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Biofuels

Part II. Thermogravimetric research of dry decomposition

Sławomir Poskrobko · Danuta Król

Bretsznajder Special Chapter

Abstract The article presents results of thermogravimetric measurements of the pyrolysis of dry biomass materials such as: grains and oats and triticale straw, energy plants called cukrosorgo. The initial phase of dry decomposition visible on the DTG curve is evaporation of moisture. The process of evaporation for the studied types of agro biomass occurred at temperatures of 65.9 °C (triticale straw) to 82 °C (oat grain). The next stage of the process concerned major transformations that for the studied cases were conducted in temperatures of 200–400 °C, and the maximum speed of transformations (the second peak is visible in the DTG graph) refers to the temperature range from 299.1 °C (oat grain) to 323.9 °C (triticale straw). The last phase of the process is characterized by the absence of mass loss, which in the case of dry biomass distribution determines the conditions of carbonizate formation. The calorific values of formed process gases ranged from 4,884 to 6,302 kJ/Nm^3. Gases of such calorific values are defined as low calorific, despite the fact they can be successfully used for energy purposes, this is for burning in boilers and gas turbines. Carbonizates are characterized with high-calorific values from 24,100 to 27,900 kJ/kg. This type of high-calorific fuels is recommended to be burnt in the boiler furnaces in a mix with fuels with a lower calorific value such as pulverized coal or wet biomass. In these processes, the combustible gas is obtained, which can be burned in power boilers and gas turbines.

Keywords Thermogravimetric · Agro biomass · Pyrolysis gas · Semi-coke · Calorific value

Introduction

Stringent emission requirements to energy sources from combustion processes, mainly restrictions to anthropogenic emissions of CO$_2$ and other greenhouse gases, have contributed to the launch of energy technologies based on renewable energy sources. It is important therefore not only to implement the most energy-efficient, cutting edge technologies (including clean coal technologies) and to improve energy efficiency in used technologies, but also to increase progressively the scope of generating electricity and heat (as well as liquid and gas fuels) from renewable energy sources. Offsetting renewable energy resources, the greatest energy potential (ca. 60 %) constitutes the biomass [1]. Due to expected high consumption of biomass in energetics, its range, in addition to forest biomass, includes biomass from agricultural sources, the so-called agro. Priority of agro biomass as a biofuel for energetics is justified, among others, by the fact that the acquisition of wood biomass is limited by the rational management of forests. Yet, using agro biomass as biofuel for power boilers poses many technological problems. The high content of alkali metal chlorides, mainly KCl, promotes the formation of high-temperature corrosion centres (chlorine) [2]. Corrosive action of chlorine significantly limits the life of structural steel boilers (e.g. screens, elements of the exchanger). Frequent replacement of these items cannot be justified from the economical point of view. The problem is

S. Poskrobko
Bialystok University of Technology, ul. Wiejska 45C,
15-351 Białystok, Poland

D. Król (✉)
Silesian University of Technology, Konarskiego 18,
44-101 Gliwice, Poland
e-mail: dankrol@wp.pl

currently the subject of many research works [3–6]. One method of limiting the corrosive effects of chlorine on the structural elements of power boilers is to carry out the thermal transformation process at relatively low temperatures, up to 600/850 °C [7]. Due to low temperature, we have to deal with thermal changes occurring in the processes of degassing (dry decomposition) without air access and the process of gasification—with limited access of air. Under such conditions, it is possible to efficiently process binding of chlorine emitted from agro biomass [8–10] in the form of HCl, by limestone sorbents. The resulting gas, in the case of pyrolysis additionally also carbonizate, in the next stage of energy production process can be co-incinerated with coal in power boilers. Examples of such solutions, based on technologies of gasification of municipal waste and wood biomass, are discussed in the literature [11, 12]. However, before the technology of agro biomass is implemented, it is necessary to conduct identity studies, which define the features of certain kinds of biomass in the environment, characteristic for the thermal transformation process. These studies primarily relate to energy efficiency, and their scope includes determining: (i) the properties of fuel (including calorific value LHV) of agro biomass, (ii) the speed of weight loss—in the case of solid fuels transition from solid to gas and (iii) the calorific value of the obtained products of degassing or gasification processes. Information on phase transformations and thermal decomposition products is provided by thermal analysis. That is why thermogravimetric study on the distribution of solid fuels is widely discussed in the literature [13–15]. Interpretation on the thermogravimetric analysis of agro biomass distribution is presented in references [13, 16, 17]. We interpreted the characteristics of dry decomposition (pyrolysis) of many kinds of biomass and among others: bagasse, corn cob, corn stalks, rice husk, rice straw, wheat straw. On the basis of TGA and DTG curves, we identified the division and the proportion of products for each kind of tested biomass, an interpretation of the process in terms of phase transformations occurring in the different types of biomass within a specified range of temperatures has been made. The ones that deserve attention are an analysis of the interaction of individual biomass components (e.g. cellulose, chemicellulose) during dry decomposition. In references [13, 18], the use of TG–FTIR method to study the feasibility of producing biofuels from several types of agro biomass is discussed. The obtained data relate primarily to the energy valuable (the possibility of obtaining a high-calorific value LHV) pyrolysis products of coconut shells, peanut shells, sugar cane bagasse and corn stalks. The essence of evaluation is the ability of the above-mentioned biomass kinds to produce liquid biofuels, in particular bio-oils. Many works focus on assessing the kinetics of the chemical processes, i.e. pyrolysis, gasification and combustion [16, 19–23]. Such analytical studies, on the one hand, are moving towards establishing optimal process conditions, which aim at the maximum possible yield of liquid products (alcohols, oils, organic acids including, e.g. acetic acid), on the other hand, they are focused on the production of process gases possibly deeply non-condensable, with high-calorific values, which translates into a measurable energetic effect of combustion in boilers and gas turbine, e.g. technologies IGGC [24–26].

