FOLIA FORESTALIA POLONICA

 Series B, Issue 38, 67-76, 2007

THERMOGRAVIMETRIC ANALYSIS AND DETERMINATION OF COMBUSTION HEAT OF RYE AND WHEAT BRAN AND PAPER ARTICLES CONTAINING THEM

Izabela Modzelewska, Monika Bartkowiak

Institute of Chemical Wood Technology
August Cieszkowski Agricultural University of Poznań

SYNOPSIS. This paper presents results of investigations concerning the heat of combustion and thermal analysis of laboratory test sheets without any filling agents and with 5% filling agent (rye or wheat). For comparative purposes, the above-mentioned analyses were also carried out for rye and wheat bran and starch.

KEY WORDS: paper test sheets, paper stock, cereal bran (rye and wheat), heat of combustion, thermal analysis

INTRODUCTION

Investigations have been carried out in recent years at the Institute of Chemical Wood Technology on the possibilities of application of cereal bran for the production of paper articles from recycled waste papers. The experiments employ by-products from the milling industry (rye and wheat bran) used as filling agents for the production, among others, of egg, vegetable and fruit trays and containers as well as paper pots for plants (Modzelewska 2006, Cofta at al. 2006).

Cereal bran is no longer used as an additive material during the production of feeds for farm animals because it does not contain any nutrients. Therefore, a problem arose what to do with considerable quantities of this by-product; its quantities in the Gdańsk mill alone reach up to 127 tons a day.

This article presents results of experiments on the possibility of utilization of cereal bran as well as by-products obtained in the course of production of paper articles with cereal bran used as a filling agent as a fuel (Werther et al. 2000). For this purpose, cereal bran as well as laboratory test sheets manufactured from pulped waste paper with and without the addition of by-products from the milling industry were subjected to thermal analysis (Sun and Sun 2002) and their heat of combustion was determined.

MATERIAL AND METHODS

Experimental material

- paper manufactured in laboratory conditions from pulped waste paper without any filling agents with the assistance of the Rapide-Köthen apparatus,
- paper manufactured in laboratory conditions from pulped waste paper with the addition of 5% rye bran with the assistance of the Rapide-Köthen apparatus,
- paper manufactured in laboratory conditions from pulped waste paper with the addition of 5% wheat bran with the assistance of the Rapide-Köthen apparatus,
- rye bran,
- wheat bran,
- starch.

Table 1. The chemical composition of cereal bran

Chemical composition [%]	Rye bran	Wheat bran
Substances soluble in cold water	37.15	45.76
Substances soluble in hot water	42.78	53.71
Substances soluble in 1% NaOH	76.68	76.60
Cellulose (Seifert)	10.01	5.00
Lignin (Tappi)	4.43	8.93
Pentosans	21.47	16.11
Starch	17.40	18.20

Research methodology

Preparation of test sheets

Test sheets of the examined paper articles were manufactured from pulped waste paper; mass additives as well as chemical auxiliary agents were also employed during the production.

Experimental pulped waste paper was ground in an open laboratory beater to 30oSR freeness and used to form test sheets of 100 ± 5 g/m^2 basis weight on the Rapid-Köthen apparatus.

Composition of the prepared stock:

- pulped waste paper,
- 5% rye or wheat loading,
- water,
- alum,
- starch.

Employed equipment:

- open beater,

– laboratory distributor-fiberiser,
– Schopper-Riegler apparatus,
– Rapid-Köthen apparatus.

Analysis of the chemical composition of cereal (rye and wheat) bran

The analysis of the chemical composition was carried out according to the PN-92 P-50092 standard "Raw materials for paper industry". The performed analysis of the chemical composition comprised the determination of the content of: substances soluble in cold and hot water, cellulose (Seifert), lignin (Tappi), pentosans and starch.

Heat of combustion

The determination of the heat of combustion was carried out according to the PN-81 G-04513 standard "Determination of the heat of combustion and calculation of the calorific value".

Thermal analysis

The TG-DSC analysis of the examined material was performed on a Labsys^{TM} thermal balance of the Setaram Company in the following measurement conditions:

– sample initial weight: 20 $\pm$1 mg,
– assumed final temperature: 600°C,
– rate of temperature increase: 3°C,
– atmosphere: helium flowing through the reaction space with the velocity of approximately 2 dm^3/h,
– reference material (DSC): Al_2O_3.

