Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 2, 637–640

PYROLYSIS OF THE WASTE BIOMASS

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The paper summarises results of several thermogravimetric experiments performed with a selected group of eight different waste biomaterials under heating rates from 2 to 50 K min^{-1}. The enthalpy of materials tested in the experiments varied from around 180 up to almost 700 kJ kg^{-1}. Certain conclusions concerning mainly the dependence of the heat exchange under the chosen conditions of the pyrolysis are drawn on the basis of measured values.

Keywords: *biomass, DSC, enthalpy, TG, warmth flow, waste*

Introduction

Pyrolysis which according to its physical–chemical substance belongs among thermic processes, is one of the ways that may lead to transformation of certain kinds of biomaterials purposely cultivated or some of waste materials into a more refined form of energy.

To the basic laboratory procedures enabling to follow in detail and record the behaviour of diverse biomaterials during the pyrolysis belong various techniques of the thermal analysis (TA), both under static (isothermal) and dynamic conditions (use of heat programme). It is for this reason that TA methods are usually, mostly very frequently, applied for the research of the thermal decomposition of biomass wastes.

While using the thermogravimetric analysis (TG) the course of the pyrolysis of pre-dried vegetable waste from food shop was modelled. The tests took place in an inert atmosphere within the temperature limits of 250–650°C. The measured data were compared with the precisely defined lignocellulose materials that fulfilled the role of standards. The main objective of these experiments was the determination of the kinetics of the pyrolysis acts. Another research work was aimed at the broad spectrum of samples of the waste biomass, on which pyrolytic tests were performed, using the TA methodology. The decomposition of the biomass was confronted with the thermolysis of the waste polymers [2].

The TG technique served in a similar way in connection with FTIR for the research of pyrolysis of wastes from palm oil production. The objective of this research was describing the course of the pyrolysis of the said waste raw material and considering the feasibility of its conversion into the energetically better usable pyrolytic gas. Waste of the heating value of 20 MJ kg^{-1} containing 50 mass% of carbon, 7 mass% of hydrogen and a very small part of ash was tested. By using TG it has been evidenced that the tested waste is easily decomposable already at low temperatures and a small gradient of the rapidity of warming. The sphere of the maximum decrease of the materiality of the sample was set to 220–340°C [3]. Research directed at the use of TG method in considering the feasibilities of the pyrolytic transformation of solid wastes into a more refined form of fuels led to similar results [4]. The untypical application of the methods of the thermal analysis in the study of other ways of handling communal waste than their direct pyrolysis is presented in [5]. In this research the behaviour of the waste composted for 132 days in three various composters was followed. Samples prepared in this way were pyrolysed thereafter in an inert atmosphere under non-isothermic conditions.

The object of an intensive TG research was also peanut peelings and hazelnut shells. Two different ways of approach were chosen in experimenting, partly isothermal pyrolysis at 350, 600 and 850°C and partly non-isothermal TG analysis with the maximum reached temperature of 920°C. The experiments proved a very good applicability of both materials for the production of adsorbents [6]. Pyrolysis of waste plant fibres from industrially processed flax and hemp was tested with a similar objective.

It is evident from what was said that TG methods represent a very effective instrument for the research directed at thermal decomposition of a broad spectrum of materials. It comes out from the quoted scientific works that especially TG techniques in connection with other analytical appliances (FTIR, MS, TG-MS) together with DSC serves for description of the thermic behaviour of biomaterials and that they furnish important information indispensable for the development of new industrial pyrolytic systems.

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1388–6150/$20.00

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Experimental

Samples and test technology

The sample basis was formed by the following group of 8 selected materials:

- Waste of amaranth processing – remnants of the whole over ground parts of the plant which remained after grains had been threshed,
- Cocoa peelings – waste of cocoa beans processing in the production of cocoa powder and chocolate,
- Barley chaff – waste of barley drying,
- Maize chaff – waste of drying,
- Coconut fibre – waste of coconut matting fabrication,
- Energetic sorrel (variety Uteusha) – ground and pre-dried over-ground parts of plants,
- Reeds – from the extensive growth of humid meadows of Southern Slovakia,
- Peanut peelings – waste of the production of roasted, peeled and salted peanuts.

Apparatus used

As an analytical device of the quantitative measuring the heat flow of pyrolyzed materials type DSC 131 (f. Setaram) was selected which measures the heat flow between the sample pan and the reference pan. With respect to the construction limit of the used calorimeter the pyrolyses in the nitrogen atmosphere were performed within the temperature range of 20–700°C. For the outline of the block of the furnace DSC calorimeter, Fig. 1.

