) and increases at higher temperatures. Between 500 to 600 °C 30-40% of the initial fuel nitrogen can be effectively removed by low temperature carbonization, and thus the potential for NO_x formation during coal combustion is reduced.

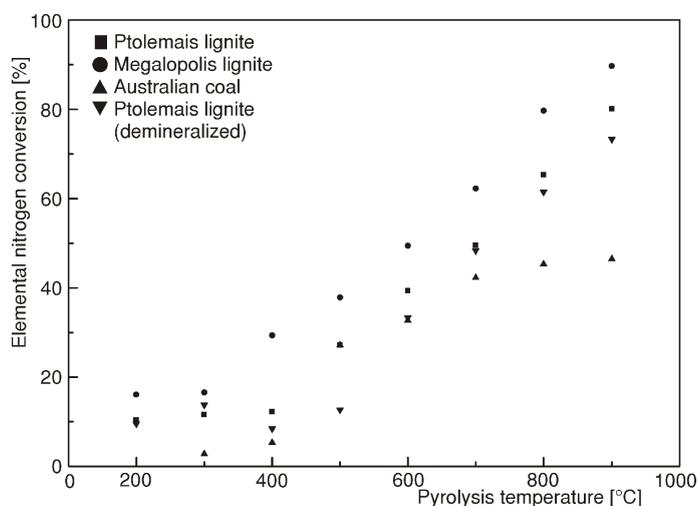


Figure 6. Effect of pyrolysis temperature on elemental nitrogen conversion of the chars

Elemental sulphur is also converted during pyrolysis and indicative results are given in fig. 7. At low pyrolysis temperatures sulphur conversion is low and increases as pyrolysis temperature increases. For Ptolemais lignite sulphur conversion increases continuously up to 400 °C and it seems to reach a plateau at about 450-550 °C. At higher temperatures discrepancies are observed, indicating that reaction of sulphur with Ca may occur, with the latter being present in high amounts in the Ptolemais lignite ash.

To account for possible effects of the inorganic matter, tests were performed also with demineralized Ptolemais lignite. Demineralization enhances sulphur removal, through pyrolysis, presumably due to the removal of inorganic sulphur during the acid pre-treatment of the coal. Furthermore, sulphur could not react with Ca, since the latter has previously been removed. The elemental sulphur conversion of the Megalopolis lignite does not increase considerably in the temperature range of 400-700 °C, while the sulphur removal of the Australian coal increases continuously up to 600 °C and reaches a plateau for higher temperatures. The extent of sulphur removal, however, depends on the properties of the parent fuel and particularly its ash content and chemical composition.

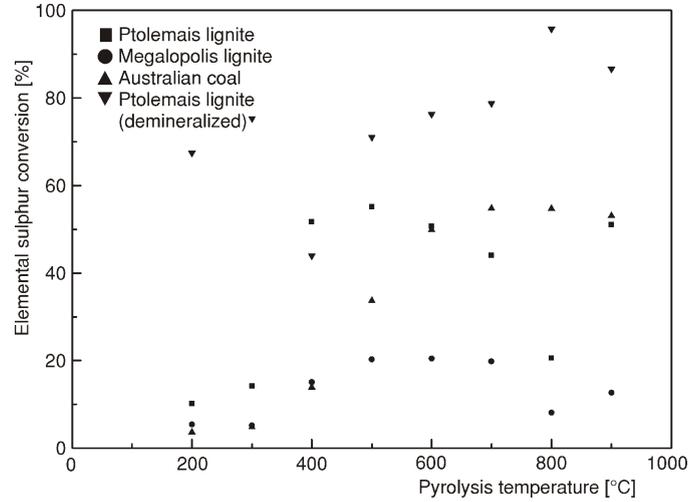


Figure 7. Effect of pyrolysis temperature on elemental sulphur conversion of the chars

Pyrolysis seems to offer a viable solution in preventive removal of mercury and chlorine from solid fuels prior to its use in solid fuel combustion power plants. Some of the results obtained are given in figs. 8 and 9. Elemental mercury conversion increases al-