DISCUSSION ON RESEARCH RESULTS

TG analysis

The first peak on the DTG curves of all samples (Fig. 1 and 2) is associated with the loss of water contained in the analysed material. The thermal decomposition of lignocellulosic materials (among others rye and wheat bran) is a two-stage process. The carbohydrate part of the material (hemicelluloses, cellulose) is the first to undergo degradation, whereas the aromatic compounds (lignin) – because of their greater thermal resistance – undergo degradation at higher temperatures (Antal 1985). This fact finds its reflection on the DTG curves registered during the thermolysis of rye and wheat bran.

The process of thermal decomposition of rye and wheat bran takes place within a single temperature area of active thermolysis which is contained within the interval of temperatures ranging from 150-360°C (Table 2). The whole area is made up of two degradation stages (Fig. 1). The stage associated with the thermal destruction of the carbohydrate part of the examined samples extends from 168-217°C for rye bran and from 152-162°C for wheat bran. The second stage of the rye bran

sample degradation begins at the temperature of 225°C, while that of the wheat bran sample – at the temperature of 180°C. In both cases, the authors recorded similar rates of thermolysis (about 2.8%/min) and the termination of the process was determined at the temperature of 360°C. At the assumed final temperature, the samples lost about 74% of their initial weight.

In the case of the starch sample (Fig. 1), the highest dynamics of the weight loss was observed at the range of temperatures from 214 to 383°C (Table 2) and the examined material underwent degradation in about 57%, whereas at the final temperature of thermolysis, it lost almost 76% of its initial weight.

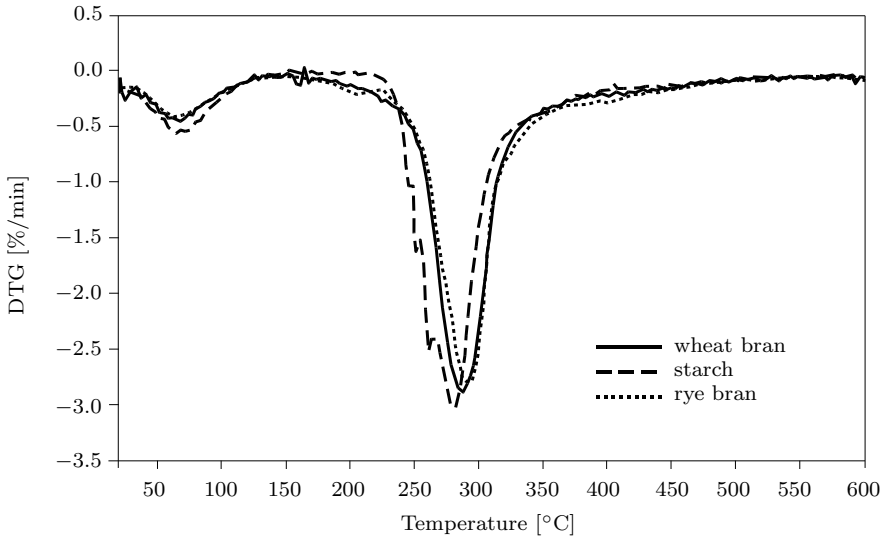

Fig. 1. DTG curves of wheat bran, starch and rye bran

The performed thermal analysis also comprised laboratory test sheets manufactured from pulped waste paper supplemented with 5% addition of rye and wheat bran as well as test sheets without the addition of such material. It was found on the basis of registered DTG curves (Fig. 2) that the area of the active thermolysis of papers manufactured with the addition of bran was contained in the interval from 190 to 368°C (Table 2).

In the case of paper samples manufactured without the addition of bran (Fig. 2), the dynamics of the thermal decomposition increased once the temperature of 168°C was achieved (Table 2). The final temperature in this instance is comparable with the temperature observed for the paper samples supplemented with bran. All the examined paper products achieved the extreme rate of thermal decomposition at the temperature of 337°C. The recorded weight losses of the examined samples at the final temperature of pyrolysis were as follows: 70.7% – paper with rye bran, 71.3% – paper with wheat bran and 72.3% – paper without any additives.

