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Kinetic Study of Thermal Decomposition and Co-Combustion of Straw Pellets with Coal

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The main goal of the present study is to assure a more effective use of CO_2 neutral fuel (wheat straw) for cleaner energy production with reduced greenhouse carbon emissions by partially replacing a fossil fuel (crashed coal) with a renewable one. This work combines experimental study and mathematical modelling of the processes developing during the co-combustion of straw pellets and crashed coal, aimed at assessment of the influence of the elemental composition and heating values of the mixture components on the main gasification/combustion characteristics, heat output from the device and on the composition of the flue gas products. The experimental study of the development of main gasification/combustion characteristics involves a complex DTG and DTA analysis of straw pellets and crashed coal and an estimation of the main steps of their thermal decomposition, combustion of volatiles, char formation and burnout, thus providing a complex kinetic study of the mixture weight loss rates and of the formation of combustible volatiles (CO, H_2) at different stages of thermal decomposition of the solid fuel mixtures. A mathematical model for the combustion of volatiles (CO, H_2) downstream the combustor has been built using the MATLAB package, with an account of the CO:H_2 molar ratio variations at the inlet of the combustor and the development of exothermic reactions for the H_2 and CO combustion dependent on the changes in straw mass load in the mixture of solid fuels.

1. Introduction

As the EU (20-20-20) clean energy targets set the 20 % limit of energy should be produced from the renewable sources, there is a growing need for wider use of alternative fuels, e.g., agriculture residues (straw) as additives in energy extraction from wood or coal (Skott, 2011). The 20 % straw additive allows to partially reduce the operational problems of boilers (Veijonen et al, 2003) and diminish the problems related to the enhanced release of polluting NO_x emission, CO and volatile organic compounds (VOCs) during the straw co-combustion with wood (Hardy et al., 2012) or with peat (Olsson, 2006) biomass. The previous experimental study of the straw co-combustion with wood or with peat (Barmina et al., 2017) has shown that the main gasification/combustion characteristics of the fuel mixtures, the heating values and the composition of the flue gas are strongly influenced by the modifications in elemental and chemical composition of the fuel mixtures, promoting the thermal interaction between the components with a direct influence on the thermal decomposition of the mixture, on the formation, ignition and combustion of the volatiles. Moreover, a chemical interaction between the fuels can occur, which affects the ash formation with an unclear ash transformation mechanism (Zheng et al., 2007). Therefore, a more fundamental study is required to gain an insight into the processes developing when co-combusting fuels of different elemental and chemical composition as the development of the components' thermal decomposition and the main combustion characteristics are strongly influenced by various factors determined by the mixture composition. With this account, the main aim of the current study is to provide detailed experimental study and mathematical modeling of the processes developing at the co-combustion of straw pellets with crashed coal which would allow to assess the main effects that influence the main combustion characteristics, the produced heat energy and the composition of the products at mixed fuel thermo-chemical conversion for various straw-to-coal mass ratios.

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2. Experimental

The effects of the wheat straw co-combustion with crashed coal were studied using a batch-size pilot device combining a water-cooled gasification section and a combustion chamber, according to the methodology described in Abricka et al. (2016). The gasifier was filled with a mixture of straw and crashed coal at various straw-to-coal mass ratios (from 100 % coal to 100 % straw). The thermal decomposition of the mixture was initiated by an external heat source – a propane flame flow with the average heat input 1.3 kW – and sustained up to 1000 s. The gasification/combustion characteristics at the thermo-chemical conversion of the mixture were studied experimentally at the average 1.6–1.7 air excess (α) in the flame reaction zone. The experimental study involves joint measurements of the main fuel characteristics (elemental composition, heating values) along with the DTG and DTA analysis of straw and coal thermal decomposition, as well as measurements of the mixture weight loss rate (dm/dt), an FTIR spectral analysis of the composition of volatiles at the combustor inlet (Zhao et al., 2017), an analysis of the flue gas composition by Testo 350 and calorimetric measurements of the cooling water separately for the gasifier and for the combustor. The elemental composition and heating values of wheat straw pellets, crashed coal and their mixtures with different straw-coal proportions are summarized in Table 1.