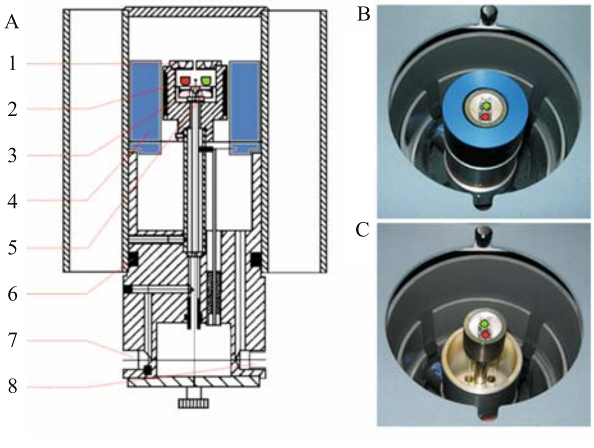

Fig. 1 Microscopic DSC: A – furnace with the convector in section, 1 – lid of the working space of the furnace, 2 – pot with the sample, 3 – comparison pot, 4 – aluminium exchanger homogenizing the heat field, 5 – silver ring of the probe, 6 – packing o – circle of the convector, 7 – inlet of the working gas, 8 – outlet of the working gas; B – an open furnace with pots in the container with a set-on homogenizer; C – open furnace with pots in the container with removed homogenizer

Results and discussion

Basic technical data summarized in Table 1 were established by the TG method, while results were verified by normalized tests based on drying and annealing of analytic samples in a muffle furnace. A fixed combustible was not determined as it can be expressed by calculation to 100%.

Table 1 Basic technical parameters of the tested samples (mass%)

Sample	Water	Ash	Volatile combustible
Amaranth	7.0	9.9	65.8
Barley chaff	8.3	6.9	71.4
Cocoa peelings	5.8	5.8	70.2
Coconut fibre	7.5	1.1	70.9
Maize chaff	9.6	1.6	74.6
Sorrel	6.3	3.8	69.6
Reeds	5.8	4.7	73.5
Peanut peelings	6.4	7.1	68.7

DSC tests were performed in a non-isothermal way with 5 various gradients of warming up samples – 2, 10, 20, 30 and 50 K min^{-1}. The final temperature of 700°C was considered to be sufficient because TG analyses performed independently and retort tests proved that this temperature guarantees conversion of the followed biomaterials overtopping in average 65% [8]. As demonstrated by TG-DTA analyses, a higher conversion would only be achieved at very high but economically already disadvantageous temperatures. Moreover, acts in progress over this limit are usually not characterised by considerable enthalpic flows caused by a decomposing process.

Data quantification took place with the help of time integration of curves of the heat flow with a forthcoming re-calculation of the heat per mass of the respective sample by the way of software Setsoft 2000. The obtained values enable mutual comparison of the heat delivered to the individual samples with various heating rates are summarized in Table 2 and graphically demonstrated in Fig. 2.

A very important factor taking part in the energetic balance of the pyrolytic action is humidity contained in the processed biomaterials which due to its big evaporation enthalpy strongly increases the endothermic painting of the whole pyrolytic process. The idea to what measure the presence of water influences the enthalpic balance of the pyrolysis can be have on the basis of Table 3 or Fig. 3.

It was verified from the comparison of the DSC curves covering warming only to the temperature of 700°C with DTA curves obtained by warming samples in a different apparatus till 1000°C [8] that most

Table 2 Enthalpy of tested materials at various heating rates (kJ kg^{-1})

Sample	Heating rate/K min^{-1}				
	2	10	20	30	50
Amaranth	283	449	519	526	575
Barley chaff	454	575	602	609	647
Cocoa peelings	476	491	603	642	664
Coconut fibres	355	454	555	595	602
Maize chaff	302	555	599	609	618
Sorrel	182	388	534	547	626
Reeds	371	549	552	553	562
Peanut peelings	302	459	530	533	537

Table 3 Enthalpy dry tested materials at various heating rates (kJ kg^{-1})

Sample	Heating rate/K min^{-1}				
	2	10	20	30	50
Amaranth	108	274	344	351	400
Barley chaff	247	368	395	402	440
Cocoa peelings	331	346	458	497	519
Coconut fibre	168	267	368	408	415
Maize chaff	62	315	359	369	378
Sorrel	25	231	377	390	469
Reeds	226	404	407	408	417
Peanut peelings	142	299	370	373	377

processes connected with heat exchange proceed at temperatures lower than is the above given construction limit of the device. Other processes connected with heat exchange happen, as established by DTA measuring, as late as at temperatures considerably exceeding 1000°C, that is in the domain which is not any more considered to be really usable for practical use of the pyrolysis of the explored waste biomaterials. DSC data obtained in the course of warming within the range of 20–700°C are, therefore, sufficiently representative for the evaluation of pyrolysis from the point of view of the energetic demands of the realization exploitation.

The value of added heat in the cases of all speeds used for warming the tested group of raw and unadjusted samples moved within 182–884 kJ kg^{-1}. In the case of values obtained for the dry substance these limits are 25–682 kJ kg^{-1}, on the average 354 kJ kg^{-1}.

