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THERMAL ANALYSIS IN COMBUSTION RESEARCH

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Abstract

Thermal analysis is widely used in combustion research for both fundamental and practical investigations. Efficient combustion of solid fuels in power plants requires understanding of properties and behavior of fuel and ash under a wide range of conditions.

At the Department of Chemical Engineering, Technical University of Denmark, thermogravimetric analysis and differential scanning calorimetry are applied in order to investigate various aspects of combustion and gasification processes: pyrolysis, char reactivity and ash melting behavior. This paper shows examples of the application of simultaneous thermal analysis in these three research areas, and it demonstrates the flexibility of this technique in combustion research.

Keywords: ash, biomass, coal, combustion, DSC, pyrolysis, reactivity, TG

Introduction

Combustion research mainly focuses on methods to increase efficiency and decrease harmful emissions. While much has been published related to coal combustion, much less is found in the literature regarding biomass. The use of biomass in thermochemical processes has found wide applications. Biomass, for example, is used as a fuel in power plants and as a reactant in pyrolysis and gasification processes in which char, tar, gas or chemicals are the major products.

Research on biomass pyrolysis has mainly been focused on the pyrolysis of wood and cellulose (the most abundant biomass constituent). However, in Denmark, straw is used as fuel in heat and power production. Straw and other biomass types deviates from coal in structure and composition, and consequently the pyrolysis and combustion behavior is significantly different. A good understanding of the pyrolysis of a fuel may result in better tools for design and optimization of pyrolysis and gasification reactors.

Fuel char reactivity during combustion in utility boilers is directly related to carbon burnout and thereby to potential high levels of unburned carbon in fly ash. This can affect boiler combustion efficiency, the operation of electrostatic precipitators and may hinder the sale of the fly ash to the cement industry for concrete applications.

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Ash from solid fuels may deposit on the steam tubes in boilers provoking corrosion and diminishing the heat transfer and thereby disturb boiler operation. The ash from different fuels behaves differently. The ash from e.g. straw contains large amounts of potassium, which lowers the ash melting temperature compared to coal ash. The low ash melting temperature results in more rapidly growing and tenacious deposits. Knowledge of the melting characteristics of ash provides information on the stickiness of ash as a function of temperature, which is a parameter of fundamental importance for the prediction of deposit growth-rate and deposit strength.

This paper shows examples of the use of thermal analysis in combustion research, from investigation of pyrolysis and char reactivity to ash melting behavior.

Experimental

The experiments were carried out in a Netzsch STA 409 C (simultaneous thermal analysis – STA), which was used in the differential scanning calorimetry/thermogravimetric analysis (DSC/TG) configuration. The STA has a vertical sample carrier with a reference and a sample crucible. In order to account for buoyancy effects, a correction measurement with empty crucibles was first conducted and then subtracted from the actual experiments. Purge gas and in some cases reaction gas were also injected in the bottom of the system and exited in the top. The system was temperature and sensitivity calibrated with metal standards, at each heating rate in the applied temperature range, at each set of conditions.

Platinum/rhodium crucibles were used. In some cases lids were placed on the crucibles. During calibration, thin alumina liners were inserted in the crucibles in order to avoid reactions between calibration metal and crucible material. In high temperature measurements, a thin alumina disc was placed beneath the crucibles in order to avoid platinum–platinum bonds between crucible and sample carrier.

Pyrolysis of biomass

In the following, a few examples of the use of the STA for pyrolysis research are given. The examples include investigation of the pyrolysis behavior and determination of the heat of reaction for two biomass types and cellulose and kinetic evaluation of the pyrolysis of wheat straw.

The STA was used with a purge gas flow of 100 mL min^{-1} nitrogen. The samples were kept at 383 K for 30 min, prior to heating at 10 or 40 K min^{-1} to a final temperature of 873 K. After 30 min at the final temperature, the char was burned in a mixture of oxygen and nitrogen in order to determine the ash content. Samples of approximately 5 mg were used. The investigated wheat straw and sunflower shells were milled using a laboratory ultracentrifugal mill (Retzsch ZM 100) mounted with a 1 mm screen. Wheat straw washed in water was included in the investigation. The washing reduced the content of salts and minerals, which have an effect on the pyrolysis.