Table 1: The elemental composition and heating values (HHV) of straw pellets, crashed coal and their mixtures (dry mass).

Fuel	C, %	H, %	O, %	N, %	Moisture, %	Ash, %	HHV, MJ/kg
Wheat straw	46.62	5.090	42.72	1.31	9.1	4.26	18.50
Crashed coal (CC)	68.96	5.120	11.60	1.99	6.6	12.33	28.40
Straw 10% + CC	66.73	5.117	14.71	1.92	6.85	11.52	27.41
Straw 20% + CC	64.49	5.114	17.82	1.85	7.1	10.72	26.13
Straw 30% + CC	62.26	5.111	20.94	1.79	7.35	9.91	25.04
Straw 40% + CC	60.02	5.108	24.05	1.72	7.6	9.10	23.99
Straw 50% + CC	57.79	5.105	27.16	1.65	7.95	8.30	22.99
Straw 80% +CC	51.09	5.096	36.50	1.45	8.6	5.97	20.17

3. Experimental results and discussion

The results of the DTG and DTA analysis of wheat straw and crashed coal have shown significant differences in thermal decomposition of the components, which can be related to their different chemical composition. The thermal decomposition of wheat straw pellets develops with the formation of the pronounced weight loss and temperature peak at T = 560 K and with comparatively smaller peaks at 650 K and at around 710 K (2.09 %). With reference to Yang et al, 2009, the thermal degradation of wheat straw at a temperature below 630 K can be related to the thermal decomposition of hemicelluloses and cellulose, whereas at T > 630 K the thermal decomposition of lignin dominates, which is highly responsible for the char formation and combustion. The combustion profile of crashed coal differs significantly from that of wheat straw. The peak attributed to the formation of volatiles vanishes from the coal DTG graph. As the char conversion stages are not exactly separated, only one pronounced weight loss peak can be found at about T = 760 K, whereas the complete combustion of crashed coal was achieved at a temperature above 850 K (Figure 1a, b). So, the results of the DTG and DTA analysis suggest that the thermal conversion regime favourable for the straw combustion is not suitable for crashed coal, the thermal decomposition of which requires higher temperatures. This was confirmed by the kinetic study of the thermal decomposition of straw pellets and crashed coal, which gives evidence of a faster thermal decomposition with the correlating release of combustible volatiles (CO, H_2) at the thermal decomposition of straw pellets, with a pronounced difference in weight loss peaks for straw pellet and for crashed coal (Figure 1c, d). The thermal decomposition of the straw pellet-crashed coal mixtures during their co-combustion is determined by the mixture composition and reaches the highest rate with a minimum value of the air excess in the gasifier for the 30 % straw mass load in the mixture (Figure 2a). The FTIR analysis of the substances obtained from the mixture thermal decomposition has shown that the weight loss rate dependence on the mixture content correlates with the subsequent increase of the peak and average values of the CO, C_2H_2 and CO_2 absorption intensity (Figure 2b). The peak value of the CO absorption intensity was observed for the 10 % straw-to-coal mass ratio. With the further increase of the straw mass load in the mixture, the CO mass fraction decreased to the minimum value along with the correlating increase up to the maximum value of the CO_2 absorption intensity, indicating so the enhanced combustion of CO attributing to the increase of the straw-to-coal mass ratio. As follows from Figure 2b, an enhanced formation of C_2H_2 can be observed increasing the mass load of straw in the mixture up to 20 % on the score of a possible chemical interaction between the hydrogen (produced at the thermal decomposition of straw) and the crashed coal.