In the case of all eight samples of the waste biomass a progressive growth of the values of heat delivered to the samples with growing speed of warming was established, whereby the most significant change

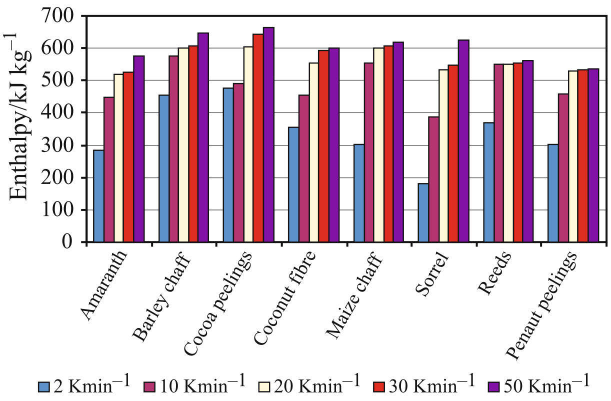

Fig. 2 Heat added to the tested samples during pyrolysis at various heating rates

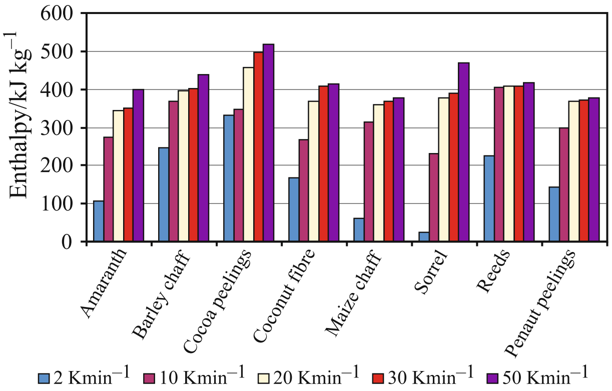

Fig. 3 Heat added to the dry substance of samples during the pyrolysis at various heating rates

of the delivered heat usually occurs between the speeds of 2 and 10 K min^{-1}.

It further follows from the comparison of the data measured at various speeds of the warming that in case of an extremely slow warming at a speed of 2 K min^{-1}, samples of the biomass released in the course of the decomposition on the average 259 kJ kg^{-1} less, which represents 40% less heat than at the quickest experimented warming (50 K min^{-1}). In the case of the dry substance the difference reached on the average 56%. It is, however, necessary to stress in this connection that it is impossible to assume in the case of a real facility that the choice of this slow speed of warming will result in energy cuts, because in case of very slow warming it will be necessary to heat the facility for a longer time than in the case of a higher speed of warming.

Conclusions

In this paper we have summarised results of several thermogravimetric experiments performed with a selected group of eight different waste biomaterials. From this group the sample of Uteusha sorrel was evaluated to be desintegrable in the easiest way with the average value of the enthalpic exchange of 455.4 kJ kg^{-1} (or 295.4 kJ kg^{-1} in the case of a dried substance). The highest difference between the enthalpies set for the slowest and fastest warming was determined also for this sorrel sample. The difference was 444 kJ kg^{-1}, which represents from 71% (initial sample) up to 95% (dried substance) of the maximal enthalpy measured for this sample at heating rate of 50 K min^{-1}.

The experiments also showed that most demanding pyrolysis from the energetical point of view was pyrolysis of cocoa peelings while recorded differences were more significant for dried substance of the observed samples than that of raw materials.

Acknowledgements

Acknowledgements are hereby expressed to the Ministry of Education, Youth and Sport of the Czech Republic for the financial support rendered for solving this project in the framework of the research project MSM 604 613 7304 and to the Grant Agency of the Czech Republic (GA ČR) for the support in the framework of project 104/05/0664.

References

1 R. Ray, P. Bhattacharya and R. Chowdhury, Can. J. Chem. Eng., 82 (2004) 566.
2 M. Staf, J. Ederová, P. Buryan and M. Schauhuberová, Aplikace metod termické analýzy ve výkumu pyrolýzy biomasy, 3rd Congress Energie z biomasy, Ostrava, 11–14 June 2004.
3 H. Yang, R. Yan, T. Chin, D. T. Liang, H. Chen and Ch. Zheng, Energy Duele, 18 (2004) 1814.
4 J. M. Heikkinen, J. C. Hordijk, W. De Jong and H. Spliethoff, J. Anal. Appl. Pyrolysis, 71 (2004) 883.
5 M. S. Crespi, A. R. Silva, C. A. Ribeiro, S. C. Oliveira and M. R. Santiago-Silva, J. Therm. Anal. Cal., 72 (2003) 1049.
6 P. R. Bonelli, E. G. Cerrella and A. L. Cukierman, Energy Sources, 25 (2003) 767.
7 P. T. Williams and A. R. Reed, J. Anal. Appl. Pyrolysis, 70 (2003) 563.
8 M. Staf, S. Skoblja and P. Buryan, Pyrolýza odpadní biomasy, Energie z biomasy, Symposium, 20–22 May, Brno 2003.

Received: September 6, 2007
Accepted: November 27, 2007

DOI: 10.1007/s10973-007-8700-9