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EVALUATION OF THE THERMAL BEHAVIOUR OF AGRICULTURAL WASTES FOR POSSIBLE USE IN THE BIOMASS PELLETS INDUSTRY

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Abstract. This paper tackles the potential uses of agricultural wastes (sawdust, sunflower seed shells, pumpkin seed shells, cherry pits, walnut shells, and green walnut shells) for the production of pellets. Combustion heat was determined for these wastes and their thermal decomposition in an air atmosphere was analysed. Five types of mini-pellets were made from different combinations of available wastes and their thermal behaviour was analysed by the microscale combustion calorimetry method. The results were compared with those obtained for pellets available on the market and it was concluded that the mini-pellets obtained from agricultural wastes can be used to maintain combustion in heating systems based on pellets boilers.

Keywords: waste, biomass pellet, combustion heat, thermogravimetric analysis, microscale combustion calorimetry.

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Glossary

CP	cherry pits
DWS	dried walnut shells
GWS	green walnut shell
PSS	pumpkin seeds shells
SSS	sunflower seed shells
S	sawdust
WF	wheat flour
Pc	pellets commercially available
HRC	heat release capacity
HRR	heat release rate
PHRR	peak heat release rate
THR	total heat release
MCC	microscale combustion calorimetry method

Introduction

The concern of the researchers to develop new ways of the use of biomass for energy purposes is continuous and is supported almost worldwide. Wood pellets are a form of biomass, however they have the disadvantage of being relatively expensive, therefore cost-effective alternatives should be proposed. Holubcik, M. *et al.* showed that woody plants such as red raspberries and black currants have similar energy properties as Norwegian spruce sawdust pellets and could be regarded as efficient replacements to wood pellets [1]. The amount of wastes originating from agriculture increases along with agricultural production. These residues could be converted to energy sources by techniques such as combustion, gasification, pyrolysis, *etc.*, however the use of these raw wastes has some disadvantages, including the low energy density, low energy efficiency, large storage capacity and problems related to transportation and distribution. In order to improve the transportation, storage and energy generation characteristics of agricultural wastes, its bulk density should be increased. Briquetting is one of the methods of increasing bulk density up to 1000-1200 kg/m^3, compared to 30-150 kg/m^3 for raw material, and the volume may be reduced by 8-10 times [2].

Increased domestic and industrial demand for biomass heat and energy production in Canada, United States, Europe and China has led, in recent decades, to a strong global pellet market and a market growth is forecast for the coming years. In the near future, agricultural wastes have great potential in the biomass pellets industry. It is, therefore, of great interest to study the characteristics of this new category of raw materials, paying special attention to the problems that they may cause in terms of both production and use. From a technical point of view, the main difference between wood pellets and agropellets is the latter's slight friability, slightly lower energy

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efficiency and higher ash content [3]. With 14.8 million hectares, Romania is the second largest agricultural producer in Central and Eastern Europe, after Poland, and currently holds one of the best positions in Europe in terms of biomass [3]. Within the country, the biomass energy sector is divided. Wood production is concentrated in the Carpathians and Subcarpathians, while agricultural by-products are produced in the southern part of the country and in the region of Moldova. In order to guarantee an independent supply of energy for the rural population, concepts have been developed to produce energy and heat from agricultural by-products. Nowadays, it appears that biomass pellets production strongly competes with direct biomass burning due to higher investment costs for pellets production [3].

In the next years, agro-pellets could play a more important role in the supply of thermal energy to households and towns/cities, after overcoming the difficulties related to agro-pellets combustion in small and medium boilers [4]. Several studies have been carried out in the last two decades that examined for example the thermochemical characteristics and performance of solid olive residues suggesting that these are a promising biomass resource, which could be used for energy [5,6]. On the other hand, Brlek, T. *et al*. suggested limiting the burning of olive processing waste pellets due to their high nitrogen content [7].