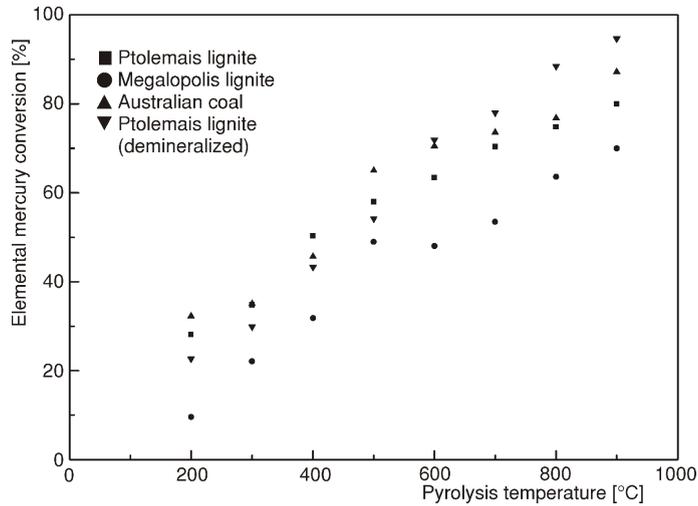


Figure 8. Effect of pyrolysis temperature on elemental mercury conversion of the chars

most linearly with pyrolysis temperature, while very high conversions are achieved at higher temperatures (up to 70% above 800 °C). About 40 to 55% and 55 to 65% of the initial elemental chlorine present in the Megalopolis lignite and Australian coal, respectively, is removed in the temperature region 400-700 °C.

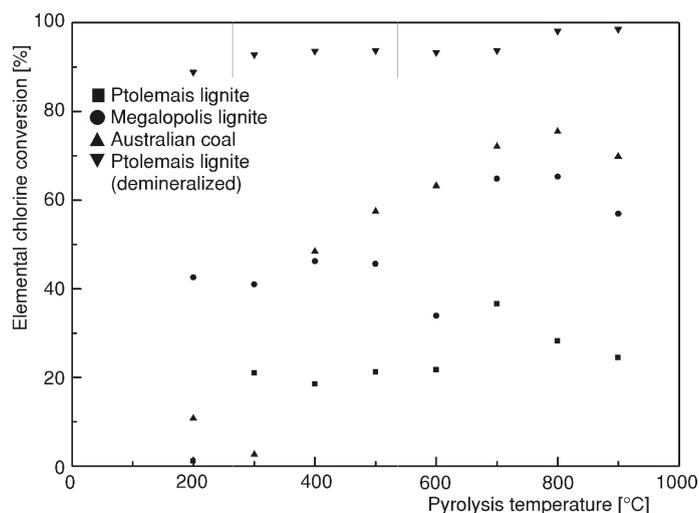


Figure 9. Effect of pyrolysis temperature on elemental chlorine conversion of the chars

However, relatively limited chlorine conversion, ~20 to 30%, was observed for Ptolemais lignite, in contrast with the demineralized Ptolemais lignite in which extremely high values, ~90%, were observed, indicating possible relation with the removal of inorganic matter.

The effect of pyrolysis residence time was studied by performing tests with Ptolemais lignite at 600 °C for various times (5-120 minutes). Char conversion is only slightly affected by the pyrolysis residence time due to the fact that fast pyrolysis reactions are completed in the first few minutes as shown in fig. 10.

Elemental nitrogen conversion reaches a plateau at ~20 minutes pyrolysis time (fig. 11). No systematic behaviour was observed for elemental sulphur conversion with pyrolysis time (fig. 12), however, it seems not to be affected by the prolongation of residence time during pyrolysis. At low pyrolysis times (up to 15 minutes) elemental mercury conversion, increases and seem to plateau at about 20 minutes residence time (fig. 13). At longer pyrolysis time elemental mercury conversion remains unaltered.