Aim of this study is to discuss methods of estimating calorific value of gaseous pyrolysis products of agro biomass, i.e. inedible grains, cereal straw and energy crops—cukrosorgo. The proposed method for determining the calorific value of after pyrolysis gases is basically a thermogravimetric analysis coupled with mass spectrometry (TG/MS). This allows to determine the calorific value of after pyrolysis gases in laboratory conditions, resulting from the decomposition of biomass fuels, rarely used in the generator processes. Undertaking such research procedure is necessary for purposes such as balancing the combustion process of such gases in power boilers and gas turbines.

Experimental

Materials

We examined agro biomass waste, that is oats and triticale straw, grain oats and triticale grain and cukrosorgo stalks. Research materials come from Polish territory (Podlasie province). Samples of tested materials were collected in accordance with the procedures for sampling solids. The preparation of representative, homogeneous laboratory samples consisted of milling and homogenization.

Testing fuel properties and thermogravimetric studies

Testing fuel properties of waste agro biomass included determination of moisture, combustible and non-combustible parts, heat of combustion and calorific value (according to Polish Standards PN-ISO 1171:2002, PN-ISO 1928:2002). Elemental composition of the flammable substance—carbon C, hydrogen (H), nitrogen (N), sulphur (S)—has been determined with the elemental analyzer CHNS, model 2400, series II made by Perkin Elmer. Chlorine (Cl) has been determined according to PN-ISO 587/2000. For the thermogravimetric studies, samples were dried to dry mass at the temperature of 105 °C. Samples weighing 14 mg were placed in a crucible with a capacity of 50 µl. The tests were performed using thermoscale Netzch STA 409 PG/2/G Luxx. Studies on dry decomposition (pyrolysis) of agro biomass were performed in argon atmosphere. Measured flow rate of argon is 50 ml/min.

Identification and measurement of gaseous products concentrations of pyrolysis were performed using a mass spectrometer Balzers QM 200 coupled with thermoscale. The process of dry decomposition of test materials placed in the thermoscale crucible was carried out at temperatures ranging from (reference temperature – room temperature) to 1,000 °C at the rate of linear temperature rise of 10 °C/min.

Results and discussion

The results of fuel properties of agro biomass tested are presented in Tables 1 and 2.

Individual values for biomass fuel properties included in Table 1 indicate that these biofuels may be suitable for use in the energy sector. High-calorific value from 15,254 kJ/$kg_{dry\ wt}$ (triticale grain) to 16,005 kJ/$kg_{dry\ wt}$ (oat grain) is the evidence. The low share of non-combustible parts, in turn, proves a small residual mass on the scraper (ash), which is the waste in the combustion process. As for the data summarized in Table 2, it is worth to mention mass share of sulphur (S) and chlorine (Cl). These elements in the biomass are found in inorganic compounds. Their content in the fuel, on the one hand, suggests the possibility of high-SO_2 and -HCl emission to the atmosphere, on the other hand, indicates the trend of corrosion outbreaks in structural steel construction elements of boiler furnace and installation of exhaust extract. Therefore, the practical rules for the selection of biofuels for power boilers often draw attention to the ratio of Cl/S. The limit is 0.454. If the Cl/S < 0.454, then the fatal corrosive chlorine action is ineffective, due to greater tendency to form mineral sulphur compounds in the furnace. This helps maintaining high-softening temperature of ash within the limits of 1,200 °C. Lowering the temperature of combustion does not allow softening of ashes, but it reduces the efficiency of the boiler. Taking into account the analysis of the data included in Table 2, agro, due to the chlorine content, are not fully valuable fuel for combustion in power boilers. When it comes to generating heat either in the form of hot water or steam, their use (because of the need to maintain low temperatures in the furnace) makes it difficult to achieve the required economic effects. It is true that the maintenance of sufficiently high temperature is possible, but for operational reasons (high-temperature corrosion, trails), it is not recommended. Therefore, agro biomass, despite the high-calorific value (Table 1), is not suitable for combustion in power boilers. However, good results of using agro biomass can be expected if it is processed in pyrolysis or gasification. In the case of pyrolysis, we obtain carbonizate, tar and combustible gas. Products of the gasification process, in an air deficiency environment, are combustible gas and ash. Thermal transformations of agro biomass in pyrolysis and gasification processes do not require high temperatures, so despite the high content of alkali metals and chlorine, there is no softening phenomenon in solid residue. In the production of combustible gases, alkali performs catalytic functions [27]. This results in a greater percentage of combustible gas components, which translates into an increase in its calorific value.