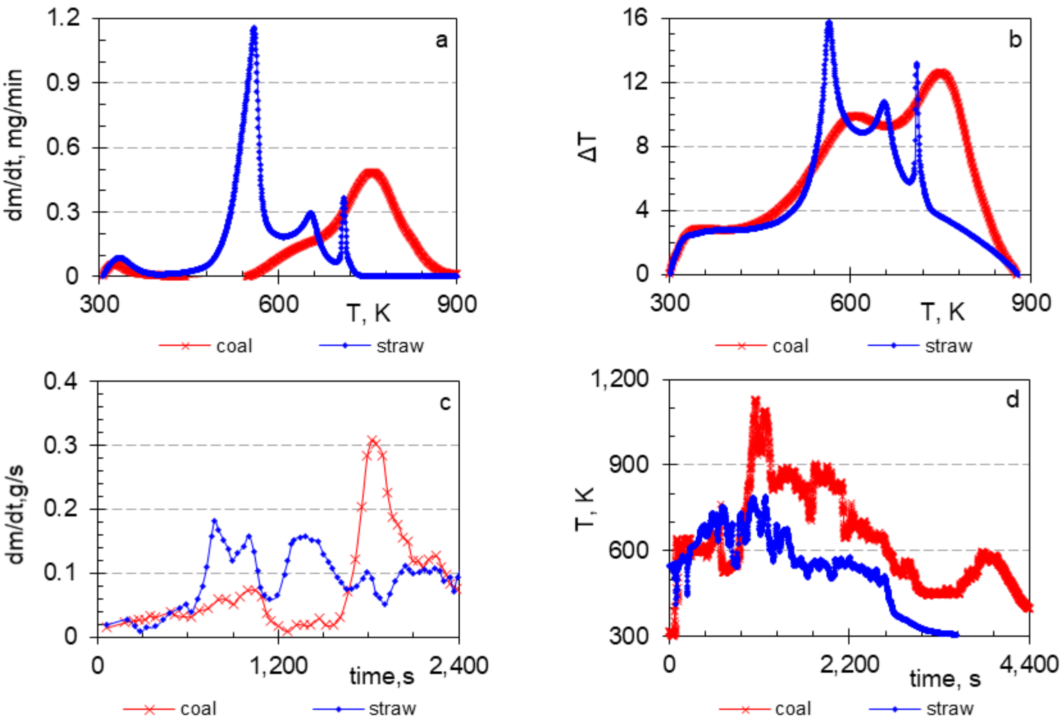

Figure1: DTG (a) and DTA (b) analysis and kinetics (c, d) of the thermal decomposition of crashed coal and wheat straw in an oxidative atmosphere.

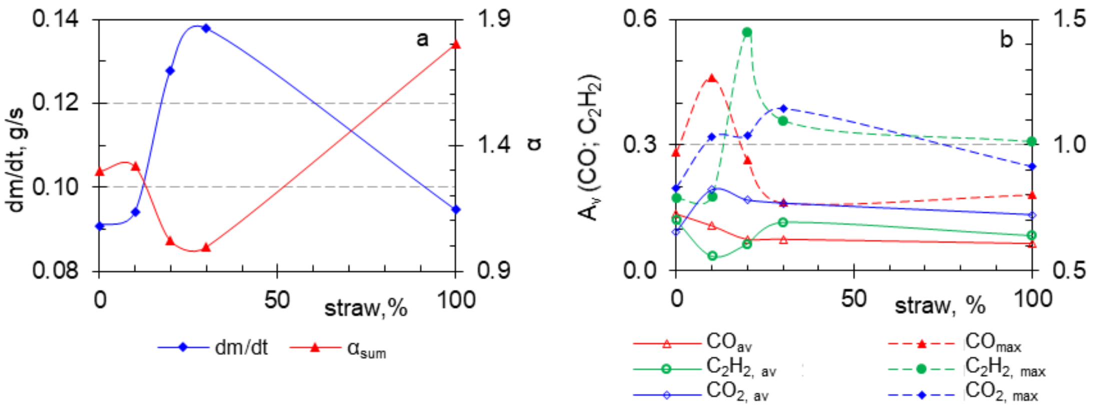

Figure 2: The thermal decomposition rate (a) and the composition of volatiles (b) released from the mixture (CO, C_2H_2, CO_2 wave numbers 2169; 730; 668 cm^{-1}) vs. variations of the mass load of straw in the mixture.