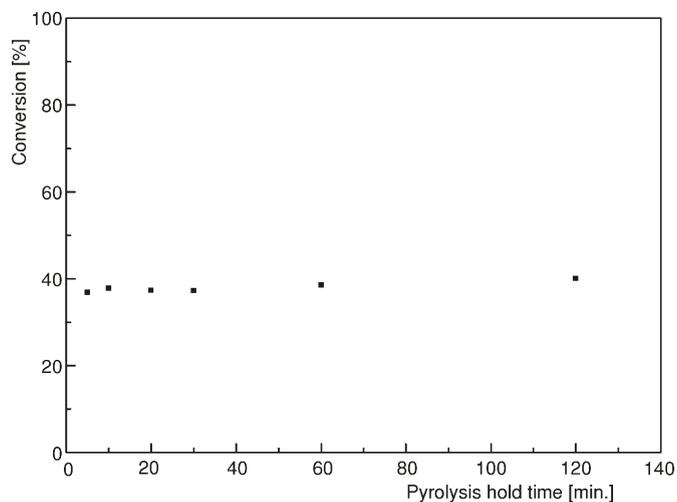


Figure 10. Effect of pyrolysis residence time on the conversion of Ptolemais chars

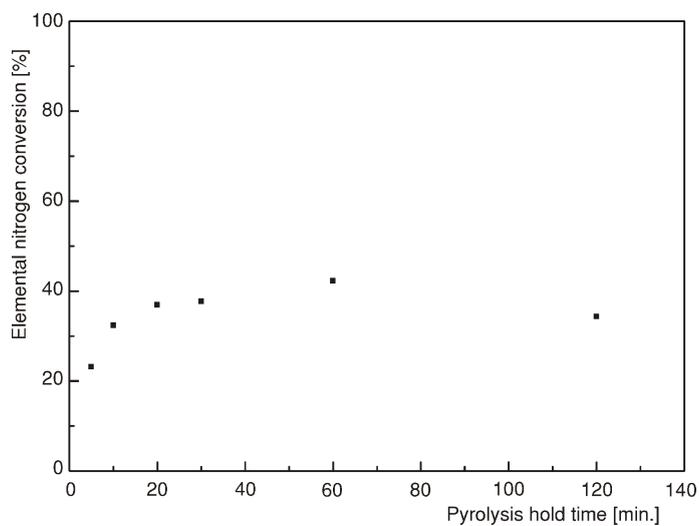


Figure 11. Effect of pyrolysis residence time on elemental nitrogen conversion of Ptolemais chars

Char oxidation

Ptolemais lignite is the most important energy source in Greece and possesses a special place in the domestic energy system since it is the main fuel for electricity produc-

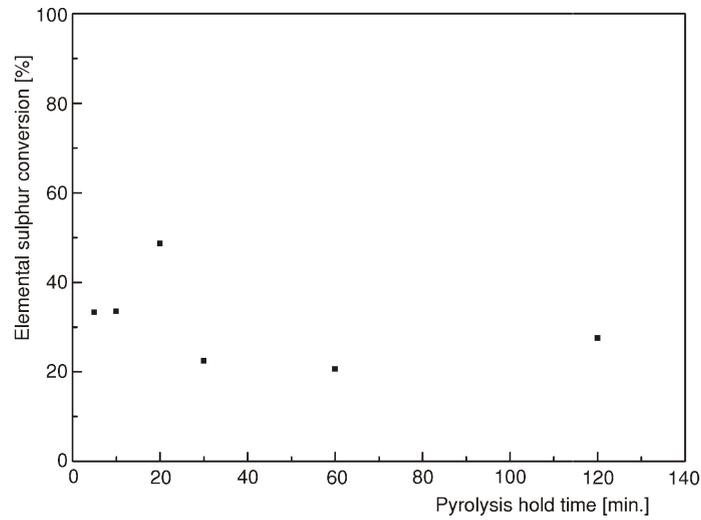


Figure 12. Effect of pyrolysis residence time on elemental sulphur conversion of Ptolemais chars