Marculescu, C. and Ciuta, S. established that over 20% of each kilogram of grapes processed for wine is waste. They analysed the thermal degradation of grape marc in a laboratory oven and found that it possesses high energy efficiency (19.7 kJ/kg) [8]. Rossini, G. *et al.* have found that tomato waste may be suitable for combustion, but its relatively high nitrogen content may cause NO_x emission problems; therefore, the authors suggested the separation of tomato waste into combustion peels and seeds for vegetable oil production [9]. González, J.F. *et al.* have studied the tomato waste combustion in a wall boiler and found that tomato residues proved more efficient in the boiler than other biomass (forest residues, sorghum, almond kernels and cane) [10]. Ruiz-Celma, A. *et al.* have studied tomato seeds and peels pellets and reported a high energy value and an energy density (approaching 8 GJ/m^3) similar to that of other biomass pellets, regardless of their low bulk density values [11]. In 2017, Brunerová, A. *et al.* have analysed the use of residual biomass from oats (*Avena sativa*), wheat (*Triticum spp*.), poppy (*Papaver somniferum*) and barley (*Hordeum vulgare L.*) residues, which were chosen because these do not require additional mechanical processing, when leaving the post-harvest processing lines. The assessment of the recorded results showed a satisfactory level of chemical quality and high energy potential of all investigated materials, yet a low level of their mechanical quality [12,13].

The goal of this study was to assesses the possible uses of specific agricultural wastes, dried walnut shells (DWS), green walnut shell (GWS), cherry pits (CP), sunflower seed shells (SSS), pumpkin seeds shells (PSS) and sawdust (S), for pellets production, respectively to obtain easily reproducible products in a household or small farm.

Experimental

Materials

Selected agricultural wastes, sawdust, sunflower seed shells, pumpkin seed shells, cherry pits, walnut shells, and green walnut shells, were assessed based on their combustion heat; additives (wheat flour - WF) were used to produce mini-pellets. The initial material consisted of various types of wastes dried at room temperature (approximately 20°C). Note that pumpkin seed shells dried slower than sunflower seed shells. The green walnut shells were already dried when these were gathered after harvesting the nuts. The dried agricultural wastes were then ground in a mortar to facilitate the formation of mini-pellets.

Pellets production

The mini-pellets were obtained by pressing/compressing a mixture of properly dried and minced ingredients. In order to improve the combustion process, approximately 6% beech wood ash (A) with an installed power of 7 KW was also included in the 5 types of mini-pellets. The ash was introduced as catalyst for the combustion process of mini-pellets [14]. The obtained mini-pellets were of 15 mm in diameter and 5 mm in length. Table 1 shows their percentage mass composition by codes. The humidity present in the 5 types of mini-pellets (Table 1) was determined indirectly from the thermogravimetric analysis. The recorded results on the obtained mini-pellets were validated by analysing the thermal behaviour of the pellets commercially available, with a diameter of 6 mm, humidity of 7.7% and calorific value declared by the manufacturer of 18.2 MJ/kg.

Table 1

Information about the mass composition (%) of the obtained mini-pellets.

Pellets		*WF, %*	*GWS, %*	*CP, %*	*DWS, %*	*PSS, %*	*SSS, %*	*S, %*	*A, %*	*Total mass, g*	*Humidity, %*
P1		30.05	31.65	-	-	-	-	32.36	5.94	0.9134	6.31
P2		27.40	27.91	-	-	-	39.03	-	5.66	0.9173	6.68
P3		22.68	-	37.30	-	-	34.12	-	5.90	0.9279	5.75
P4		27.20	32.29	-	34.53	-	-	-	5.98	0.9372	7.68
P5		18.45	38.50	-	-	37.00	-	-	6.05	0.8375	5.05

Methods

The *combustion heat* of agricultural wastes was determined using a Berthelot calorimeter. The samples were compressed and burned in a platinum crucible. The used calculation ratio (Eq.(1)) [15]:

$$\Delta H^0_{C,298} = \frac{-C \cdot \Delta T - m_{Fe} \cdot \Delta H^0_{C,298}(Fe)}{m_s} \quad (1)$$

where, *C*- heat capacity of the calorimeter ($1.04 \cdot 10^4$ J/K);

ΔT- temperature difference accompanying the combustion (°C);

m_{Fe}- mass of the burned Fe thread (g);

$\Delta H^0_{C,298}(Fe)$ - iron standard enthalpy of combustion ($-6.658 \cdot 10^3$ J/g);

m_s- mass of the sample submitted to combustion (g);

$\Delta H^0_{C,298}$ - standard enthalpy of combustion of the sample submitted to thermal degradation.