Different biomass types behave differently during pyrolysis. Figure 1 shows mass loss as a function of temperature during the pyrolysis of cellulose, wheat straw, washed wheat straw and sunflower shells at a heating rate of 40 K min^{-1}. The figure shows that the pyrolysis of cellulose occurs over a small temperature range and the mass loss rate curve shows a single, more or less, symmetrical peak. The char yield is very low, about 5 mass% (dry ash free basis – daf). The pyrolysis of wheat straw occurs over a wider temperature range, and in this case a single mass loss rate peak is also observed; however, it is not symmetrical and it has a long tail. The char yield is much higher than for cellulose, approximately 26 mass% (daf) at 750 K. The pyrolysis of washed wheat straw shows that the mass loss rate divides into two peaks. The char yield in this case is much lower than that of the raw straw, 15 mass% (daf) at 750 K. The pyrolysis of sunflower shells shows a more complex behavior. The pyrolysis begins at a much lower temperature, with a peak at approximately 500 K, followed by an asymmetrical peak at approximately 625 K. As for straw and washed straw, a long tail is observed. The char yield is 24 mass% (daf) at 750 K. The figure shows that although cellulose is the main constituent of the biomass, there is a large difference between the pyrolysis behavior of cellulose and the biomass, especially with regard to the onset of the pyrolysis and the char yield. A more detailed discussion of the pyrolysis of the biomass types in Fig. 1 is given in [1–3].

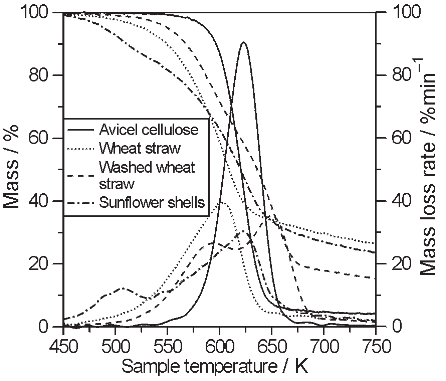

Fig. 1 Pyrolysis of different biomass types at 40 K min^{-1}

DSC measurements were carried out simultaneously with TG and were used to estimate the heat of reaction for the pyrolysis. It was found that the pyrolysis of cellulose was endothermic (660 J g^{-1} daf initial mass), while no peak was detected for the pyrolysis of wheat straw, and a small peak (too small for quantification) was found for the pyrolysis of washed wheat straw. In order to obtain better DSC-conditions a few experiments were carried out with a reference material in the reference crucible (in this case 10 mg γ-Al_2O_3) and with lids on the crucibles. The lids had three small holes in them, in order to let the product gas out. This resulted in a more distinct DSC-signal with a flatter baseline. Figure 2 shows the pyrolysis of cellulose both with and without lids on the crucibles. In this case the measured heat of reaction for the pyrolysis of cellulose was 620 J g^{-1} daf initial mass, while the pyrolysis of wheat straw showed a small exothermic peak (too small for quantification), and the pyrolysis of washed wheat straw showed an endothermic peak (310 J g^{-1} daf initial mass). In all three cases a larger char yield was observed; for cellulose it was twice that of the pyrolysis without lid. This confirms the trend observed by [4, 5]. The experiments show that without lids the DSC-signal is less distinct, however, if a lid is placed on the crucibles in order to achieve a better DSC-signal, the TG-curve changes. Consequently, these errors have to be estimated in order to choose the best conditions for the determination of heat of reaction for the pyrolysis of biomass.