Opportunity to evaluate the efficiency of physicochemical transformations in the pyrolysis process of flammable substance was obtained by thermogravimetric analysis. Figures 1, 2, 3, 4 and 5 show thermogravimetric curves TG and DTG for the studied types of agro biomass. TG curves record weight loss Δm as a function of temperature during heating of the fuel sample. Using the differential of TG curve, we obtain the first derivative $dm/dt = f(T \text{ or } t)$ (rate of weight loss where: T—temperature, t—time), what is

Table 1 Fuel properties related to dry mass

Sample type	Fuel properties			
	Humidity/%	Combustible parts/$\%_{dry\ wt}$	Ash/$\%_{dry\ wt}$	Calorific value/kJ/$kg_{dry\ wt}$
Oat grain	10.37	97.35	2.65	16,005
Oat straw	5.93	94.69	5.31	15,745
Triticale grain	10.81	97.86	2.14	15,245
Triticale straw	4.98	96.91	3.09	15,658
Cukrosorgo	5.94	95.03	4.84	15,660

Table 2 Elemental composition of flammable substance (mass of dry ashless fuel)

Sample type	Elemental composition of flammable substance/$\%_{dry\ wt}$					
	C	H	N	S	Cl	O
Oat grain	45.15	7.19	2.38	1.07	0.02	44.19
Oat straw	46.18	6.40	1.35	0.94	0.056	45.07
Triticale grain	43.72	6.89	1.83	1.03	0.03	46.50
Triticale straw	46.41	6.50	1.32	0.92	0.05	55.21
Cukrosorgo	46.88	6.26	1.13	0.96	0.09	43.83

shown in Figs. 1, 2, 3, 4 and 5 by the differential thermogravimetric curve DTG. Based on the analysis of DTG, we identified the stability of thermal decomposition of biomass processes, the rate with which changes occur in the measurement of mass and the maximum values of the rate of changes on the DTG curve indicate the extreme (peak), which corresponds to points of inflection on the TG curves. The initial phase of dry decomposition visible on the DTG curve is evaporation of moisture. The process of evaporation for the studied types of agro biomass occurred at temperatures from 65.9 °C (triticale straw) to 82 °C (oat grain). The next stage of the process concerned major transformations, that for the studied cases were conducted in temperatures of 200–400 °C and the maximum rate of transformations (the second peak is visible in the DTG graph) refers to the temperature range from 299.1 °C (oat grain) to 323.9 °C (triticale straw). The last phase of the process is characterized by the absence of mass loss, i.e. d$m = 0$, which in the case of dry biomass distribution determines the conditions of coke formation. The percentage of dry residue, i.e. coke (curve for d$m = 0$), is read from the TG curve, where the final temperature of the pyrolysis process was about 1,000 °C. Analysing the DTG curve, we can remark different temperature conditions of coke creation, where d$m \rightarrow 0$. In the case of pyrolysis of the oat straw, triticale straw and cukrosorgo, semi-coke is created in the temperature range 400–600 °C. As for the distribution of dry oat grain and triticale grain, semi-coke formation temperature range ranks between 400 and 500 °C.

Table 3 contains the process values, characteristic for the studied types of agro biomass. These are the

