

INVESTIGATION OF THE PYROLYSIS AND GASIFICATION OF A TURKISH COAL USING  
THERMAL ANALYSIS COUPLED WITH MASS SPECTROMETRY

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**Abstract**

Clean conversion of coal into gaseous and liquid fuels and chemicals is of utmost importance along with its direct utilization via combustion in a sustainable manner. Pyrolysis is an important intermediate stage in coal combustion and gasification and also a simple and an effective method for a clean conversion of coal. Coal gasification is applied in IGCC systems for power generation and for the production of a range of fuels from hydrogen to diesel.

TA/MS (thermal analysis coupled with mass spectrometry) was applied to the pyrolysis and gasification of a Turkish coal. Pyrolysis experiments were carried out in argon atmosphere while air was used as the gasification agent. The samples were heated from room temperature up to 1000°C. The main evolved products were identified through the on-line recorded mass spectra. The thermal and evolution behavior of the coal sample was compared for selected heating rates and gas flow rates. The gas flow rate was changed between 5 and 70 mL/min whereas the heating rate was selected from 10 to 40 °C/min. Two different sample masses (5 and 10mg) were used to check any effect of the mass on the thermal analysis results.

The on-set, shape and off-set of the DTG curves combined with the evolution temperatures of the major gaseous products such as H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S and SO<sub>2</sub> clearly show differences in the thermolysis behavior at different atmospheres, gas flow rates and heating rates. These differences in thermolysis behavior indicate when and under which conditions pyrolysis and/or partial oxidation (gasification) and/or oxidation might be occurring. The TA/MS results are also indicative of the reactivity of the coal sample to the selected atmosphere at various temperatures. Results can be utilized to determine kinetic parameters via various methods. Care should be taken to avoid mass transfer limitations. The results prove that the gasification of coal consists of two major reactions: pyrolysis and gasification of in situ formed char. The rate of the latter reaction is much slower than that of the former reaction. The volume of the gasifier is therefore primarily dependent on the gasification rate of char. For this reason, kinetics of char gasification obtained by TA/MS plays a key role by providing valuable information for the proper design and operation of gasifiers.



## 1. Introduction

The qualitative and quantitative compositions of the organic and inorganic coal matrices determine in a way the thermolysis behavior of coals. Global coal reserves contain a very broad scope of coals ranging from high quality bituminous coals to low quality lignites.

Major thermolysis processes are combustion, gasification and pyrolysis [1-3]. Combustion is used to extract energy directly from coals. Gasification is a thermochemical process by which the organic coal matrix is converted to gaseous products with useable heating value; the gasification products can be further processed to liquid fuels or to chemicals. (primarily carbon monoxide and hydrogen in a controlled oxidizing atmosphere. Pyrolysis is the first chemical step in nearly all coal thermolysis processes, such as combustion, gasification and liquefaction, and has a significant influence on the subsequent process stages [4-5]. Therefore, understanding pyrolysis behavior is important in improving existing and developing new coal utilization technologies. Accurate knowledge of coal thermolysis behavior is of utmost importance in the sustainable utilization of coal.

Pyrolysis means the decomposition of coal while being heated to elevated temperature in an inert atmosphere and produces a hydrogen-rich volatile fraction which consists of gases, vapor and tar components and a carbon-rich solid residue, called char. The characteristics of the resultant char control subsequent processes, including combustion, and in particular gasification. The reactivity and kinetics of coal char with various combustion (oxygen and/or air) and gasification (air/oxygen/steam/carbon dioxide etc.) atmospheres provide valuable information and have been widely studied [6].

Thermogravimetric analysis (TG) is one of the most common techniques used to investigate the thermal events and associated conversion kinetics during pyrolysis, gasification and combustion of coals in defined atmospheres with selected heating programmes. Non isothermal TG measures the weight of a sample with respect to the change in temperature and represents a quantitative weight change associated with a thermally induced transition. In TG the loss in weight is recorded as a function of temperature or time while the derivative thermogravimetric analysis (DTG) represents the rate of mass loss based on TG data [7-10]. TG data can be used to obtain kinetic information.

Combining TG with gas-analytical techniques significantly enhances the possibilities for interpreting the formation thermolysis process products [11]. The knowledge about the temperatures and rates of formation of desired and undesired gaseous species in a given thermolysis atmosphere can be used for improving/redesigning /designing various processes such as thermal coal desulfurization, tar minimization during gasification, carbon combustion efficiency improvement, methane formation minimization, enhancement of hydrogen production etc.