Thermogravimetric analysis was performed dynamically, in air with a flow rate of 20 cm^3/min, with a heating rate of 10°C/min, within the 25-700°C temperature range and the sample weight between 3.8 and 4.3 mg. The Mettler Toledo TGA-SDTA851^e equipment was used, and the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal (DTA) curves were processed using Mettler Toledo's STAR software. The operating parameters were kept constant for all types of analysed wastes, in order to obtain comparable data. The main thermogravimetric and thermal characteristics considered were: T_{onset} - the temperature at which the thermal degradation starts at every stage; T_{peak} - the temperature at which the thermal degradation is maximum; T_{endset} - the temperature at which the degradation process ends for each stage; *W*- percentage weight loss and DTA characteristic (exo- or endothermal processes).

The *flammability behaviour* of the samples was tested using an FTT Micro Calorimeter with microscale combustion calorimetry (MCC) method. The weight of the analysed samples ranged between 3.64 mg and 5.15 mg, and they were heated at a rate of (1°C/s) in a nitrogen atmosphere with a flow rate of 80 cm^3/min; the resulting gases were mixed with oxygen with a flow rate of 20 cm^3/min and then fed into the combustion chamber heated to 900°C. The oxygen consumption rate was measured continuously and the heat release results were calculated as the mean of five measurements for each sample. Note that ASTM D7309-2007 (method A) was applied, which involves sample degradation in a nitrogen atmosphere; then, as specified above, the flue gases are fed into a combustion chamber where these are thermally oxidized until exhausted [16]. By applying these tests, the following parameters were measured: *HRR* (heat release rate), T_{PHRR} (peak heat release rate temperature), *PHRR* (peak heat release rate), *THR* (total heat release) and *HRC* (heat release capacity). The residue remaining after the analysis was weighed and reported as a percentage [17,18].

Results and discussion

Combustion heat determination

Heats of combustion are usually determined by burning a known amount of the material in a bomb calorimeter with an excess of oxygen, and the heat of combustion can be determined by measuring the temperature change. Table 2 compares the combustion enthalpies obtained using a Berthelot calorimeter for the analysed types of wastes and also presents values from the literature. The combustion heat was determined for the studied starting material originating from agricultural wastes, the obtained results are graphically represented in Figure 1.

According to literature data, wood combustion enthalpy ranges between 18800 and 20100 J/g [15]. The results shown in the Table 2 prove that the combustion enthalpy values recorded for pumpkin and sunflower seed shells are only slightly lower than the values for wood. The combustion heat of the analysed samples increases in the following order: green walnut shells < dried walnut shells < cherry pits < pellets available on the market < sunflower seed shells < pumpkin seed shells < sawdust.

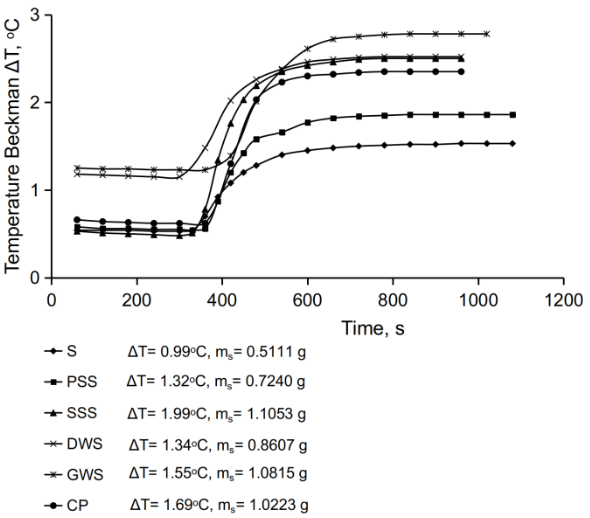

Figure 1. Temperature variation in the calorimeter for the analysed wastes.