Table 2. Thermal characteristics

Material	Area of active thermolysis [°C]	Degradation stages [°C]	Temperature of maximum degradation rate [°C]	Maximum rate of degradation [%/min]	Weight loss [%]		
					in the area of active thermolysis	in degradation stages	up to 600°C
Rye bran	30-127		65	0.40	7.83		74.10
	168-360	168-217	209	0.26	52.76	2.58	
		225-359	292	2.79		49.72	
Wheat bran	36-125		64	0.44	7.70		74.60
	152-360	152-162	158	0.10	54.91	0.28	
		180-360	286	2.84		54.33	
Starch	21-122		68	0.55	10.13		76.21
	214-383	214-264	259	2.70	57.67	14.56	
		266-383	280	3.00		41.49	
Paper without cereal bran	25-115		58	0.33	5.36		72.30
	168-369		337	4.12	57.40		
Paper with the addition of 5% wheat bran	22-113		58	0.36	5.72		71.30
	199-368		337	4.03	55.41		
Paper with the addition of 5% rye bran	23-112		55	0.32	5.65		70.70
	190-366		337	3.77	54.45		

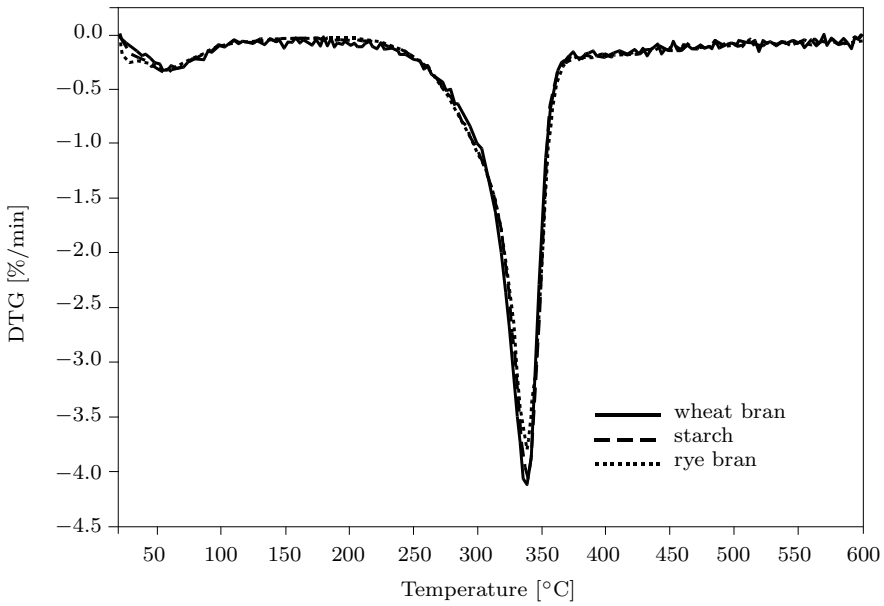

Fig. 2. DTG curves of paper, paper with wheat bran and paper with rye bran

DSC analysis

Differential scanning calorimetry involves measurements of the difference between the energy supplied to the examined substance and the standard one in the function of temperature regulated in accordance with a definite program. The recorded DSC curve shows the quantity of heat exchanged by the sample with the surrounding in a unit of time in the time or temperature function. DSC methods provide a possibility of a rapid determination of the reaction enthalpy and the change of molar heat together with temperature.

The amount of the absorbed or given off heat is expressed in µJ/mg of the examined substance. The quoted measure of the heat effect is connected with the method of measurement in the applied apparatus and differences of temperatures between the examined sample and the applied standard.

The evaporation of water contained in the examined material (the first peak on the DTG curve) is associated with the supply of heat energy to the system. This fact is visible on the DSC curves (Fig. 3 and 4) which indicate the endothermic nature of the process.

The performed theromogravimetric analysis revealed that the thermal decomposition of the examined rye and wheat bran occurred within one area of active thermolysis: respectively 168-360°C and 152-360°C (Table 2). The DSC curves recorded in these areas point to the exothermic nature of the occurring changes (Fig. 3). The quantity of the secreted heat during the thermolysis process of rye

and wheat bran amounted to: (−) 208.24 µJ/mg and (−) 121.90 µJ/mg, respectively (Table 3). In both cases, the extreme of the heat effect, in comparison with the extreme of the degradation rate, is moved towards lower temperatures.