The results presented here are for Soma lignite - a quite good quality Turkish lignite with 400Mtonnes reserve. Our previous and on-going TG-MS studies indicate quite different thermolysis behaviour for Turkish coals which range from high to low quality lignites .

## 2. Methodology

### 2.1. Coal

Soma lignite has a lower heating value of 4462 kcal/kg on dry basis. It has 40% volatile matter, 31% fixed carbon and 29% ash on dry basis. The total sulfur content is 1,34% again on dry basis. The comprehensive properties of Soma lignite are available elsewhere [12].



## 2.2. Gases

Argon and air are supplied by the Turkish gas company HABAS as 5 grade high purity gases (99,999% pure).

## 2.3. TG-MS System

The TG apparatus used in this study is NETZSCH Simultaneous Thermal Analyser STA 409 PC which can be operated under selected inert, oxidative and reactive atmospheres in the temperature range of 25°C-1500°C at heating rates up to 50K/min. Inert gases (N<sub>2</sub>, Ar, He), oxidative gases (air, O<sub>2</sub> enriched air, O<sub>2</sub>/air with inert gases), reactive gas mixtures (CO<sub>2</sub>/ CO /O<sub>2</sub>/inert gas/limited amounts of H<sub>2</sub>/H<sub>2</sub>S/SO<sub>2</sub>/COS ) can be used. It is also possible to introduce water vapor into the TG atmosphere with the other thermal analysis instrument – NETZSCH STA F3 Jupiter H<sub>2</sub>O.

Both TG systems are coupled with quadrupole mass spectrometers (QMS 403C). Hence, along with TG/DTG measurements evolved gases can be analysed simultaneously. The transfer lines between the TG and MS were heated to 250°C in order to avoid condensation of the gaseous products.

### 2.3.1. Parameters affecting the TG-MS measurements

Prior to coal thermolysis analyses with the TG-MS system appropriate operation parameter ranges were determined, primarily to avoid diffusion control considering kinetic studies and to achieve appropriate heat and mass transfer throughout the sample .

#### 2.3.1.1. Sample Mass

As the amount of the sample used increases, several problems may arise. The whole sample used may not come into contact with the surrounding atmosphere; e.g. in oxidative atmosphere the upper and bottom portions of the sample in the crucible may undergo different reactions. The usage of too small amounts of samples with coal can cause homogeneity related problems. In the literature, sample masses as low as of 5 mg are used for coal based thermal analysis studies [13-16]. The weight of Soma lignite for this study was kept at about 10 mg.

#### 2.3.1.2. Particle Size

If the particle size of the sample is too small, some sample can be lost during the evacuation of the TG furnace. On the other hand diffusion limitations affect measurements, if the particle size of the sample is too large. In the literature, the particle size used for thermal analysis experiments is in the range of 100-250 µm [17-22]. Soma lignite at the size of <250µm was selected for this study.

#### 2.3.1.3. Heating Rate and Temperature Programme

The main practical difference between rapid and slow heating rates is that rapid heating may reduce the time needed to attain a specified weight loss. Big differences in heating rates (1K/min and 500K/min) may also affect thermolysis mechanism. In the heating rate ranges of our studies (1-50K/min), increasing the heating rate appears to increase the on-set and off-set temperatures of thermolysis peaks rather than changing the thermolysis mechanism. Soma lignite was heated from 25°C to 1000°C at a constant heating rate of 40° C/min in this study.

#### 2.3.1.4. Thermolysis atmosphere and flow rate

In pyrolysis and inert gas containing reactive atmosphere thermolysis applications inert gases such as Nitrogen, Argon and Helium can be used. Helium has the highest thermal and mass diffusivity; the former is desired, however, the latter makes Helium the least suitable gas



giving rise to changes of the shape and intensity of the MS signal. Nitrogen and Argon are preferred to Helium due to their similar properties concerning their application in TG-MS systems in pure form or as mixtures [23]. Argon usually contains less impurity than Nitrogen and is preferred for quantitative MS applications.  $N_2$  has the same molecular mass as CO and makes CO determinations by mass spectrometry problematic [24]. In this study, Argon was used as carrier gas for pyrolysis and air as gasification atmosphere.