Fig. 1 Curves TG and DTG for oat grain

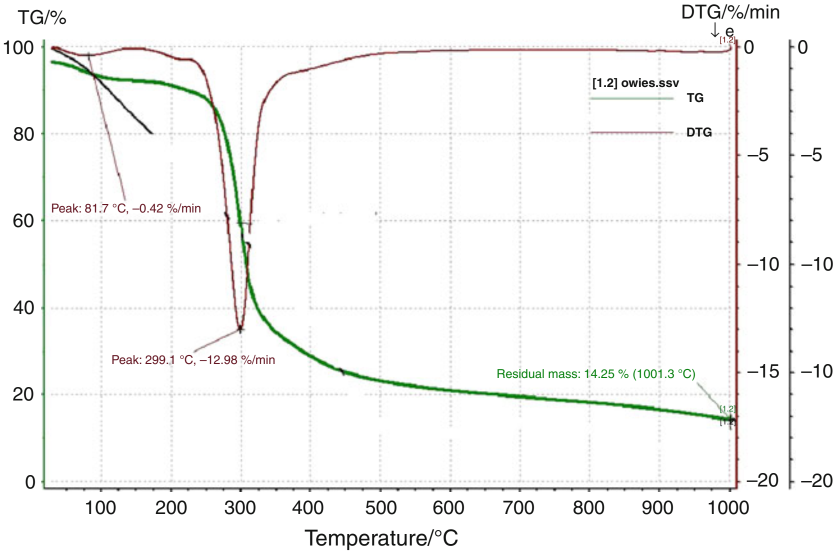

Fig. 2 Curves TG and DTG for oat straw

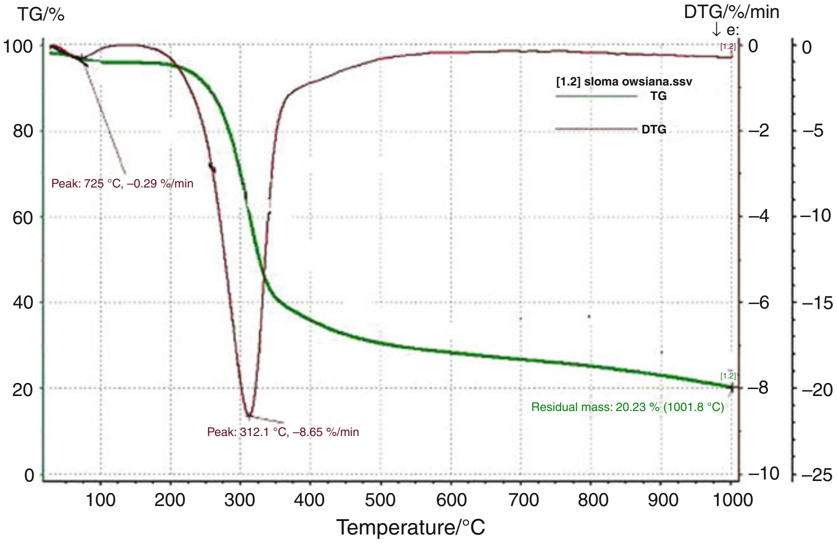

Fig. 3 Curves TG and DTG for triticale grain

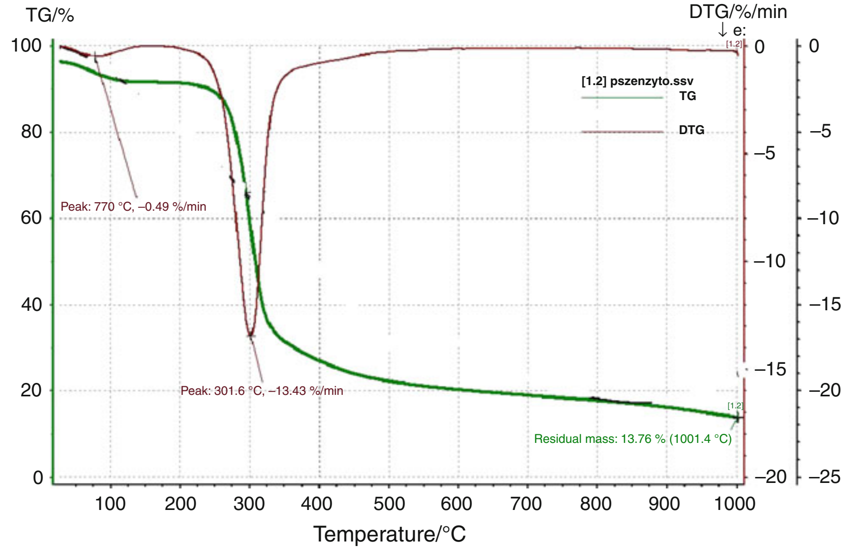

Fig. 4 Curves TG and DTG for triticale straw

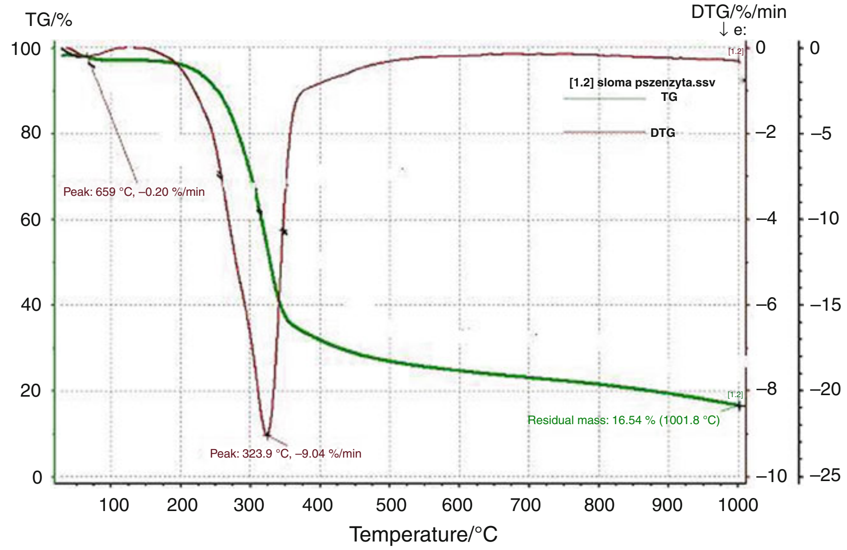

Fig. 5 Curves TG and DTG for cukrosorgo

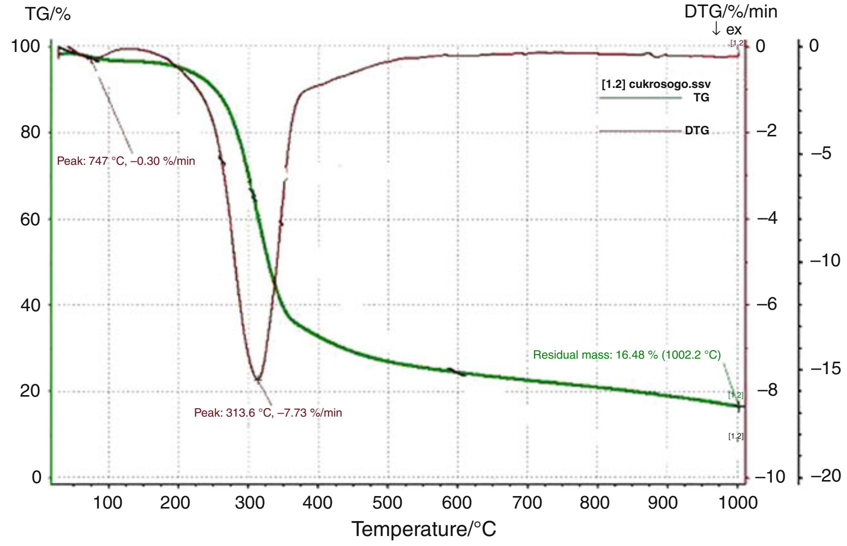

Table 3 Rate of mass loss data as the function of temperature

Sample type	Peaks on DTG curve			Global rate loss/%	Residue/%
	Reaction group	Temp./°C	Rate of mass loss/%/min		
Oat grain	I	81.7	−0.42	85.75	14.25
	II	299.1	−12.98		
Oat straw	I	72.5	−0.29	79.77	20.23
	II	312.1	−8.65		
Triticale grain	I	77	−0.49	86.24	13.76
	II	301.6	−13.43		
Triticale straw	I	65.9	−0.20	83.46	16.54
	II	323.9	−9.04		
Cukrosorgo	I	74.7	−0.30	83.52	16.48
	II	313.3	−7.73		

temperatures of phase transitions in groups I and II of reactions, the total mass loss and percentage of mass solid residue, i.e. coke with the mineral residue (ash).

Qualitative and quantitative analysis of gaseous transformation products

In order to identify the gaseous products, dry decomposition of agro biomass mass spectrometer has been used, coupled with thermoscale. Measurements were performed in a continuous manner, to the full extent of thermal transformation of biomass, i.e. from the room temperature (20 °C) to the stabilization temperature of the coking process (100 °C), this is for dm/dt = 0. We received changes in selected concentrations, i.e. affecting the calorific value of after pyrolysis gas, gaseous products (as the change in the ionic current for the given m/z—mass to charge of corresponding ion). Identified basic pyrolysis products for the above-mentioned range of temperatures, with drawn DTG curve, are shown in Figs. 6, 7, 8, 9 and 10.

Table 4 shows the shares of elemental products of phase transitions in [$\%_{mas}$], derived from the decomposition of studied biomass materials (Figs. 6, 7, 8, 9 and 10). In addition to gaseous products, a solid product was included (as carbonizate).

Water evaporating in the initial phase of the pyrolysis process at temperatures up to 150 °C constitutes moisture in the test biofuel sample, while the reaction water is released from the sample mass in the temperature range of the main transformations.