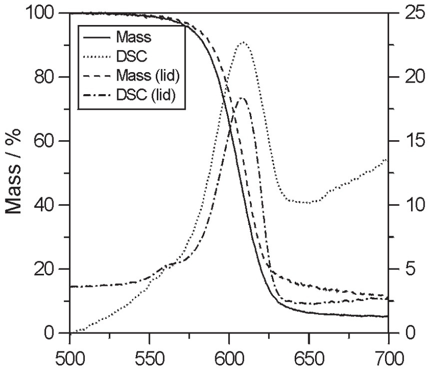

Fig. 2 Pyrolysis of cellulose at 10 K min^{-1} with and without lids on the crucibles

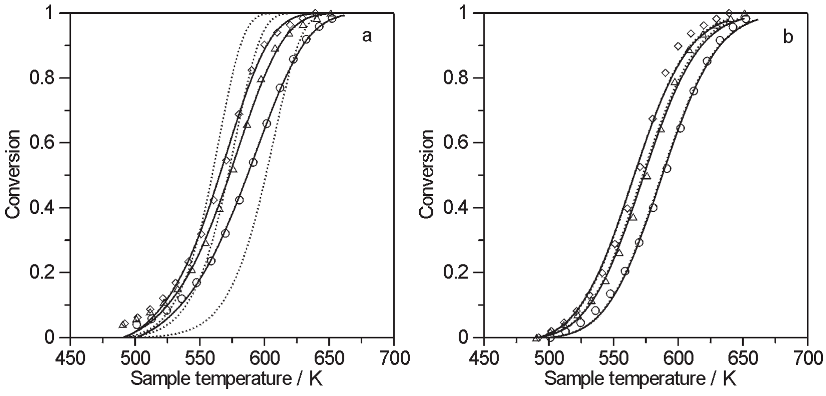

Fig. 3 The pyrolysis of wheat straw at 5, 10 and 40 K min^{-1}. Kinetics fitted to the individual curves and simultaneously to all curves for a – a single first order reaction model and b – the distributed activation energy model

The curves for wheat straw in Fig. 1 indicate that the kinetics for the pyrolysis is not a simple first order reaction, however, simple kinetic models are often wanted when included in more complex process models. The wheat straw pyrolysis was fitted using a single first order reaction model (2 parameters) and a distributed activation energy model (3 parameters), for which a normal logarithmic distribution was applied [3, 6]. Kinetics was fitted to experiments at three different heating rates individually and simultaneously. Figure 3 shows the experimental data as well as the fits. Figure 3a shows that while the individual fits agree well with data, the simultaneous fits do not. However, the distributed activation energy model (Fig. 3b) shows good agreement with data for both individual and simultaneous fits. It was observed that if kinetics are needed to describe the pyrolysis at a single heating rate, the single first order reaction works reasonably well, however, at different heating rates, the distributed activation energy model is needed.

Char reactivity

STA is a useful tool for the investigation of char reactivity. As an example, the reactivity of chars from six fuels including coals of different rank, petroleum coke as well as washed Danish straw was investigated by measuring sample mass change during oxidation as a function of temperature. For comparison purposes the oxidation behavior of commercial graphite and carbon extract (Cerrejon) from the fly ash of a coal-fired boiler unit were also determined.

STA was used in the DSC/TG configuration, with the gas flow exiting in the top. In most cases, less than 5 mg of fuel particles sieved to a size of 90–105 μm were spread out carefully on the bottom of a platinum crucible. The experiments were divided into separate pyrolysis and char oxidation steps. The chars were pyrolysed in nitrogen at a heating rate of 45 K min^{-1} to different heat treatment temperatures (HTT) in the range 973–1673 K with a hold time of typically 15 min. After pyrolysis the chars were cooled down to 473 K and kept at this temperature for 45 min to stabilize the temperature. Thereafter, the oxidative gas (10 mol% oxygen with nitrogen as balance) was injected directly into the crucible region. The char oxidation proceeded at a pre-set heating rate of 1, 5, or 20 K min^{-1}. For most cases oxidation measurements at 5 and 20 K min^{-1} could be used, but for some chars, particularly the very reactive washed straw, measurements at 1 and 5 K min^{-1} were employed.