To determine the appropriate flow rates for Argon and air atmospheres the flow rate range of 5-70 ml/min has been covered for Soma lignite at a constant heating rate of 40K/min. The flow rate has only a minor effect on pyrolysis results; under the oxidative atmosphere changing the flow rates definitely affects the results. As the flow rate of the oxidative gas increases the thermolysis behaviour changes from gasification to combustion. A similar but definitely not so pronounced effect was observed as the heating rate decreased from 50K/min to 10K/min. Details can be found elsewhere [25].

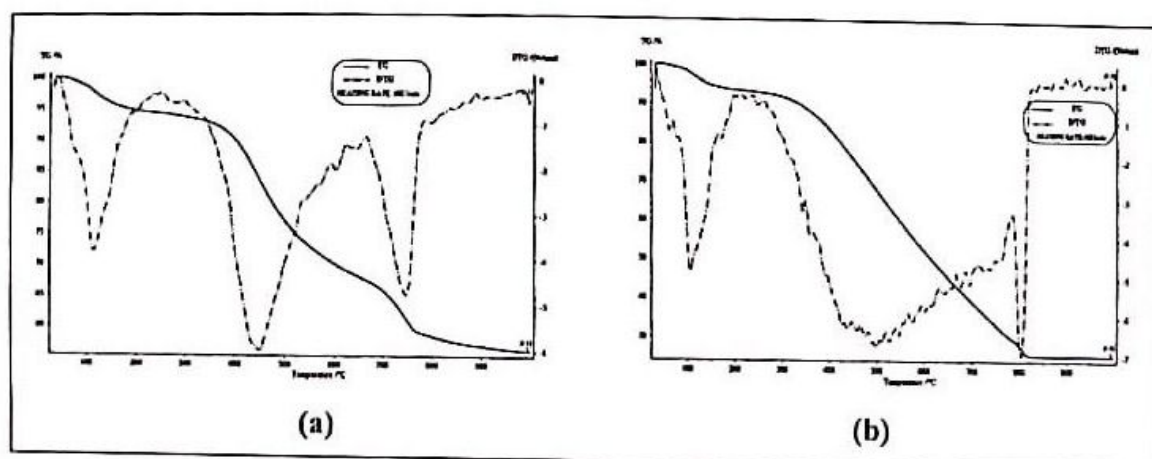
The flowrates used in the literature with oxidative atmospheres cover a broad range from 5ml/min to 100ml/min [14,26-29]. For pyrolysis, generally, flowrates in the range of 40-50 ml/min are used [7,13,30-33]. In this study the final Argon and air flow rates have been determined as 40 and 20ml/min, respectively.

#### 2.4. MS Signals

In this study the MS signals simultaneously determined along with the TG-DTG signals for the temperature range 25-1000°C are as follows: 2 ( $H_2$ ), 16 ( $CH_4$ ), 18 ( $H_2O$ ), 28 (CO), 44 ( $CO_2$ ) and 34 ( $H_2S$ ), 60 (COS) and 64 ( $SO_2$ ).

### 3. Results

Pyrolysis and air gasification TG-DTG results with Soma coal are presented in Fig. 1. Pyrolytic decomposition is observed first at 300°C and continues up to around 900°C as indicated by the TG-DTG-MS results for Soma lignite (Figures 1-3). Chemical reactions begin to occur around 250°C and end around 800°C during air gasification. Pyrolytic weight loss is much less than the weight loss of air gasification; only about 54% of the organic coal matrix is pyrolysed versus the 97% of the air gasified organic matrix. It should also be mentioned that 38% of the organic matrix of Soma lignite is converted to gaseous products up to 650°C while about 67% of the organic matrix is lost during air gasification for the same temperature interval. Moreover pyrolysis reactions leading to gaseous products appear to occur primarily in two distinct peaks while air gasification appears primarily as a very broad peak followed by a sharp one around 800°C.