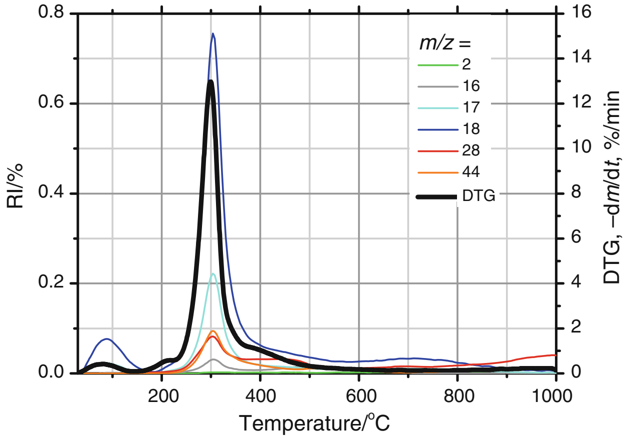

Fig. 6 Oat grain changes in the concentration of elemental gas products

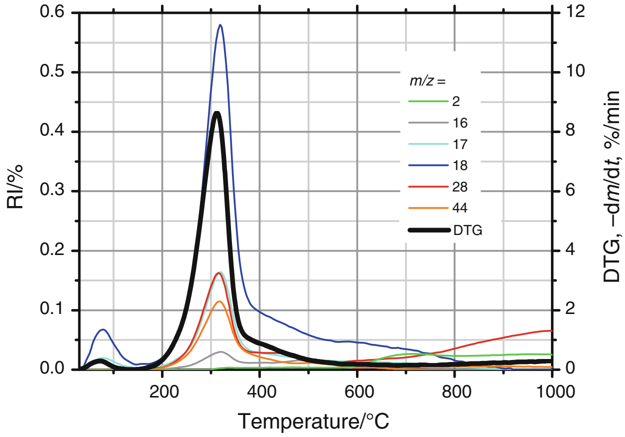

Fig. 7 Oat straw changes in the concentration of elemental gas products

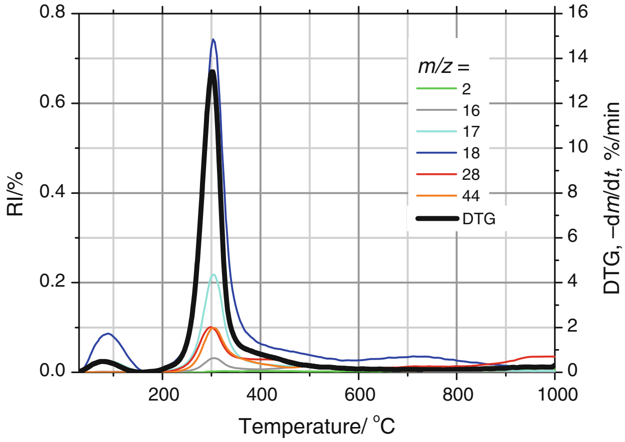

Fig. 8 Triticale grain changes in the concentration of elemental gas products

Identification of NH_3, in presented case, suggests the possibility of using agro biomass as a reburning fuel used in solid fuel combustion processes to reduce NOx emission. Such conditions are also fulfilled by the presence of combustible CH_4.

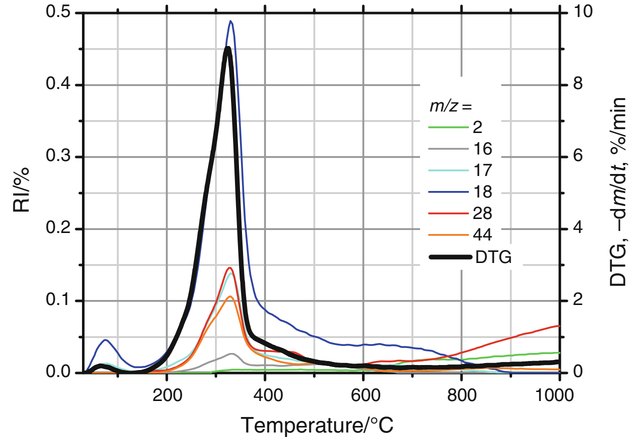

Fig. 9 Triticale straw changes in the concentration of elemental gas products

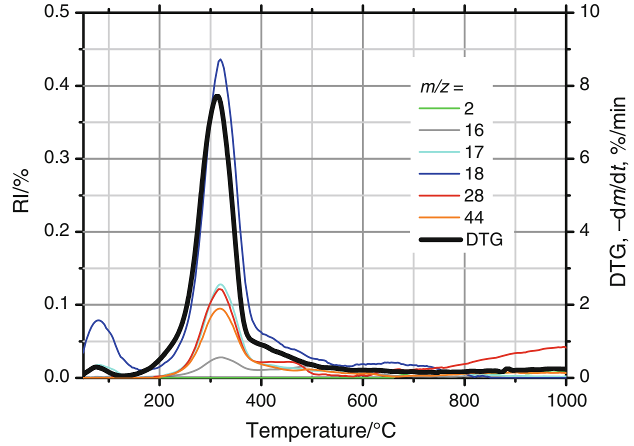

Fig. 10 Cukrosorgo changes in the concentration of elemental gas products

After pyrolysis gases apart from the main components (which reflect the changes in concentrations of Figs. 6, 7, 8, 9 and 10, together with the values of *m/z*), we identified other gaseous products. Table 5 summarizes the quantitative analysis results of only gaseous decomposition products of combustible materials. Apart from the linking carbon and hydrogen elements (H_2, CH_4, H_2O, CO, CO_2, C_2H_6 $m/z = 30$; C_2H_4 $m/z = 28$; C_2H_2 $m/z = 26$), the linkings of nitrogen in the form of NH_3 ($m/z = 17$) and HCN ($m/z = 27$) were also given. These compounds are of importance in the organization of low-emission solid fuel combustion process as reburning fuels, because they participate in the autonomous reduction of nitrogen oxides emission.