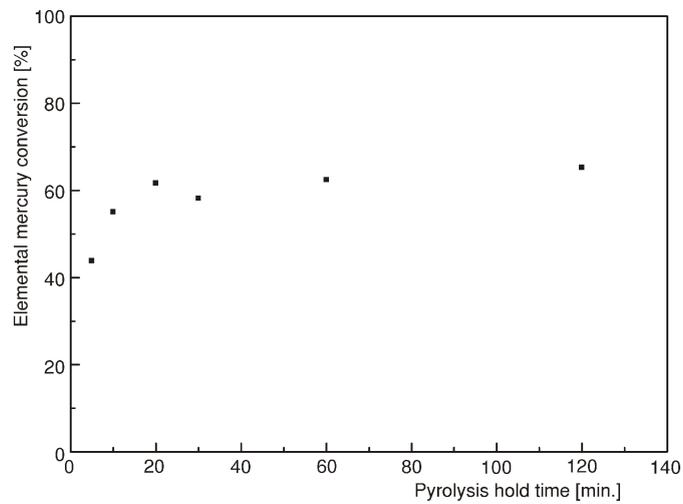


Figure 13. Effect of pyrolysis residence time on elemental mercury conversion of Ptolemais chars

tion. For that reason the combustion behaviour of the partially pyrolyzed chars originated by Ptolemais lignite was investigated by thermogravimetry.

Char reactivity in oxygen atmosphere is strongly affected by the pyrolysis conditions at which chars prepared. It is well established that significant variations occurred

between the differential thermogravimetric (DTG) profiles of pure fuels and their chars [11-13] with the former being more reactive than the partly burned chars.

Because of the findings reported in these earlier studies chars from Ptolemais lignite were prepared from 200 to 900 °C and examined under oxidative conditions for kinetic evaluation. The representative results for the specific Greek lignite are exhibited at figs. 14 and 15.

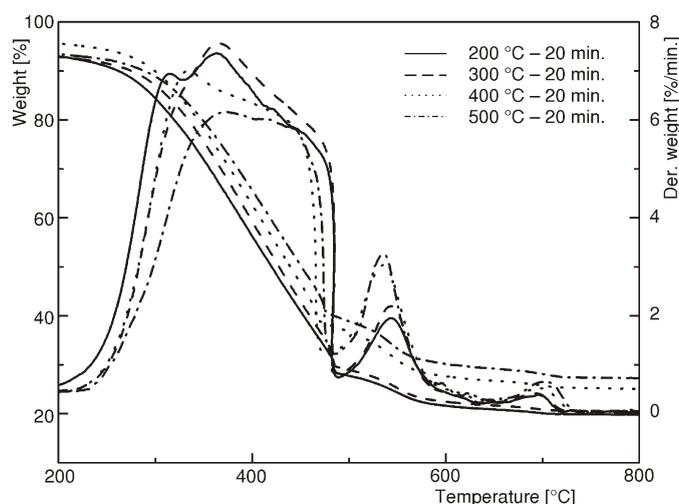


Figure 14. Weight loss and rate of weight loss as a function of temperature for the combustion of Ptolemais lignite chars prepared at 200-500 °C for 20 minutes

The figures illustrate that chars prepared at higher pyrolysis temperature showed lower conversion and an increase of temperatures at which the combustion occurred. The time – temperature history of the pyrolysis has been reported by many authors [13-15] to exhibit strong effect to the char reactivity. This finding agrees also well with the results of Sentorun *et al.* [11] who attributed the increase of the combustion temperatures to the volatile matter reduction and to the ash components increment, taking place during the carbonization stage. It may also be noted that temperatures at which combustion of the chars started, increased in respect to the temperatures that partially pyrolyzed samples were generated.