**Figure 1.** Pyrolysis (a) and air gasification (b) TG-DTG results for Soma lignite

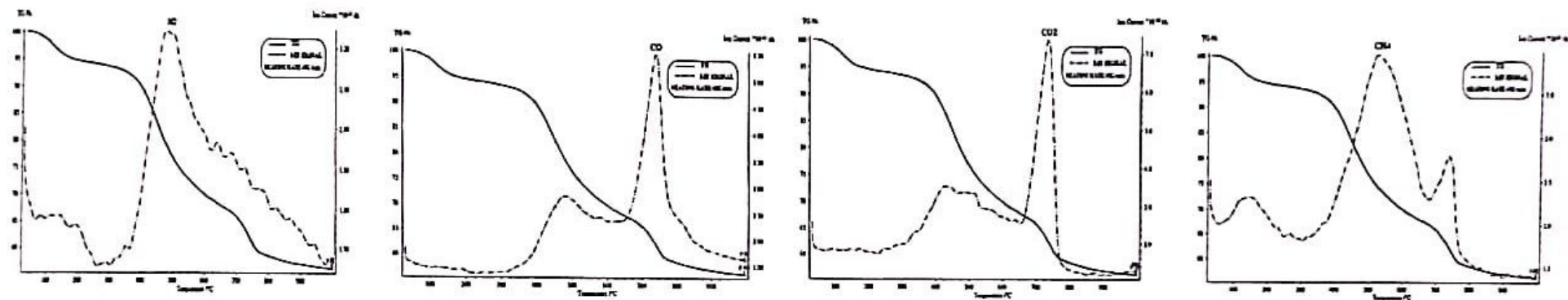
Figures 2 and 3 present the evolution of pyrolysis and gasification products of Soma lignite. All gaseous products are observed at higher temperatures for pyrolysis case compared to air gasification in line with the TG-DTG results. Hydrogen production covers a much broader temperature range with several peaks for gasification versus one broad peak in pyrolysis. Carbon monoxide and is formed as one small broad low temperature and one sharp high temperature peak for pyrolysis while CO formation is shifted to lower temperatures for the gasification case. Carbon dioxide evolution occurs in two stages giving a small broad peak at the temperature of 427°C and a sharp peak at 735°C in pyrolysis. In air gasification CO<sub>2</sub> evolution occurs in a much broader temperature range with a peak shoulder at 440°C and a second peak at 702°C.

Methane formation is observed for both pyrolysis and gasification as one broad major peak followed by a second small one at high temperatures.

Hydrogen sulfide is the sulfurous product of pyrolysis while COS and SO<sub>2</sub> both are observed during air gasification. H<sub>2</sub>S evolves in one relatively big peak (peak temperature : 450°C) and one small peak (peak temperature: 550°C) during pyrolysis. TG-MS results for air gasification indicate that H<sub>2</sub>S production peaks around 340°C and diminishes around 450°C; some minor H<sub>2</sub>S evolution may occur above 800°C. COS formation begins around 300°C in air gasification and peaks around 373 and 445°C. Sulfur dioxide begins to form around 400°C, peaks at 474°C and diminishes sharply at 500°C.



### SOMA ARGON TG-MS



### SOMA AIR TG-MS

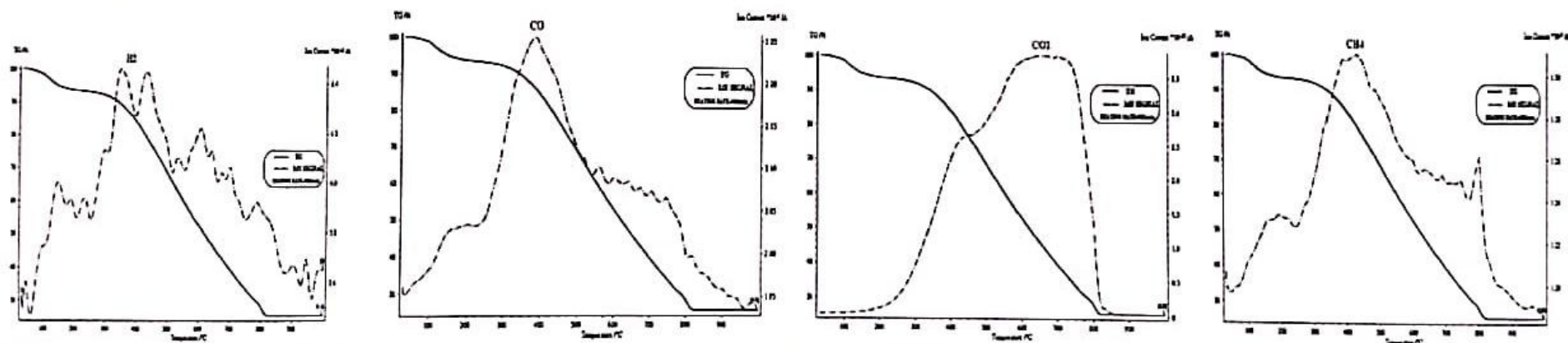
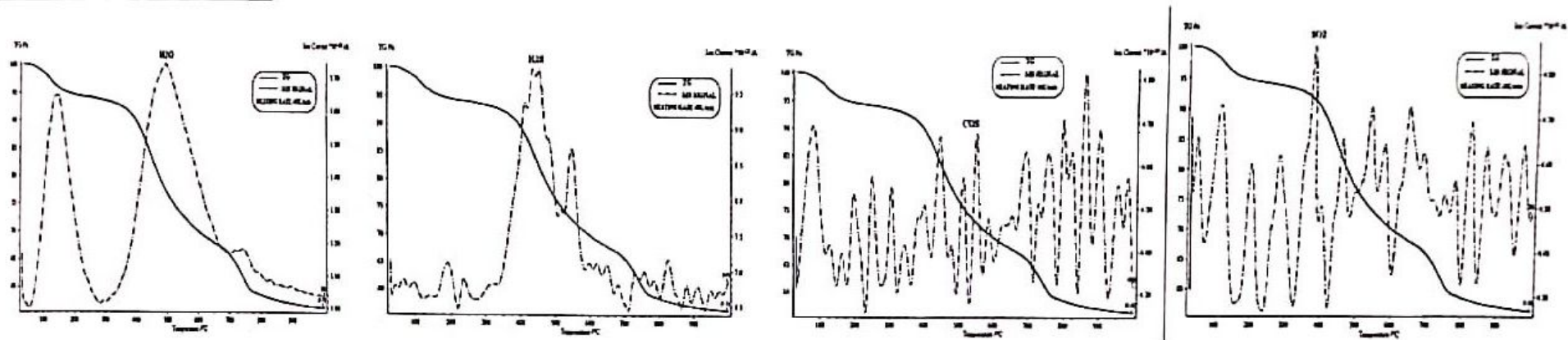


