

THERMOGRAVIMETRIC STUDY OF THERMAL AND OXIDATIVE PROCESSES OF A LOW RANK GREEK COAL

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ABSTRACT

The aim of the work was to investigate the thermal and oxidative processes relevant to combustion of a Greek Lignite.

Non isothermal thermogravimetric analysis coupled with DSC and analysis of evolved gas by MS was carried out on the raw coal under both inert and oxidizing conditions in order to study pyrolysis and oxidative pyrolysis and on pre-pyrolysed char in order to study the combustion process.

Appropriate kinetic models were proposed for each reactive process under investigation and the relative kinetic parameters were evaluated.

Results are analysed in order to assess the network of pyrolytic/oxidative reactions that is most suitable to describe the behaviour of Greek Lignite upon heating in a combustion environment.

Topical area: Combustion of Solid Fuels

Keywords: 1. Pyrolysis; 2. Combustion; 3. Lignite.

INTRODUCTION

Brown coals constitute the major energy resource in Greece. Of the 6.7 billion tons of proven reserves, 3.85 billion tons are minerable, while indicated reserves amount to 1.6 billion tons and inferred reserves are estimated at 2.3 billion tons. The annual lignite production is over 63.5 million tons, which makes Greece the second-largest lignite producer in the European Community market¹. This amount covers 70% of the demand for electricity production; however, it is characterized by high ash contents (30-50%), which results in a lower availability and a higher running cost of the plants as well as in environmental pollution.

Knowledge of the thermal behaviour and of the reactivity of a fuel in a combustion environment, is very important for the effective design and operation of the thermochemical conversion units. Past literature has extensively addressed pyrolysis and combustion of carbon rich solid materials (solid fuels), including coals, biomass and polymers. However recently Senneca et al. [2-4] have shown that the common description of pyrolysis and char combustion as sequential steps fails to describe the behaviour of some solid fuels in a combustion environment. Experiments carried out on a set of solid fuels including biomass, polymeric material and bituminous coal indicated that for some of them oxidation takes place in parallel with pyrolysis. This obviously affects the reaction times, the products yield and distribution, the patterns of heat release inside the reactors.

The present paper aims to extend the analysis to Greek Lignite. Pyrolytic and oxidative processes have been studied by means of thermoanalytical techniques. In particular non isothermal thermogravimetric analysis (TGA) was used to investigate the process of pyrolysis of Lignite coal under inert and oxidizing conditions and the process of combustion of its pre pyrolysed char. Analysis of the evolved gases by on line MS and DSC was also performed to further investigate the similarities and discrepancies of pyrolysis under inert and oxidizing conditions.

EXPERIMENTAL

A high volatile low sulfur lignite from the Ptolemais basin, in north Greece, was used in this work. Its properties are summarized in table 1. Lignite was ground and sieved to the sizes of -250 μ m before experiments.

Table 1. Proximate analysis, ultimate analysis, and calorific value of lignite on a dry basis

Volatile (%)	matter	Fixed carbon (%)	Ash (%)	C (%)	H (%)	N (%)	O (%)	S (%)	HHV (MJ/kg)
47.9		38.5	13.6	54.6	5.4	1.9	24.1	0.4	20.5

Two different experimental apparatus have been used to perform thermogravimetric analysis, namely a Perkin-Elmer thermobalance and a Netzsch STA 409 DC TG/DSC equipped with an online Bakzers MS quadrupole (0..300 a.m.u). The first apparatus was used to perform experiments of inert pyrolysis in nitrogen and of char combustion in air. The second apparatus was used to perform experiments of inert pyrolysis in He and experiments of oxidative pyrolysis with 5 and 21% oxygen in He with simultaneous analysis of evolved gas (EGA). Notably this apparatus is equipped with a special skimmer device that ensures a negligible transfer time of the product gas to the MS and therefore rules out the possibility of secondary reactions in the gas phase.

All experiments were carried out at atmospheric pressure with a gas flow rate of 50ml/min. Small masses (8-25mg) of each material were taken, in order to reduce the effects of eventual side reactions and mass and heat transfer limitations.