Calorific value of after pyrolysis gases

Since the implementation of new technologies in the energy processes based on thermal transformation of solid fuels including a wide range of biomass, importance has been attributed to pyrolysis and gasification. In these processes, the combustible gas is obtained, which can be burned in power boilers and gas turbines. The use of different types of biomass, including waste agro biomass, gives such opportunities, especially important for the development of small power capacity energetics of local scope (dispersed energetics). Economic efficiency of such solutions, already at the stage of fuel selection, requires the development of clear and comparable methods for assessing the conversion of solid fuel in the gas fuel and energetically valuable solid residue (carbonizate). The above-described TG/MS studies allow to estimate the caloric properties of gaseous fuels obtained in the pyrolysis process. Based on the composition of combustible gases, we calculated their calorific value (LHV_g) according to formula (1). Individual components of after pyrolysis gases: CO, H_2, CH_4, C_2H_2, C_2H_6 (Table 5) are expressed in molar percentage shares. Subsequent transformations of the biomass fuel in the secondary fuel (Figs. 1, 2, 3, 4 and 5) lead to the formation of after pyrolysis coke (solid residue). The calorific value of carbonizate (solid residue), expressed in kJ/kg, Table 6, also affects the efficiency of the studied process.

$$\begin{aligned} LHV_g = {} & 282984 \cdot CO + 241818 \cdot H_2 + 802300 \cdot CH_4 + \\ & + 1255600 \cdot C_2H_2 + 1323100 \cdot C_2H_4 + \\ & + 1427800 \cdot C_2H_6 \ [\mathrm{kJ/kmol}] \end{aligned} \tag{1}$$

Values obtained according to (1) have been recalculated so as to obtain the values of LHV_g which is expressed in [$\mathrm{kJ/Nm^3}$].

Calorific values LHV_g^* of after pyrolysis gases have been calculated using the formula (2) presented in references [28, 29]:

$$\begin{aligned} LHV_g^* = {} & 126.36 \cdot CO + 107.98 \cdot H_2 + 358.18 \cdot CH_4 + \\ & + 590.36 \cdot C_2H_4 + 637.72 \cdot C_2H_6 \ \left[\mathrm{kJ/Nm^3}\right], \end{aligned} \tag{2}$$

where (as present authors [29–31]) CO, H_2, CH_4, C_2H_4 and C_2H_6 were the molar percentages of components of the product gas. Formula (2) does not include hydrocarbon C_2H_2. Calculated LHV_g according to formula (1) and LHV_g^* according to formula (2) are presented in Table 6.

The results of calorific values of agro biomass pyrolysis products, presented in Table 6, indicate that the gaseous biofuels can be successfully used for combustion in gas turbines and power boilers. Higher calorific values are gained by after pyrolysis gases LHV_g, obtained from the decomposition of straw oats, triticale and cukrosorgo, and lower values from grain. This is due to the smaller share of reaction water in the gas obtained from cereal straw and cukrosorgo stalks (Figs. 7, 9, 10; Table 5). The proportion of reaction water can be made dependent on the content of

Table 4 Shares of elemental products in [$\%_{mas}$], created in the temperature range RT (reference temperature − room temperature) ÷ 1,000 °C

Sample type	Gas products/$\%_{mas}$						Solid residue
	H_2	CH_4	Vapour H_2O	CO	CO_2	Other	
Oat grain	0.1	0.8	21.4	8.3	10.4	44.8	14.3
Oat straw	0.4	0.8	22.2	12.7	12.1	31.5	20.2
Triticale grain	0.1	0.7	22.4	7.7	11.3	44.1	13.8
Triticale straw	0.1	0.6	19.4	11.3	8.7	43.4	16.6
Cukrosorgo	0.1	1.0	17.7	9.1	12.1	43.4	16.5

Table 5 Quantitative shares of gaseous transformation products, created in the temperature range RT (reference temperature − room temperature) ÷ 1,000 °C (given as molar percentages)

Sample type	Gas products/$\%_{mol}$										
	H_2	CH_4	Couple H_2O	CO	CO_2	C_2H_6	C_2H_4	C_2H_2	NH_3	HCN	Other
Oat grain	2.1	3.9	49.7	15.1	8.4	2.2	0.9	0.2	14.9	0.3	2.3
Oat straw	6.2	3.4	43.2	19.3	8.3	2.0	1.0	0.2	12.6	0.3	3.5
Triticale grain	1.4	3.5	50.5	13.8	9.0	1.9	0.7	0.2	14.9	0.3	3.8
Triticale straw	5.9	3.2	42.6	19.5	9.3	1.9	1.0	0.2	12.0	0.3	4.1
Cukrosorgo	1.8	5.1	40.6	16.6	9.7	1.5	1.7	0.3	12.6	1.2	8.9

Table 6 Calculated calorific values of after process gases and carbonizate

Sample type	Oat straw	Triticale straw	Cukrosorgo	Oat grain	Triticale grain
LHV_g acc. to (1)/kJ/Nm^3	6,302	6,160	6,247	5,577	4,884
LHV_g^* acc. to (2)/kJ/Nm^3	6,192	6,049	6,079	5,466	4,774
LHV_k of carbonizate/kJ/kg	24,100	26,500	24,900	26,600	27,600

hydrogen (H) in the studied biomass. According to the data of Table 2, the reduced hydrogen content was observed in straw and cukrosorgo, and higher content in grains. Therefore, we may assume that for the studied biomass fuels with similar calorific values and similar proportion of carbon, the greatest influence on differences of calorific values in the fuel gas had hydrogen contained in these biofuels. Thanks to the reaction of hydrogen with fuel oxygen, the share of reaction water in the gas produced from oat grain and triticale grain has increased. Probably at the expense of the reaction of hydrogen with oxygen, the share of CO and C_2H_4 in the gas was decreasing, which is presented by the data included in Table 5.