The kinetic study of the effect of the straw co-combustion with coal on the main flame characteristics has shown that an increase in straw mass load in the mixture results in a faster increase of the flame temperature and heat output up to their peak values, along with a faster burnout of the mixture (Figure 3a, b). The measurements of the elemental composition and heating values of the mixtures have shown that an increase of the straw mass load results in linear decrease of the carbon and hydrogen content in the mixture with the correlating decrease of the heating value of the mixture (Table 1, Figure 4). The kinetic study of the heat output from the device and CO_2 volume fraction in the flue gas has shown that with the increase of the straw mass load in the mixture the thermal interaction between the components leads to the deviation from graph linearity for the average heat output and produced heat energy per mass of burned mixture, with the deviation peak value at the 10 % straw mass load (Figure 4a) when the mass fraction of volatiles (CO, H_2) approaches its peak value (Figure 2b).

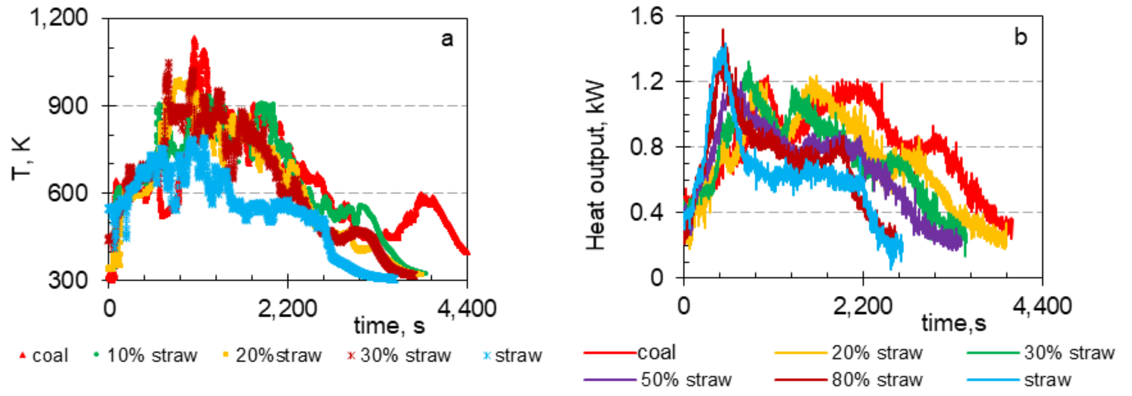

Figure 3: The kinetics of the flame temperature (a) and heat output from the device (b) vs. variations of the mass load of straw in the mixture.

This suggests that the heat produced by the combustion of volatiles released during the thermal decomposition of straw pellets maintains the enhanced heating of the crashed coal, thus increasing the heat output from the device and the produced heat energy per mass of burned mixture. A less pronounced deviation from linearity was observed for the CO_2 volume fraction in the flue gas increasing the straw mass ratio in the mixture (Figure 4b).