Within the temperature area of starch active thermolysis, the DSC curve indicates an exothermal character of the degradation process (Fig. 3). The recorded cumulative heat effect equals (−) 49.21 µJ of the secreted heat per 1 milligram of the examined sample (Table 3).

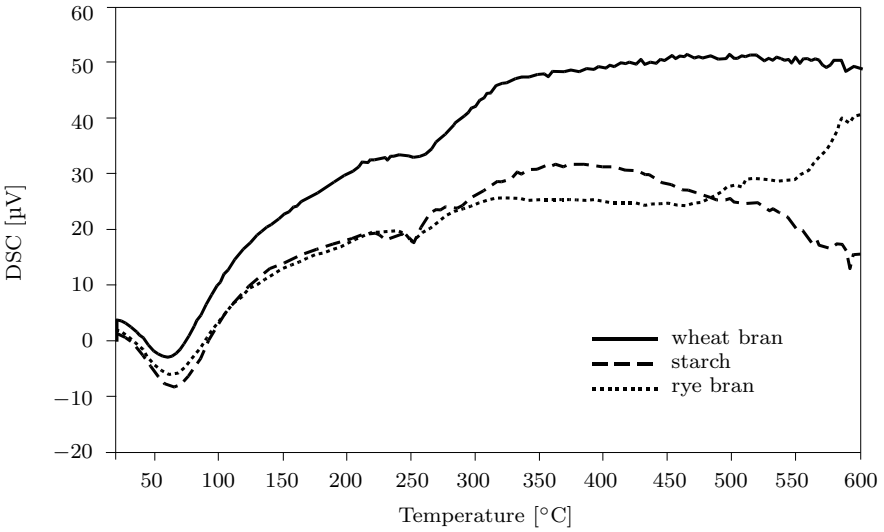

Fig. 3. DSC curves of wheat bran, starch, and rye bran

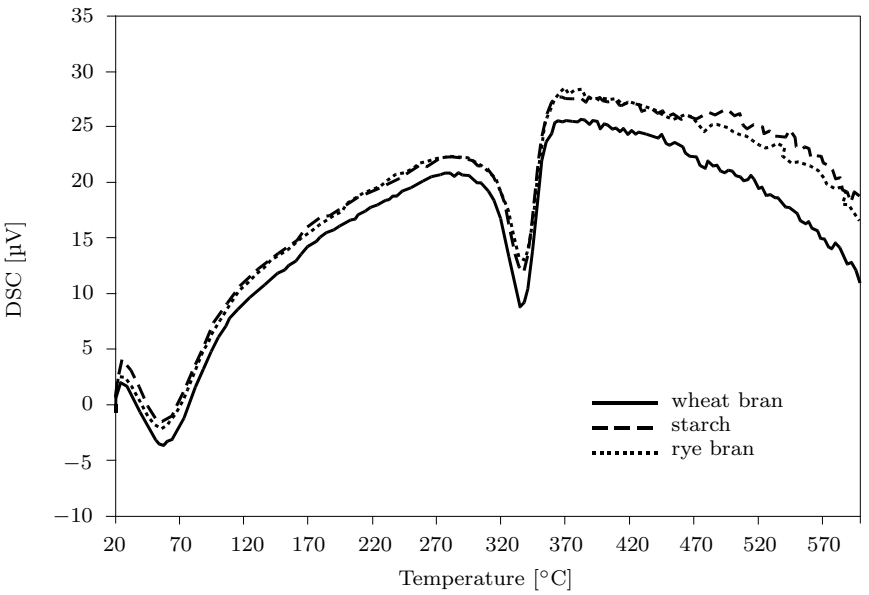

Fig. 4. DSC curves of paper, paper with wheat bran and paper with rye bran

Table 3. DSC analysis

Material	Area of active thermolysis [°C]	Heat [µJ/mg]	Temperature [°C]		Weight loss in the area of active thermolysis [mg]
			maximum of thermal effect	maximum of decomposition rate	
Rye bran	30-127	(+) 469.48	63	65	1.59
	168-360	(−) 208.24	251	292	10.75
Wheat bran	36-125	(+) 393.62	59	64	1.57
	152-360	(−) 121.90	254	286	11.20
Starch	21-122	(+) 622.34	64	68	2.07
	214-383	(−) 49.21	250		11.76
Paper without cereal bran	25-115	(+) 319.53	58	58	1.09
	168-369	(+) 319.65	337	337	11.71
Paper with the addition of 5% wheat bran	22-113	(+) 258.72	58	58	1.17
	199-368	(+) 365.75	337	337	11.30
Rye bran	23-112	(+) 297.98	57	55	1.15
	190-366	(+) 416.92	337	337	11.05