The temperature at which chars produced also provoked an inversely proportional decrease of the total conversions as presented by the TG curves. Furthermore, as fig. 14 and 15 illustrate, for the combustion of Ptolemais chars produced up to 600 °C for 20 minutes, a second peak appears between 500 to 600 °C. This peak was annihilated at the DTG profile of Ptolemais chars generated at 800 and 900 °C for 20 minutes giving rise to a unique peak at the temperature region of 300-600 °C. In order to establish a veri-

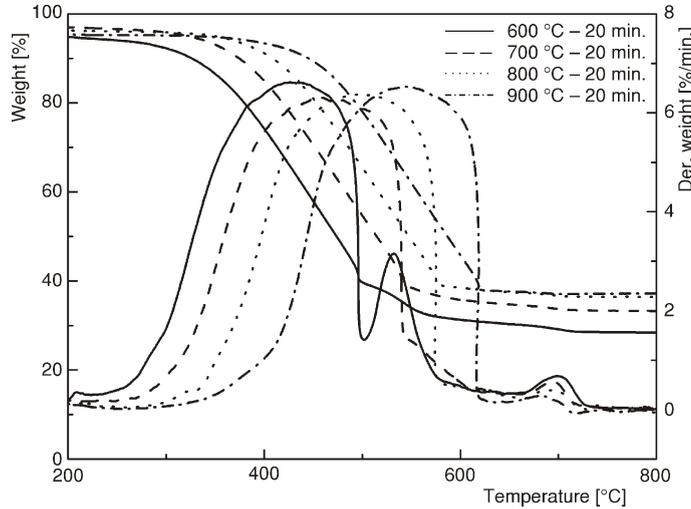


Figure 15. Weight loss and rate of weight loss as a function of temperature for the combustion of Ptolemais lignite chars prepared at 600-900 °C for 20 minutes

fication of the reactivity the method used by Russell *et al.* [16] was employed. According to this model the pre-exponential factor of the Arrhenius equation was used to characterize the reactivity of each sample. From the mathematical point of view char reactivity was defined as $\ln A_0$ which arise by the equation:

$$\frac{dW}{dt} = A_0 e^{-\frac{E}{RT}} W \quad (3)$$

where A_0 is the pre-exponential factor at 50% conversion and E should be constant (130 kJ/mol). Russel *et al.*, showed that many coals had activation energies near this value. T is the temperature in K and R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$). Figure 16 shows the correlation between the reactivity and the combustibles (fixed carbon and volatiles) in the generated chars. Increased reactivities were observed for chars with increased volatile and fixed carbon content. As reported above, it is already well known that pyrolysis temperature strongly affect in inversely proportional manner mainly the volatile content of the partly pyrolyzed chars. These observations confirm the previously discussed reactivity decrease in respect to the char generation temperature.

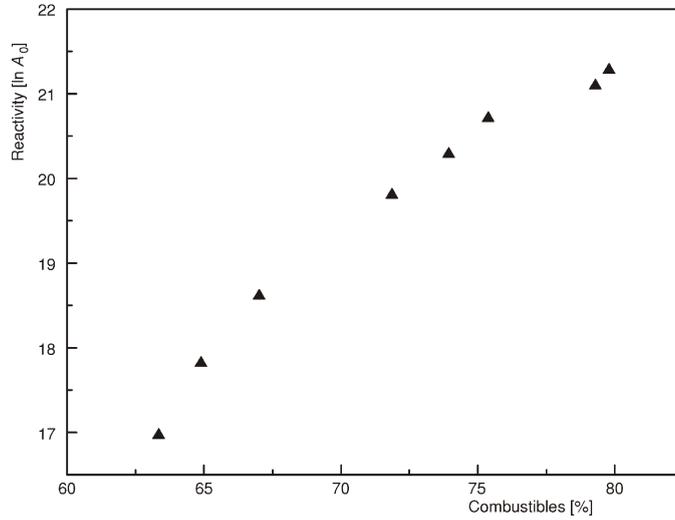


Figure 16. Reactivity of Ptolemais lignite as a function of combustibles (fixed carbon and volatiles) concentration in chars

As already mentioned, pyrolysis time affect the characteristics of the produced chars. Figure 17 provides the TG/DTG curves obtained from the combustion of