The experimental procedure for obtaining a typical thermogram was as follows: the sample under test was uniformly spread and weighed directly into the crucible. The temperature was increased to 110°C/150°C in order to dry the sample. After a drying period of 30min, the temperature was increased to the desired value of 850°C at the pre-selected heating rate and held constant at this value, until steady conditions were obtained. Heating rates have been varied between 5 and 100°C/min.

Experiments of char combustion were carried out in sequence with inert pyrolysis. In this case after the pyrolysis run had been completed, the furnace was cooled down to ambient temperature, the nitrogen stream was switched to air and the temperature was again increased to 850°C, until the char was completely burned.

Experiments were replicated at least twice to determine their reproducibility, which was found to be very good.

EXPERIMENTAL RESULTS

Typical thermograms obtained during inert pyrolysis, oxidative pyrolysis and char combustion are reported in figures 1-3.

The DTG curve in nitrogen (fig.1) shows a first stage of weight loss below 200°C followed by a second one in the range 200-600°C with peak at approximately 405°C. A sharper peak appears at 700°C. Notably the low temperature weight loss has not been observed in experiments where the dehumidification step was carried out at 150°C rather than 100°C, suggesting that this step was mainly due to release of water.

The DTG in air of the pre-pyrolised char (fig.2) reveals that the weight loss starts at temperatures above 350°C. A major peak is observed at approximately 430°C followed by a second peak at 510°, and of a third shallow one at 710°C.

The DTG of oxidative pyrolysis shows that the weight loss starts at 200°C with a peak at 405°C. Follows a second rather shallow peak at 510°C and a third one at 660°C.

The weight loss upon inert pyrolysis was approximately 48%. The overall weight loss upon char combustion was approximately 75%, which is equivalent to about 37% of the dry lignite. The weight loss obtained during oxidative pyrolysis was approximately 85%, indicating that both volatiles and char were depleted.

From a qualitative point of view the DTG of oxidative pyrolysis appears intermediate between that of inert pyrolysis and of char combustion. The temperature of the main peak is the same for oxidative and inert pyrolysis, but not the value of the rate of mass loss, which is higher in oxidative pyrolysis, consistently with a more severe weight loss within the same temperature range. The temperature of the second peak is the same for oxidative pyrolysis and char combustion although this peak is more pronounced in char combustion than in oxidative pyrolysis. The third peak of oxidative pyrolysis is also shallower than in char combustion and is anticipated by approximately 50°C.

Results of EGA during inert pyrolysis indicate a massive release of species with molecular weight 18 up to the 200°C. In the second large peak the molecular mass 28 becomes very evident. Attributing the mass 18 to H₂O and the mass 28 to CO a H₂O/CO molar ratio of 1:0.3 is measured throughout the experiment. Smaller amounts of other species are observed as the temperature is increased: around 400°C species with molecular weight around 60 a.m.u. and at 600°C species with molecular weight around 80-100 a.m.u. suggesting the release of alkenes first and ciclo-alkanes later. A distinct increase of the mass 2 typical of hydrogen is observed starting at 500°C up to 750°C suggesting the occurrence of a transformation within the solid matrix which opens the way to secondary pyrolysis in the last stage of weight loss at 700°C. At this temperature the MS reveals the appearance of modest amounts of species with molecular weight 202 typical of poliaromatic compounds such as pyrene.

The EGA by MS performed during oxidative pyrolysis shows an increasing contribution of CO₂. The molar ratios between the major gaseous products are reported in table 2. The MS profiles as regards these species is also reported in figure 4.

Table 2 Molar ratio of H₂O: CO: CO₂ evolved during pyrolysis and oxidative pyrolysis

Experiment	(Molar ratio in the evolved gas)
Inert pyrolysis (He 100%)	1: 0.3: 0
Oxidative pyrolysis (O ₂ 5%, He 95%)	1: 0.23: 2.62
Oxidative pyrolysis (O ₂ 21%, He 95%)	1: 0.16: 2.56

It can be observed that CO and CO₂ are released mainly in the first two peaks. Traces of the molecular weights 128-164-267 are observed in the temperature region corresponding to the first and the second peak. 112-128-202-218-228 are observed at higher temperatures. The release in H₂ observed at high temperature during the pyrolysis in nitrogen is not observed during oxidative pyrolysis. Moreover a wider variety of high molecular species is observed when pyrolysis is carried out under oxidative rather than under inert conditions.