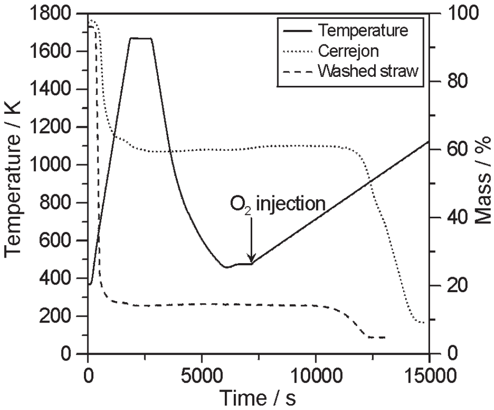

Fig. 4 TG measurements of Cerrejon coal and washed straw

Figure 4 shows a typical TG measurement for coal (Cerrejon) and washed straw pyrolysed at 1673 K with the subsequent oxidation occurring at 5 K min^{-1}. Each mass loss measurement can be regarded as a fingerprint of the combustion behavior of the fuel.

From the mass loss data of the char at two heating rates during oxidation, a volumetric reaction model (VRM) [7] was used to model the experimental char oxidation rates:

$$\text{rate}=1/(1-X)\text{d}X/\text{d}t=k_0 e^{-E_a/RT} \tag{1}$$

$X=1-W/W_0$ is the char conversion on a dry-ash-free basis, with W representing the char mass at any time and W_0 the char mass at time zero, k_0 is the pre-exponential factor (s^{-1}), E_a the activation energy (kJ mol^{-1}), R the gas constant (kJ mol^{-1} K^{-1}) and T the reaction temperature (K). The pre-exponential factor k_0 is interpreted here as the char reactivity.

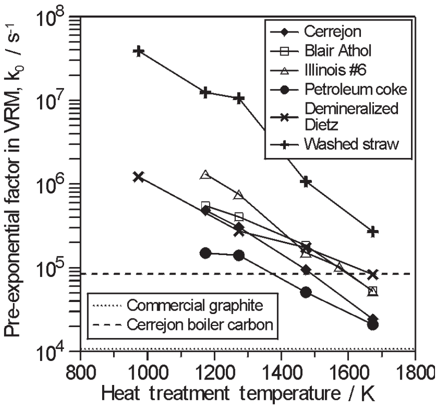

Fig. 5 Char reactivity for the fuel chars investigated

Initially, the pre-exponential factor and the activation energy of each char were determined by non-linear least squares fitting. Subsequently, a common activation energy of 135 kJ mol^{-1} – corresponding to the average value of the calculated activation energies for all chars – was fixed and the pre-exponential factor was refitted. Thereby the pre-exponential factor permits a straightforward comparison of the relative reactivity of the chars prepared at different conditions. In Fig. 5 plots of k_0 as a function of HTT for all the chars investigated are showed. k_0 decreases with up to two orders of magnitude when increasing the HTT from 973 to 1675 K, and the reactivities approach that of the commercial graphite. Noteworthy is the fact that the Cerrejon coal char prepared at 1673 K has a reactivity that is comparable to that of the fly ash carbon extract, hence indicating the capability of the STA apparatus to produce chars which reactivity resemble that of chars collected in full scale boiler units.