Figure 2. H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> evolutions during Argon pyrolysis and air gasification of Soma lignite



### SOMA ARGON TG- MS



### SOMA AIR TG- MS

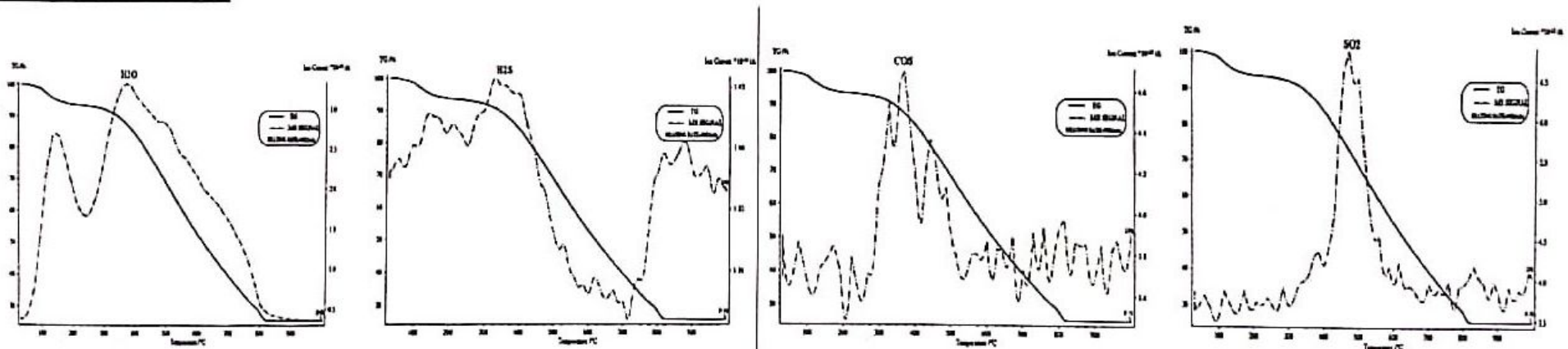


Figure 3. H<sub>2</sub>O, H<sub>2</sub>S, COS and SO<sub>2</sub> evolutions during Argon pyrolysis and air gasification of Soma lignite



#### 4. Concluding Remarks

TG-DTG-MS data indicates quite well the dependency of the qualitative and quantitative product formation of coals and other hydrocarbons in selected atmospheres and heating regimes. The temperature and atmosphere related formation data is of utmost importance for primary evaluation of coals towards clean coal thermolysis technologies as well as for designing custom fit processes. Data about sulfurous product formation is important in terms of their removal considering not only environmental limitations but also their poisoning effect on catalysts in further process stages following pyrolysis or gasification. Data taken for several Turkish lignites and their mixtures with biomass at various heating rates and atmospheres are being kinetically analysed (iso conversion , model fitting and regression ) and will be published in the near future.

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