Thermogravimetric analysis

The TG, DTG and DTA curves given comparatively in Figures 1S and 2S (Supplementary material) and Figure 2 enabled determining the main thermogravimetric characteristics of the analysed wastes presented in Table 3. According to the obtained results, in stage I, humidity is removed from wastes and varies between 4 and 11%. After humidity removal, the thermal decomposition of sawdust (S) and sunflower seed shell (SSS) samples takes place in two stages. In the case of sawdust, according to literature, the mass loss in the second stage may be associated with the total decomposition of hemicellulose and cellulose and with the partial decomposition of lignin. The last stage corresponds to the decomposition of the remaining lignin and the burning of carbon residues [24]. As expected, the main thermogravimetric characteristics obtained for commercial pellets (Pc) are close in value to those of S. The amount of residue obtained at 700°C is 9.48% for S and 6.10% for Pc. The main decomposition stage of SSS occurs within the 252-333°C temperature range and is accompanied by a 48.43% mass loss. Compared to S, the SSS thermal decomposition onset at this stage occurs earlier with a deviation of 15°C, probably due to the higher hemicellulose content, which is rich in poor etheric bonds that are thermally unstable and produce volatile combustible species, capable of homogeneous combustion in the gaseous phase [25,26].

A different behaviour was noted in the case of the thermal decomposition in air of pumpkin seed shells, which, at temperatures higher than 350°C, undergo a two-process transformation, with decomposition rate temperatures peaks at 459 and 514°C, respectively. At the end of the second stage, up to a temperature of 437°C, a series of stable intermediates are probably formed. In the case of this type of seeds (PSS), a twice higher amount of residue was obtained, compared to the other samples (S and SSS).

Table 2

Combustion enthalpy values for the analysed wastes (J/g).

Sample	*This work*	*Literature data*
Sawdust (S)	19826.93	19700 [19], 19482 [20], 9573 [21]
Sunflower seed shells (SSS)	18549.64	18674 [22]
Pumpkin seeds shells (PSS)	18780.16	-
Green walnut shells (GWS)	14785.18	-
Cherry pits (CP)	17071.47	19870 [22]
Dried walnut shells (DWS)	16157.44	17800 [23]
Pellets commercially available (Pc)	-	18200*

**value declared by the producer*

The largest amount of residue at 700°C is produced by GWS. In the last stage, this sample saw a highly exothermal thermooxidation process (Figure 2), accompanied by a considerable mass loss within the 580-630°C temperature range. At the end of the third decomposition stage, GWS also forms a stable intermediate whose decomposition starts at a temperature greater than 580°C. Both DWS and CP have comparable residual amounts, which are four times lower than those of SSS and S; however, as shown above, their caloric capacities are lower than those of the latter types of wastes. After removal of the humidity, the thermal decomposition of the DWS takes place in two stages with temperatures at which the degradation rate is maximum at 285 and 472°C respectively. The last stage of degradation is the thermooxidation process which ends at the temperature of 507°C and is accompanied (according to the DTA curve shown in Figure 2) by a highly exothermic process. Dried walnut shells were analysed by applying the TG/GC/MS (thermogravimetry/gas chromatography/mass spectrometry) technique in a helium atmosphere, within 25-900°C temperature range, by Fan, F. *et al.*, who found that in an inert atmosphere (helium) the thermal decomposition of walnut shells takes place in a single stage with a 347°C peak degradation rate temperature [27]. The TG/GC/MS technique applied on these dried walnut shells samples has helped to the identification of more than 20 different substances in pyrolysis gases, of which can be mentioned furan, furfural, benzene and long chain alkanes, *etc*. Petuhov, O. analysed the thermal decomposition of walnut shells in a nitrogen atmosphere and found that the process takes place in several stages. In the first stage, the removal of humidity and volatile substances takes place and is accompanied by a mass loss of 7.1%. In the following stages, hemicellulose, cellulose and lignin decompose [28]. In the case of wheat flour used as an additive to produce mini-pellets, thermal decomposition in an air atmosphere takes place in three stages. The first stage characterized by an endothermal process, according to the DTA curve (Figure 2), which corresponds to approximately 10% of moisture removal. Starch decomposition in disaccharides occurs during the second stage, within the 274-317°C temperature range, with a 54.34% mass loss. The process continues at temperatures higher than 420°C, with depolymerisation of amylose and amylopectin [29].

Considering the decomposition onset temperature as a thermal stability criterion, obviously disregarding humidity removal, the following thermal stability increase sequence for the analysed materials was obtained: green walnut shells < sunflower seed shells < pumpkin seed shells ≈ dried walnut shells < cherry pits < sawdust < wheat flour.