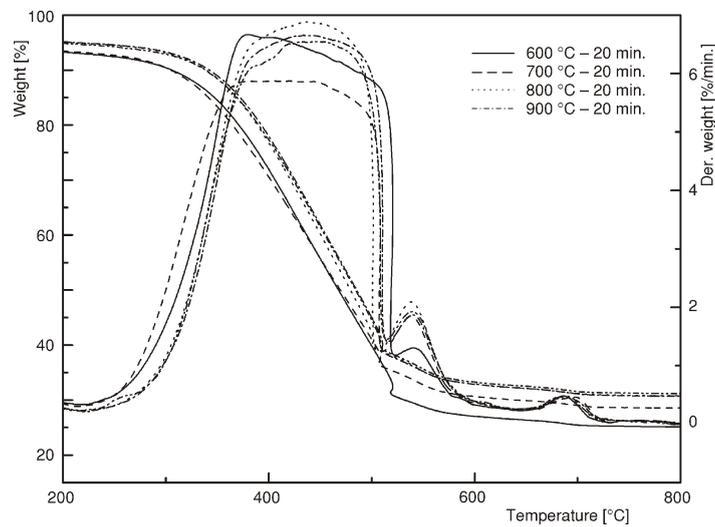


Figure 17. DTG curves as a function of temperature for the combustion of Ptolemais lignite chars prepared at 600 °C for various times

Ptolemais chars generated at constant temperature (600 °C) for various times ranging from 5 up to 120 minutes.

As it is clearly shown two main combustion behaviours could be ascribed. The first refers to the combustion of chars generated by the pyrolysis of Ptolemais lignite in short time intervals and the ones produced at higher pyrolysis residence times. In general, chars obtained at 600 °C and lower pyrolysis times (5 and 10 minutes) appear to be more reactive than the others partially pyrolyzed at elevated times. It may also be noted that the chars prepared at 5 and 10 minutes exhibited higher total conversions than the others generated at higher pyrolysis times. The latter presented almost the same conversions. As fig. 17 outlines three combustion stages could be distinguished. The first one is takes place between ~300 and 500 °C and is represented by the highest shoulder of the DTG curve. Lower conversions are observed for the second (~500-600 °C) and the third (650-700 °C) combustion stages. In the first and second stages chars presented the same combustion behaviour. At the third region DTG curves of all the chars coincided reflecting that combustion at about 700 °C is not affected by the pyrolysis time variation. In essence, combustion time seems to have a little effect to the combustion behaviour of Ptolemais chars.

Conclusions

Low temperature carbonization is an effective option for clean coal production by removing a significant amount of the existing polluting compounds contained in coal, although slight reduction of the produced char's reactivity was observed. The latter is concluded from TGA combustion experiments performed with chars produced from Ptolemais lignite. Produced char reactivity is mostly affected by the carbonization temperature conditions. As pyrolysis temperature increased, higher peak temperatures were observed reflecting the reduced reactivity of the samples. Carbonization time seems to have a minor effect on char reactivity. Moreover, the prolongation of carbonization time above 20 minutes does not affect the elemental conversion of the pollutants. Thus, carbonization conditions of 500-600 °C and ~20 minutes may be considered sufficient for clean coal production from poor quality coals.

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Authors' addresses:

G. E. Skodras^(1,2,3), *P. Natas*⁽³⁾, *P. Basinas*⁽³⁾, *G. P. Sakellaropoulos*^(2,3)

¹ Institute for Solid Fuels Technology and Applications,
Ptolemais, Greece

² Laboratory of Solid Fuels and Environment,
Chemical Process Engineering Research Institute,
Thermi, Thessaloniki, Greece

³ Chemical Process Engineering Laboratory,
Aristotle University of Thessaloniki,
Thessaloniki, Greece

Corresponding author (G. E. Skodras):

E-mail: skodras@vergina.eng.auth.gr

P. O. Box 1520, 54124 Thessaloniki, Greece

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