A deactivation ratio can be defined as the ratio of k_0 at any HTT to k_0 at the lowest HTT of each fuel data set. These ratios can be used as input data for determination of parameters in a transient char thermal deactivation model (annealing model), which accounts for the gradual loss of char reactivity during heat treatment due to microstructural changes within the char matrix. The details of such a model can be found elsewhere [8]. Based on this model, the deactivation ratio, or reactivity loss of chars prepared in laboratory reactors operating at much higher heating rates and temperatures than the STA can be predicted. The model requires knowledge of the accurate temperature–time history of the char samples and this is possible in reactors such as the STA, wire mesh reactors (WMR) and more recently in the so-called heated strip reactor [9] and all-graphite transient heating device [10]. The deactivation ratios provided by the annealing model were compared to the experimental deactivation ratios of representative fuels heat-treated in the all-graphite transient heating device and WMR. In the former reactor, chars are prepared at heat treatment temperatures ranging from 973 to 2700 K with hold times at the corresponding peak temperature of ~2 s and heating rates of ~1000 K s^{-1}, while in the WMR [11, 12], chars are typically prepared at a heating rate of ~10^4 K s^{-1} up to peak temperatures of 2073 K with hold times of 1–5 s. Such conditions resemble those of full scale boilers. Overall, the loss of reactivity obtained with the annealing model were in reasonable agreement with the experimental deactivation ratios obtained on high heating rate equipment [8], suggesting that STA can be a valuable tool for the estimation of char kinetic constants to be applied in combustion modeling.

Ash melting properties

The STA was recently applied in the investigation of the melting properties of ash from coal and biomass co-firing [13]. Nitrogen flow through the reactor was kept at 100 mL min^{-1}. Samples of approximately 20 mg were used. About 25 mg γ-Al_2O_3 was used as reference material. Lids were used in order to obtain a more uniform temperature distribution. Alumina discs were placed between the crucible and the sample carrier. The temperature was increased up to 1673 K at a heating rate of 10 K min^{-1}.

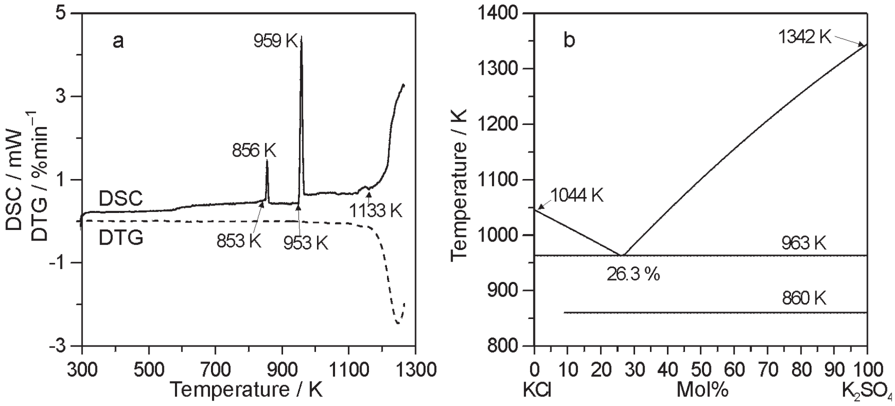

Fig. 6 STA of a mixture a – KCl–K_2SO_4; phase diagram for b – KCl–K_2SO_4 mixture (adapted from [14])

When dealing with ash samples the occurrence of reactions among the ash components can be neglected. Therefore, all processes accompanied by heat absorption at zero mass change can be assumed to be a phase change, rather than chemical reactions.

In the following, two examples of the use of STA for the evaluation of the melting properties are given. The first example is the melting of a synthetic mixture of 6.1 mg of KCl and 13.9 mg of K_2SO_4. The molar ratio of the mixture is 44 mol% KCl and 56 mol% K_2SO_4. At 26.3 mol% of K_2SO_4, the mixture forms a eutectic that melts at 963 K. Figure 6a shows the result of the DSC-TG on the mixture. The DSC evidences a first peak starting at 853 and peaking at 856 K, which corresponds to the phase transition of K_2SO_4 between the α- and the β-configuration, expected at 860 K (Fig. 6b). A second peak, starting at about 953 K and peaking at about 959 K, corresponds to the formation of the eutectic. The STA of this sample corresponds very well with the theoretical behavior of the synthetic mixtures as obtained from the study of the phase diagram of the mixture KCl–K_2SO_4 (Fig. 6b) [13]. In fact, applying the lever rule, it appears that about 60% of the mixture melts at the eutectic temperature. The remaining fraction gradually melts only if the temperature is raised, and the liquid temperature is reached at 1134 K. The theoretical and experimental melting curves (as molten fraction in mol% *vs*. temperature) are compared in Fig. 7 (adapted from [13]).