The calorific value of carbonizate (Table 6) depends on the content of non-combustible (ash) parts in the examined biofuels (Table 1). With the increase of non-combustible parts (ash) LHV_k increases. Referring to the calorific values of gas obtained in the pyrolysis (Table 6), we assume good compatibility of calculations made according to formulas (1) and (2) (LHV_g and LHV_g^*). Formula (2) does not include hydrocarbon C_2H_2. In literature, which formula (2) is used, these values for biomass fuels are: frame $LHV_g = 3{,}350 \div 4{,}798$ kJ/Nm^3 [30], tobacco waste $LHV_g = 11{,}900$ kJ/m^3 [29] (twice as fast heated sample) and sludge $LHV_g = 6{,}600 \div 8{,}600$ kJ/Nm^3 [30]. The after pyrolysis gas calorific value is highly influenced by heating speed. In the processes of fast pyrolysis of biomass, calorific value of gases is estimated at about 15,000 kJ/Nm^3 [28, 31]. Thus, our own experiences in the field of industrial pyrolysis of wood indicate that the heating value of non-condensable gases can reach about 6,000 kJ/Nm^3, with the gas composition expressed in volume %: $CO_2 = 60$ %, $CO = 30$ %, $H_2 = 2$ %, $H_2O = 3.2$ %, $N_2 = 0.5$ %, $CH_4 = 3$ %, $C_2H_4 = 1$ %, $C_3H_6 = 0.3$ %.

Conclusions

Action towards reducing CO_2 emissions to the atmosphere encourages the development of energy technologies, where more and more attention, in addition to combustion processes, is paid to processes such as pyrolysis and gasification. Due to the continuous trend of increasing the efficiency of energy processes enforced by economic and environmental condition, pyrolysis and fuel gasification technologies require more subtle methods to assess their effectiveness. In this article, we presented the possibility to test analytically the pyrolysis process efficiency of agro biomass. The studied biomass consisted of crops that are not suitable for the consumption and cereal straw and stalks energy plant called cukrosorgo. As part of the analytical research on dry decomposition of biomass, mass loss as a function of temperature (TG curves) and mass loss rate (DTG curves) have been determined. On the basis of the results, quantity of solid residue (carbonizate) and the temperature range of major transformations of tested biomass materials have been estimated. Their thermal decomposition at temperatures up to 1,000 °C (in oxygen-free atmosphere), in the range of the main transition temperatures (200–400 °C), shows a very similar course.

Elemental gaseous products of pyrolysis were identified, i.e. CO, CO_2, CH_4, H_2, NH_3, and their concentrations are presented in Table 4. On the basis of the data contained in Table 4, estimated gas calorific value does not reflect the actual calorific value. Further research identification showed the presence in the after process gas, next to methane, of other highly calorific hydrocarbons such C_nH_m, as shown in Table 5. Based on the data given in Table 5, we estimated calorific value of gaseous products of pyrolysis for different types of biomass. The obtained values are within the limits from 4,884 kJ/Nm^3, gas from triticale grain, to 6,302 kJ/Nm^3, oat straw gas. Gases of such calorific values are defined as low calorific, despite that fact they can be successfully used for energy purposes, this is for burning in boilers and gas turbines. The differences in after process gas calorific values are caused by varying water content in the reaction gases. The greater amount of water has been created during the decomposition of cereal grains, straw and stalks than cukrosorgo. Hence the calorific values of gases from the pyrolysis of grains are smaller. Higher reaction water content in the gases from grains suggests a higher gram share of hydrogen (H) marked on the elemental composition of grain flammable substance (Table 2).

When it comes to carbonizate, it is characterized with high-calorific values from 24,100 kJ/kg, oat straw, to 27,900 kJ/kg, triticale grain. These values depend on the content of non-combustible (ash) parts in the studied biomass. This type of high-calorific fuels (after pyrolysis carbonizate) is recommended to be burnt in the boiler furnaces in the mix with fuels with a lower calorific value such as pulverized coal, wet biomass and sewage sludge. Extended spectrometric analysis of after process gas composition presented in Table 5 has also enabled the identification of higher hydrocarbons C_nH_m, NH_3, oraz HCN. It suggests that these gases can be used in reburning method [32] of NOx emission reduction in combustion processes of, e.g. coal dust in boilers OP type, very popular in the Polish energy sector.

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