The DSC curve for oxidative pyrolysis is also reported in figure 4. It shows two exothermic reactions in correspondence with the first two peaks and a change in slope, typical of a change in sample heat capacity in the temperature range corresponding to the third peak. The DSC curve obtained for inert pyrolysis is not reported in the figure, however a negligible heat release was observed in inert pyrolysis compared to oxidative pyrolysis.

KINETIC MODEL

An independent parallel reactions model was used to describe the kinetics of pyrolysis, oxidative pyrolysis and char combustion according to equations (1) (2) (3) and (1) (2) (4) respectively

$$m(t) = \sum_{j=1}^n c_j [1 - a_j(t)] + m_{\infty} \quad [m(0)=1] \quad (1)$$

$$-\frac{dm}{dt} = \sum_i c_i \frac{da_i}{dt} \quad i=1,2,3 \dots N \quad (2)$$

$$\frac{da_j}{dt} = A_j \exp(-E_j / RT) (1 - a_j) \quad (3)$$

$$\frac{da_j}{dt} = A_j \exp(-E_j / RT) g(P_{O_2}) (1 - a_j)^{n_j} \quad (4)$$

where, m is the sample mass normalized by the initial sample mass, n is the number of components, c_j is the fraction of combustibles or volatiles in component j , $a_j(t)$ is the reacted fraction of component j in time t and m_{∞} is the normalized amount of the solid residues at the end of the experiment (char in the end of inert pyrolysis and ash in the end of oxidative pyrolysis and char combustion).

In the kinetic analysis the nonlinear least squares algorithm was used to calculate the kinetic parameters for the reactions of inert pyrolysis and char combustion. This method identifies kinetic

parameters that minimize values of the objective function: $O.F. = \sum \left[\left(\frac{dm}{dt} \right)^{\text{exp}} - \left(\frac{dm}{dt} \right)^{\text{calc}} \right]^2$ where

$(dm/dt)^{\text{exp}}$ is the experimentally observed DTG curve and $(dm/dt)^{\text{calc}}$ is the calculated DTG curve, obtained by numerical solution of the kinetic differential equation with the given set of parameters.

The Kissinger method based on the shift of the temperature of the DTG peaks with heating rate was used instead to obtain the kinetic parameters relative to oxidative pyrolysis. Results of experiments at 5-10-20°C/min were used for this analysis.

The results of the kinetic analysis are reported in table 3. It can be noted that the kinetic parameters obtained for the major peak of inert pyrolysis are very close to those obtained for the first stage of oxidative pyrolysis. The kinetic parameters obtained for the second stage of weight loss of oxidative pyrolysis are very close to those obtained for the corresponding stage of char combustion.

Table 3. Calculated kinetic parameters for the pyrolysis and combustion of lignite.

Reaction	Reaction 1 A/A*g(pO ₂) (1/min) E (KJ/mol) c(%) n	Reaction 2 A/A*g(pO ₂)(1/min) E (KJ/mol) c(%) n	Reaction 3 A/A*g(pO ₂)(1/min) E (KJ/mol) c(%) n	Reaction 4 A/A*g(pO ₂) (1/min) E (KJ/mol) c(%) n	Reaction 5 A/A*g(pO ₂) (1/min) E (KJ/mol) c(%) n
Pyrolysis in nitrogen	5.4*10 ³ 52.5 20.7 1	1.1*10 ⁵ 77.7 23.3 1	5.9*10 ² 56.3 24.8 1	8.2*10 ¹⁹ 374.9 5.8 1	4.9*10 ³ 91.0 18.6 1
Oxidative pyrolysis with 5% O ₂ in helium	1.9*10 ⁵ 78 0.85 1	2.8*10 ⁷ 139 0.1 1	nd		
Char combustion in air	1.4*10 ¹⁰ 143.9 62.3 2.0	3.8*10 ⁷ 125.8 30.4 0.6	nd		