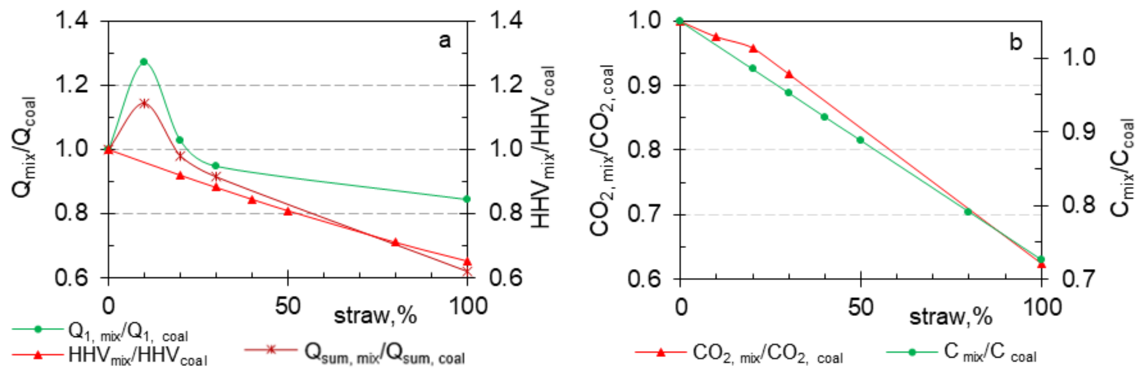

Figure 4: The produced heat energy per mass of burned mixture in the combustor ($Q_{1,\ mix}/Q_{1,\ coal}$), vs. the total amount of produced heat energy ($Q_{sum,\ mix}/Q_{sum,\ coal}$) and the CO_2 volume fraction in the products at mixture thermo-chemical conversion vs. variations of the mass load of straw in the mixture.

4. Results of mathematical modelling and numerical simulation

For a more thorough analysis of the processes developing when co-combusting straw with crashed coal, mathematical modelling and numerical simulation of the processes were performed using two dominant second-order chemical reactions of the volatile combustion:

$$H_2 + OH \rightarrow H_2O + H; \qquad E_1 = 14360\ {}^{J}/_{mol}; \qquad A_1 = 216\ {}^{m^3}/_{mol\cdot s} \tag{1}$$

$$CO + OH \rightarrow CO_2 + H; \qquad E_2 = 30787\ {}^{J}/_{mol}; \qquad A_2 = 960\cdot 10^3\ {}^{m^3}/_{mol\cdot s} \tag{2}$$

In accordance with the obtained experimental data, the average values of C_1 (H_2) and C_5 (CO) at the inlet of the combustor are determined by the mixture composition and are the following: for coal H_2 = 0.74 mol/m^3, CO = 1.27 mol/m^3; for 10 % of straw in the mixture H_2 = 0.46 mol/m^3; CO = 0.9 mol/m^3; for 20 % of straw H_2 = 0.45 mol/m^3; CO = 1.01 mol/m^3; for 30 % of straw H_2 = 0.29 mol/m^3; CO = 0.75 mol/m^3; for 100 % of straw H_2 = 0.32 mol/m^3; CO = 0.84 mol/m$_3$. In the mathematical model, the following values are used: the mass fraction of the concentration C_k = 1(1)6 for the initial conditions C_1+ C_2 + C_5 = 1 (C_2 is the mass fraction of OH), C_3 = C_4 = C_6 = 0 (2.5 times decreasing the concentration values). The production rate for the k-th species is expressed using the following approximation (Smooke et al, 1987):

$$\Omega_k = \sum_{j=1}^{2}[(\nu''_{jk} - \nu'_{jk})R_j(T)\prod_{n=1}^{6}(\frac{\rho C_n}{m_n})^{\nu'_{jn}}],\ k \in [1,6], \tag{3}$$

where $R_j(T)$ is a rate constant modified with the Arrhenius temperature dependence for the forward path of the chemical reaction

$$R_j(T) = A'_j T^{\beta_j} \exp(-E_j / RT), \tag{4}$$

where A'_1 = 216 and $A'_2 = 0.96 \cdot 10^6$ m^3/(mol·s) are the reaction rate pre-exponential factors, R = 8.314 J/(mol·K) is the universal gas constant, ν''_{jk} and ν'_{jk} are the stoichiometric coefficients of the k-th species appearing as products and reactants in j-th reaction, $\beta_j = 0$ is the order for temperature, $m_1 - m_6$ denote the molecular weights of the species (g/m^3). In the equation for the mass fractions of the concentration C_k the source term is $m_k \cdot \Omega_k/\rho$ [1/s]. In the expression for the temperature

$$\frac{1}{m\rho c_p}\sum_{k=1}^{6} h_k m_k \Omega_k \ \text{(K/s)}, \tag{5}$$

where

$$m = \frac{1}{6}\sum_{k=1}^{6} m_k \text{ and } h_1 = 0,\ h_2 = 39.46,\ h_3 = -242,\ h_4 = 218,\ h_5 = -111,\ h_6 = -394 \text{ (kJ/mol)} \tag{6}$$

are the enthalpy of the species, c_p = 1000 J/(kg·K) is the specific heat at constant pressure (for H_2 the specific heat at constant pressure is approximately 14 kJ/(kg·K).