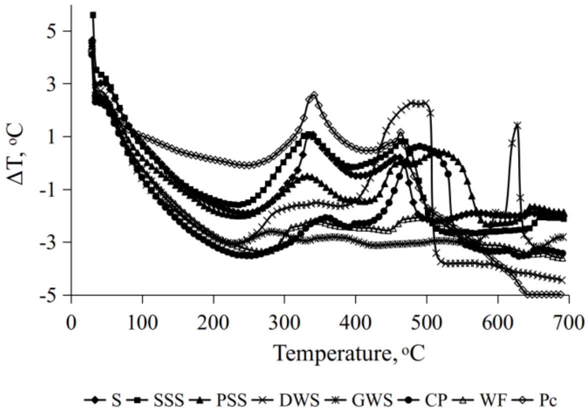

Figure 2. DTA curves of the analysed wastes.

Microscale combustion calorimetry analysis of the obtained pellets

The MCC was used to analyse the 5 mini-pellets whose composition was described in Experimental section (Table 1) and a type of wood pellets available on the market used in heating systems based on pellets boilers. The mini-pellets taken for analysis had a mass ranging between 4.11 mg and 5.15 mg and were heated at a rate of (1°C/s) in a nitrogen atmosphere with a flow rate of 80 cm^3/min; the resulting gases were mixed with oxygen at a flow rate of 20 cm^3/min, then introduced into the combustion chamber of the device heated to 900°C. The variation of the heat release rate (*HRR*) of the tested samples was calculated as a function of time shown in Figure 3. The diagrams prove that only for the mini-pellet denoted P1 the curve separates two peaks, but at much lower values of the *HRR*, compared to the other mini-pellets. The microscale combustion calorimetry was previously used by Agarwal, G. *et al.* to analyse the energetic properties of coal, biomass and mixtures. This is one of the few studies identified in the literature in which the microscale combustion calorimetry method is used to study the thermal behaviour of residues from agriculture [30]. The *HRR* peak obtained for corn biomass is 37.5 W/g, whereas the *HRR* of corn – leached biomass, in which inorganic salts were removed by washing with distilled water for two hours at 110°C and then dried under air at the same temperature, increased to 58.2 W/g [30]. According to the data shown in

Figure 3 and Table 4, the *PHRR* value, 60.78 W/g, was obtained for the mini-pellet marked P3 containing WF, CP, SSS, S and A. The mini-pellet marked P3, has the highest HRC value, and also a higher heat release rate peak temperature (Figure 3S, Supplementary material). The pellet containing 100% wood material (Pc), available on the market, obviously had a high *PHRR* value, *i.e.* 99.07 W/g, which was higher than that of mini-pellets made of different agricultural vegetable waste.

Table 3

Thermogravimetric characteristics of the analysed wastes.

Sample	*Stage*	T_{onset}, °C	T_{peak}, °C	T_{endset}, °C	*W*, %	*Residue*, %
S	I	52	69	95	4.23	9.48
	II	267	327	339	51.37	
	III	339	454	476	34.92	
SSS	I	57	78	113	4.05	8.18
	II	252	299	333	48.43	
	III	333	464	491	39.34	
PSS	I	56	76	106	5.38	17.26
	II	258	320	349	43.79	
	III	437	459	501	19.34	
	IV	501	514	561	14.23	
GWS	I	51	70	99	8.93	22.9
	II	219	278	302	30.79	
	III	302	369	450	18.00	
	IV	583	624	631	19.38	
CP	I	58	81	156	8.39	2.26
	II	262	290	320	26.08	
	III	320	344	369	27.38	
	IV	458	511	533	35.89	
DWS	I	54	84	120	8.91	2.54
	II	258	285	349	52.76	
	III	414	472	507	35.79	
WF	I	44	66	105	10.15	3.86
	II	274	301	317	54.34	
	III	428	495	542	31.65	
Pc	I	48	65	95	5.48	6.10
	II	268	331	349	56.08	
	III	410	457	498	32.34	