RESULTS AND DISCUSSION

Analysis of experimental results and of the kinetic analysis suggest that when Greek Lignite is heated in an inert environment three pyrolysis events can be identified in the low, medium and in high temperature region respectively. When Greek Lignite is heated in an oxidizing environment, typical of most thermochemical conversion units, the first process to take place appears to be the breakage of bonds and chains within the solid matter, typical of a primary pyrolysis. However the presence of oxygen induces a prompt reaction of the primary pyrolysis products with production of H_2O , CO and CO_2 and a marked exothermicity. Notably oxidation takes place within the solid matter itself since the possibility of volatiles combustion in the gas phase is ruled out by the very peculiar configuration of the experimental apparatus, which ensures a virtually zero transfer time from the sample to the MS analyser. Approximately 85% of the carbon content of lignite (both fixed and volatile) is lost by this process that can be regarded as pyrolytic and oxidative at the same time. Another 10% is lost in a second stage that can be regarded instead as a char combustion stage. A third stage is observed at higher temperatures. This last event appears to be more similar to a high temperature solid phase reaction such as aromatisation, indeed it is not exothermic, it does not produce CO and CO_2 and releases instead high molecular weight aromatic compounds.

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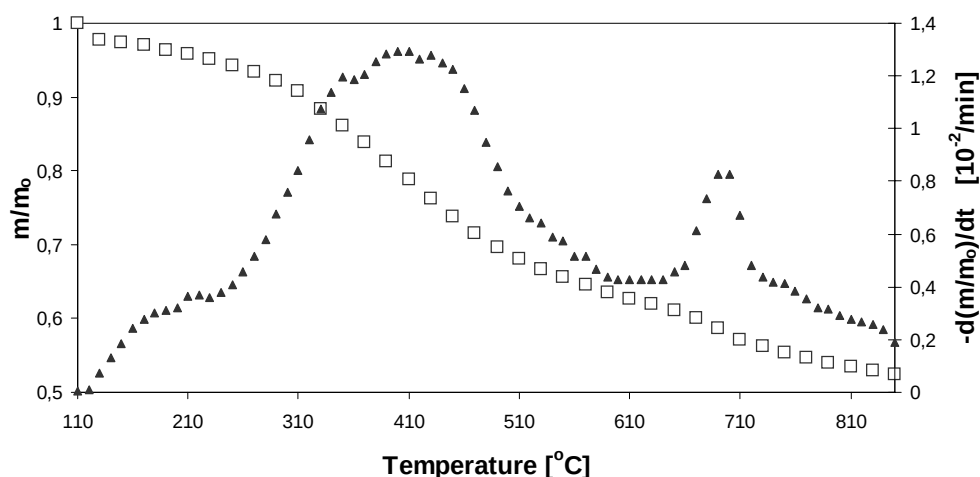


