



# Investigation of heat of biomass pyrolysis and secondary reactions by simultaneous thermogravimetry and differential scanning calorimetry



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## HIGHLIGHTS

- TG–DSC technique was re-examined to determine the heat of biomass pyrolysis.
- Temperature-dependent specific heat was measured for biomass and char samples.
- The primary pyrolysis was found to consist of endothermic and exothermic stages.
- Linear relations were found between the biomass pyrolysis heat and conversion ratios.
- The heat of secondary reactions could be up to 2500–4000 J/g for the biomass samples.

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## ABSTRACT

The heat of pyrolysis reactions is of great importance not only for its impact on biomass pyrolysis process but as a fundamental parameter for modelling biomass thermochemical conversion. Previously frequently-used technique that integrates DSC heat flow curves to determine the heat of pyrolysis actually presented the enthalpy change of pyrolysis within a temperature range. This enthalpy change in effect took no account of the sensible heat of the volatiles leaving the crucible before reaching the upper limit of the temperature range. This work was attempted to determine both the heat of biomass pyrolysis as a function of conversion ratios or temperatures and the heat of secondary reactions. To this end, the conventional simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) technique was re-examined to investigate thermal behaviour of cellulose, xylan, lignin and four lignocellulosic biomass samples using a TG–DSC analyser. Selected samples around 3.3 mg were thermally decomposed in a crucible either with or without a pierced lid at a heating rate of 10 °C/min to a maximum temperature of 500 °C. Specific heat capacities of all the original biomass and char samples were measured through DSC analyses. Temperature-dependent formulas were developed for extrapolating the specific heat of both biomass and char samples at high temperatures. The heat of pyrolysis as a function of conversion ratios was characterised by the derivative of the enthalpy change versus mass changes during pyrolysis. Thus-obtained heat of biomass pyrolysis represented the difference between the enthalpies of formation of the products and reactants at a specific temperature or conversion ratio instead of a temperature range. The results showed that the heat of pyrolysis reactions changed from high endothermic values, via moderately endothermic values and finally rapidly to high exothermic values as the conversion ratios increased. Linear relations were established between the heat of biomass pyrolysis and conversion ratios ranging from 0.2 to 0.8. The heat of secondary reactions was about 80–280 J/g for cellulose and increased with conversion ratios up to 2500–4000 J/g for the lignocellulosic biomass samples.

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## 1. Introduction

As the only carbon-based renewable energy resource, biomass is potentially more compatible with existing energy conversion

and utilisation technologies than other renewables. Among various biomass conversion technologies, pyrolysis is one of the important and promising thermochemical conversion processes that can transform biomass into biofuels. Pyrolysis is also the primary and fundamental step to combustion and gasification. Consequently, there have been great research interests to achieve better

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## Nomenclature

|                  |                                |            |  |
|------------------|--------------------------------|------------|--|
| $c_p$            | specific heat capacity (J/g K) | $m$        | per unit mass change                         |
| $m$              | mass or weight (g)             | $t$        | time (s)                                     |
| $\dot{m}$        | mass flow rate (g/s)           | $T$        | temperature (K)                              |
| $h$              | enthalpy (J/g)                 | $Y$        | yield of products from biomass pyrolysis (%) |
| $q$              | heat per unit mass (J/g)       | $\alpha$   | conversion ratio                             |
| $Q$              | heat (J)                       | $\beta$    | heating rate (K/s)                           |
|                  |                                | $\gamma$   | mass ratio of char to the initial sample     |
| <i>Subscript</i> |                                | <i>py</i>  | pyrolysis                                    |
| $b$              | unconverted biomass            | <i>rad</i> | radiation                                    |
| $c$              | char                           | $s$        | substance in the sample crucible             |
| <i>DSC</i>       | DSC signal                     | $t$        | termination point                            |
| $e$              | end of the pyrolysis process   | $V$        | vapour products of biomass pyrolysis         |
| $i$              | intermediate point             |            |  |

understanding of biomass pyrolysis process in order for technology development and optimisation [1–3]. Among the various fundamental knowledge related to biomass pyrolysis, the heat of pyrolysis is one of the most important factors for reactor design, model simulation, process optimisation, and economic evaluation [3–6]. It is thus essential to quantitatively determine the thermal characteristics of biomass pyrolysis.