The thermolysis of the examined paper articles takes place in one area of increased degradation dynamics. On the basis of the DSC curves, an endodermic nature of the pyrolysis process was established (Fig. 4). The amount of heat energy necessary for the thermal decomposition of paper supplemented with rye bran amounted to (+) 416.92 µJ/mg, while for the paper manufactured with the addition of wheat bran – (+) 365.75 µJ/mg (Table 3). The demand for heat energy during the thermolysis of the paper without bran supplementation was at the level of (+) 319.65 µJ/mg. It was found that the extreme values of heat effects (337°C) of the examined paper products coincide with the extreme values of the degradation rates (337°C).

Heat of combustion

Following the determination of the heat of combustion, of both rye and what bran, very high results were obtained (Table 4). Rye bran turned out to be energetically better but the difference between the two discussed cases was rather small, of the order of 650 J/g.

Table 4. Heat of combustion of what and rye bran

Heat of combustion Q_s, [J/g]	Cereal bran	
	wheat bran	rye bran
	18 565.72	19 210.81

CONCLUSIONS

On the basis of the performed thermal analysis (TG/DSC), the following conclusions were drawn:

- variations in the values of weight losses during the first stage of thermolysis of both rye and wheat bran as well as the lower range of temperatures for this stage in the case of wheat bran can be associated with the lower cellulose content in this material in comparison with rye bran,
- the thermal decomposition of rye bran begins at higher temperature in comparison with wheat bran,
- the active thermolysis of the milling by-product takes place at a lower range of temperatures in comparison with starch thermal degradation,
- weight losses of the examined milling by-product during the final temperature of thermolysis are comparable and only slightly lower in relation to starch weight losses,
- the thermal decomposition of the examined bran and starch is of exothermal nature, and values of heat effects differ considerably,
- the thermal degradation of laboratory test sheets manufactured with the addition of the milling by-product begins at higher temperatures in comparison with the test sheets without the inclusion of cereal bran,
- no clear differences in the final weight losses of the examined laboratory test sheets were observed,
- the thermal decomposition of paper products is of endothermic nature; the smallest quantity of heat energy needed to degrade test sheets was used in the case of test sheets without the addition of the milling by-product.

The recorded high results of the heat of combustion of both rye and wheat bran indicate that the examined raw materials can be used as biofuels for energetic purposes.

REFERENCES

Antal M.J.Jr. (1985): Biomass pyrolysis: a review of literature. Part 2. Lignocellulose pyrolysis. Adv. Solar Energy: 175-255.

Cofta G., Modzelewska I., Fuczek D. (2006): Investigations on the resistence of selected paper products containing cereal bran to the infestation by microfungi. Ann. Warsaw Agric. Univ. SGGW For. Wood Technol. 59(1): 110-113.

Modzelewska I. (2006): Selected strength properties of paper products with the addition of cereal bran. Ann. Warsaw Agric. Univ. SGGW For. Wood Technol. 59(2): 87-90.

Modzelewska I., Adamska K. (2006): Application of cereal bran in production of paper products – initial investigations. Acta Sci. Pol. Silv. Colendar. Rat. Ind. Lignar. 2(2): 175-184.

PN-92 P-50092. Surowce dla przemysłu papierniczego.

PN-81 G-04513. Oznaczanie ciepła spalania i obliczanie wartości opałowej.

Prosiński S. (1984): Chemia drewna. PWN, Warszawa.

Sun R.C., Sun X.F. (2002): Structural and thermal characterization of acetylated rice, wheat, rye and barlay straws and poplar wood fibre. Ind. Crops Prod. 16: 225-235.

Werther J., Saenger M., Hartge E.U., Ogada T., Siagi Z. (2000): Combustion of agricultural residues. Progr. Energy Combust. Sci. 26: 1-27.

Received in July 2007

Authors' address:
Dr. Izabela Modzelewska
Dr. Monika Bartkowiak
Institute of Chemical Wood Technology
August Cieszkowski Agriculture University of Poznań
ul. Wojska Polskiego 38/42
60-637 Poznań
Poland