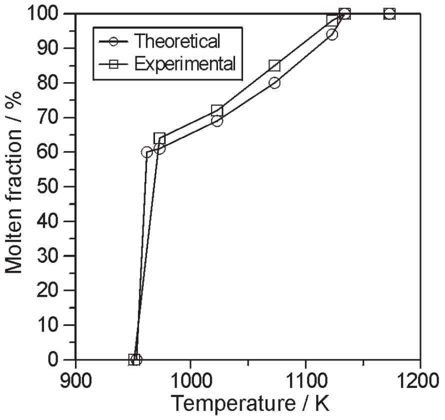

Fig. 7 Theoretical and experimental melting curves for the KCl–K_2SO_4 mixture (adapted from [13])

The second example describes the result of the STA on real ash samples. Ash was obtained from an experimental campaign at a straw-fired utility boiler, the Slagelse combined heat and power production plant. In this case, the plant fired several different types of straw, and ash was sampled in several locations (for details see [15]). The samples analyzed here are bottom ash (BA) originating from combustion of wheat and barley (respectively samples ‘Slagelse 1’ and ‘Slagelse 3’ in the original reference). The bulk compositions of the mineral matter are compared in Table 1. Particularly relevant are the differences in the cases of silicon and potassium. In Fig. 8, the STA analysis of the two ash types is compared. Evaporation from the sample was negligible in this temperature range, since very little condensable material is

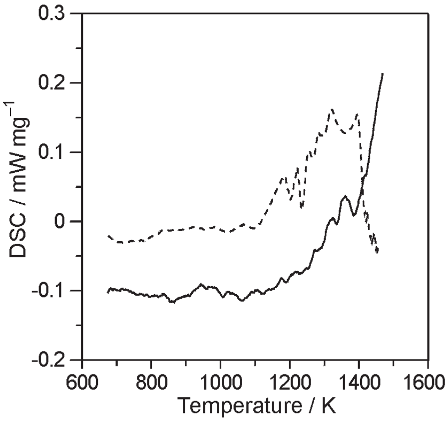

Fig. 8 DSC analysis of bottom ash from combustion of straw. The wheat was silicon-rich while the barley was potassium-rich;
BA of wheat, KCaSi=30%, quartz=47%, Si-rich=21% (—)
BA of barley, KCaSi=84%, quartz=5%, Si-rich=6% (---)

deposited on bottom ash. In the figure only the result of the DSC analysis is plotted. The bottom ash starts melting at about 1123 K in both cases. However, while the BA of barley has completed melting already at about 1523 K, the BA of wheat has not. The mineralogical analyses of the ash obtained with computer controlled scanning electron microscopy revealed that the BA of wheat is mainly made by quartz and silicon-rich compounds, while the BA of barley contains mostly potassium/calcium-silicates (see the legends). Particularly potassium silicates possess lower melting points (T_{melt} between 1040 and 1320 K) than silicon rich compounds (T_{melt} of quartz is about 2000 K [16]). Due to the different melting behavior, the barley ash has a definite higher tendency to become sticky and produce deposits with a greater tenacity respect to the wheat ash.

Table 1 Bulk composition of wheat and barley (mass%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5
Wheat	70	0.81	0.42	11	1.4	0.37	8	1.5	0.98
Barley	25	0.35	0.19	13	1.4	1.7	46	1.4	1.6

Conclusions

The STA instrument is widely applicable in combustion research, for both fundamental and practical research. Thermal analysis can be used to describe the pyrolysis behavior as well as to estimate the heat of reaction. The STA was also used to determine the parameters in an annealing model that describes the influence of pyrolysis conditions on the char oxidation. The model is capable of predicting the deactivation ratios of chars prepared at different conditions in reactors operating at much higher temperatures and heating rates than the STA. Finally, the STA was used in the investigation of ash melting properties and the results were found to agree well with theory.

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