Figure 1. TG-DGT curves of lignite pyrolysis in nitrogen at 10°C/min

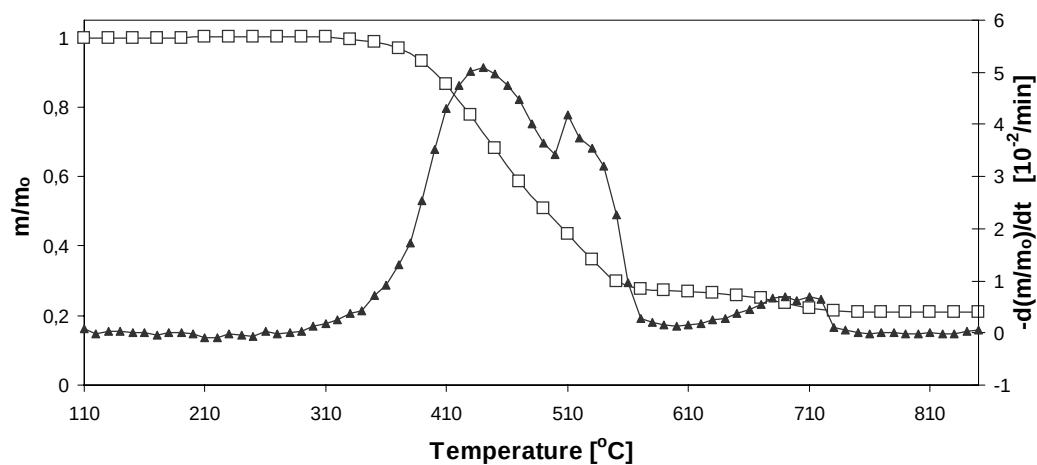


Figure 2. TG-DGT curves of combustion of lignite char in air at 10°C/min

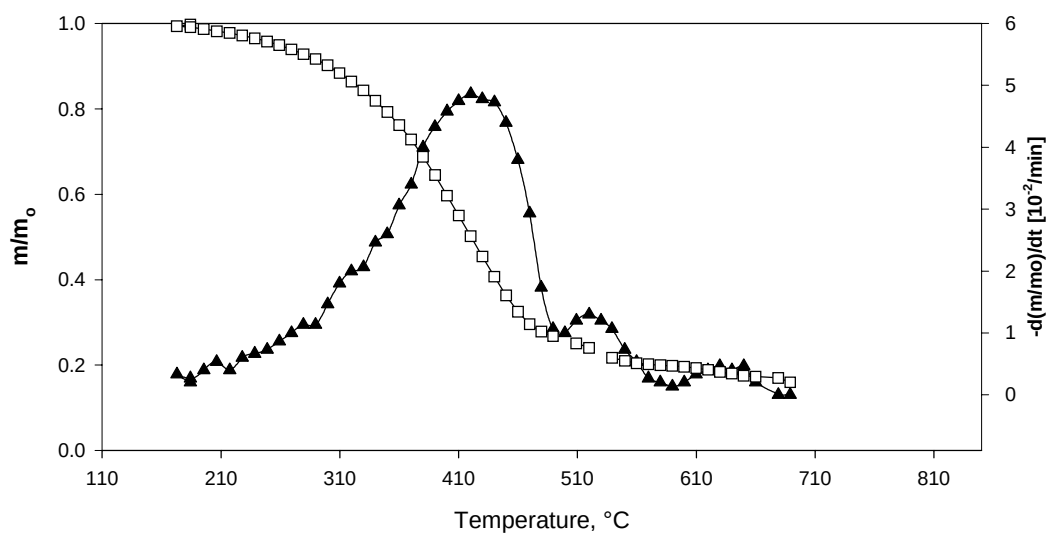


Figure 3. TG-DGT curves of oxidative pyrolysis of lignite in 5% oxygen at 10°C/min

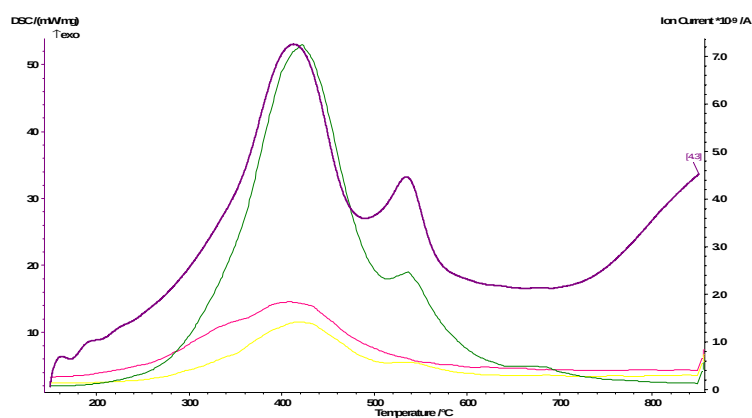


Figure 4. DGT-DSC-MS curves of oxidative pyrolysis of lignite. Purple line DS
Green line 44 a.m.u. Red line 18 a.m.u. Yellow line 28 a.m.u.