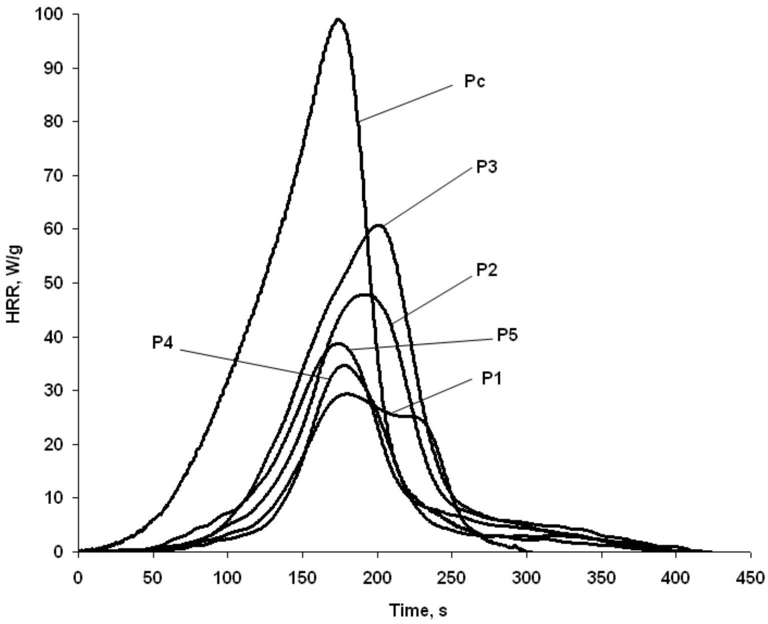

Figure 3. Time-dependent *HRR* curve representation for the obtained pellets.

Table 4

Microscale combustion calorimetry results for the obtained pellets.

Pellets	*Mass, mg*	*THR, kJ/g*	*PHRR, W/g*	T_{PHRR}, °C	*HRC, J/gK*	*Residue, %*
P1	5.12	3.28	29.34	328.46	29.96	14.84
P2	5.15	4.67	47.86	336.06	49.22	22.71
P3	4.11	5.77	60.78	355.34	61.03	20.19
P4	4.60	2.78	34.65	324.80	35.37	20.21
P5	4.40	3.72	38.72	329.93	38.78	24.09
Pc	4.30	8.42	99.07	375.59	122.64	17.67

P1 generated the smallest amount of residue. All mini-pellets obtained from plant wastes produce heat for about 350 seconds, according to time-dependent HRR curve (Figure 3). The results show that the latter had a higher *HRC* than our mini-pellets and also a higher heat release rate peak temperature. Pellets available on the market, marked Pc in the diagram in Figure 3, produce heat for about 275 seconds. Based on the results achieved in this study, it was shown that *HRC* is lower for mini-pellets than for commercial wood pellets, however, the duration of the combustion process is greater in their case, and the amount of ash obtained is comparable. Nonetheless, it can be concluded that mini-pellets made from agricultural waste can be used together with wood pellets to maintain combustion in heating systems based on pellets boilers.

Conclusions

This paper is devoted to the evaluation of the combustion heat of specific agricultural wastes, dried walnut shells, green walnut shell, cherry pits, sunflower seed shells, pumpkin seeds shells and sawdust, which may be used for pellets production. Their thermal decomposition in an air atmosphere was analysed within the 25-700°C temperature range.

Combustion heat and thermal stability increase sequences for the analysed materials were thus established. Combustion heat values greater than 18000 J/g were obtained for: sunflower seed shells, pumpkin seeds shells and sawdust. A different behaviour was noted in the case of the thermal decomposition in air of pumpkin seed shells, which, at temperatures higher than 350°C, undergo a two-process transformation. At the end of the second stage, a series of stable intermediates are probably formed up to a temperature of 437°C. It has also been noted that the largest amount of residue at 700°C was produced by green walnut shells. At the end of the third decomposition stage, green walnut shells also formed a stable intermediate whose decomposition starts at a temperature greater than 580°C.

Five types of mini-pellets were made from different combinations of selected wastes and their thermal behaviour was analysed by the microscale combustion calorimetry method. The mini-pellet, marked P3, containing wheat flour, cherry pits, sunflower seed shells and ash has shown the best energy performances and the better flammability behaviour. In comparison to commercially available pellets, the five prepared mini-pellets have a longer combustion time.

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Supplementary information

Supplementary data are available free of charge at http://cjm.asm.md as PDF file.

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