To date, there have been a number of studies investigating the heat of pyrolysis for biomass [4,6–11]. However, as the value of this quantity depends heavily on feedstocks, temperature ranges, the extent of secondary reactions among primary pyrolysis products and even on measurement conditions, accurate characterisation of the heat of pyrolysis is difficult [8]. Various inconsistent results have been reported ranging from endothermic to exothermic values. Some of these results were recently summarised in the literature [12]. Most studies on the heat of biomass pyrolysis have been carried out using differential scanning calorimetry (DSC) or simultaneous thermogravimetry (TG) and DSC [7,9–11]. DSC provides a convenient method for measuring quantitatively the heat flow to a sample as the temperature of the sample varies. The heat of pyrolysis is then determined by integrating the heat flow curves against time. Lee et al. [13] investigated wood pyrolysis process in laser radiation and calculated the heat of pyrolysis using obtained information of decomposition rates, temperature and pyrolysis gas compositions. The overall mass weighted endothermic heat of wood pyrolysis was about 610 J/g at low heat flux [12]. Most recently, Yang et al. [4] employed thermodynamic calculations to estimate the heat required for biomass pyrolysis in a screw-conveyor reactor after measuring the yields and composition for gaseous, volatile and char products.

However, it should be mentioned that most of the results reported in the literature were indeed the enthalpy change of biomass pyrolysis within a specified temperature range. These values indicated the energy released or required for biomass pyrolysis during this temperature range. Essentially, mathematical modelling for biomass pyrolysis prefers the heat of reaction as a function of temperature or conversion for solving energy conservation equations [3,12]. Still, to the best of the authors' knowledge, no such results for the heat of pyrolysis reactions have been reported so far. Therefore, the main objective of this study was to re-examine the TG–DSC technique and to characterise the heat of reactions with respect of the biomass pyrolysis process. The impacts of secondary reactions on the heat of pyrolysis were also investigated. These goals were achieved by conducting simultaneous TG–DSC tests for pyrolysis of seven selected biomass samples.

In order to determine the heat of pyrolysis reactions, specific heat capacities of both biomass feedstocks and their derived chars

need to be specified. A few attempts have been made to measure the heat capacities of various biomass samples using DSC [14], adiabatic calorimetry [15] or the laser flash method [16]. Similar to the situations for the heat of pyrolysis, however, the reported heat capacity values for cellulose and wood samples were inconsistent among different studies. Moreover, even fewer studies have been conducted to measure the heat capacity of char derived from biomass pyrolysis. The specific heat of wood char was usually assumed to be that of graphite [17]. In this study, the heat capacities of biomass and char samples were carefully measured by TG–DSC analyses before biomass pyrolysis tests were carried out. The ratio method, a comparative technique, was used to determine the specific heat capacities of all the studied samples with powdery  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a standard reference. This method could minimise the effects of thermal lag arising from variations in heating rates and sample sizes on the results [18].

## 2. Material and methods

### 2.1. Samples

Four lignocellulosic biomass feedstocks, including poplar wood chips, pine wood bark, corn stalk and rice straw, were selected for this study. These are commonly available forestry and agricultural residues in China and could potentially be used for massive biofuel production. All these biomass samples were ground to pass a 0.5 mm sieve. In addition, individual biomass constituents, namely cellulose (medium fibres, Sigma–Aldrich), hemicellulose (beechwood xylan, Sigma–Aldrich) and alkali lignin (Tokyo Chemical Industry Co., Ltd., Japan) samples were also used for comparison with the biomass samples. The fractions of the main components, the proximate and ultimate analyses of the samples are listed in Table 1. All these samples were oven-dried at 105 °C for 24 h.

99.99% pure aluminium oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) was used as a standard material for heat capacity measurements. The aluminium oxide sample was heated to 1200 °C for 3 h before use. Some char samples were also prepared by heating above-mentioned biomass samples (5–10 g) loaded in 20 ml alumina crucibles with lids to 700 °C for 30 min in a muffle furnace. These char samples were used for  $c_p$  measurements and to characterise the radiation effect in TG–DSC tests (as mentioned in Section 2.2).

### 2.2. TG–DSC analyses for biomass pyrolysis and specific heat measurements

A Netzsch STA 449F3 thermal analyser (Fig. 1) was used for simultaneous TG–DSC measurements. Biomass pyrolysis tests

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