For mathematical modelling, a system of nine parabolic type partial differential equations was used to describe the formation of 1D compressible reacting swirling flow and the flame temperature. The boundary conditions were given at inlet (x = 0): ρ = w = T = 1, $C_3 = C_4 = C_6 = 0$, $C_1 = C_{10}$, $C_2 = C_{20}$, $C_5 = C_{50}$ (dependent on the pellets). These values were used for the initial conditions at t = 0 for all x values in the segment [0; 2]. At outlet, the uniform zero derivative conditions were used. Numerical results, dependent on (x, t), were obtained for $0 < x < 2$, $0 < t < 1$ and are summarized in Table 2, where w_{max} = max(w), w_{end} = w[2; 1], T_{max} = max(T), T_{end} = T[2; 1], $C_{k,\,end} = C_k[2; 1]$, k = 1(1)6, $C_{10} = C_1[x; 0]$, $C_{50} = C_5[x; 0]$, $C_{20} = C_2[x; 0]$.

Table 2: Values of $C_{k,\,end}$, w_{max}, w_{end}, T_{end}, T_{max} at thermo-chemical conversion of straw, coal and their mixtures $C_{2,\,end}$ = 0.

Species	Straw	Coal (CC)	Straw 10 % + CC	Straw 20 % + CC	Straw 30 % + CC
$C_{1;0}$ (H_2)	0.13	0.29	0.19	0.18	0.12
$C_{5;0}$ (CO)	0.34	0.51	0.36	0.40	0.30
$C_{2;0}$ (OH)	0.53	0.20	0.45	0.42	0.58
$C_{1,\,end}$ (H_2)	0.09	0.28	0.16	0.16	0.07
$C_{3,\,end}$ (H_2O)	0.35	0.03	0.25	0.19	0.32
$C_{4,\,end}$ (H)	0.03	0.01	0.03	0.03	0.03
$C_{6,\,end}$ (CO_2)	0.53	0.45	0.57	0.63	0.57
w_{max}	5.73	4.85	6.29	6.71	6.04
w_{end}	3.06	2.88	3.15	3.23	3.13
T_{end}	3.32	2.60	3.76	4.12	3.60
T_{max}	5.20	3.76	6.32	7.39	5.95

The results represented in Table 2 (the maximum values of the temperature (T_{max}), axial flow velocity (w_{max}), mass fraction of CO_2 and H_2O) were obtained with the 20 % straw-coal mixture co-combustion model numerical simulation (Figure 4). Referring to the data of the experimental study, the increase of the flame maximal temperature, flow velocity and CO_2 mass fraction correlates with the enhanced thermal decomposition of the mixture with the 10–30 % straw mass load resulting in an enhanced combustion of the volatiles (Figure 2), with the correlating increase of the produced heat energy at the thermo-chemical conversion of the mixture (Figure 4). With the constant primary and secondary air supply rates, this leads to a decrease of the air excess ratio in the reaction zone from 1.4 to 1.1, improving so the combustion conditions and thus completing the combustion of volatiles. This is confirmed by the results of the mathematical modelling, i.e. the mass fraction of the reactants CO, OH decreased to zero at t = 0.5 s. It should be noted, however, that the enhanced thermal decomposition with the enhanced release of combustion volatiles results in an about 16 % increase of the produced heat energy in the flame reaction zone along with an increase of the total produced energy during the burnout of the mixture by about 14 %. According to the results of the mathematical modelling, the 10–20 % straw load is a recommended mass fraction in the straw-coal mixture.

5. Conclusions

With the aim to achieve the more effective use of straw as a fuel for energy production and to assess the effect of the straw co-combustion on the development of the thermal decomposition of mixtures, on the formation and combustion of volatiles, the complex experimental study and mathematical modelling of the processes developing at straw-crashed coal co-combustion were carried out. The results of the experimental study make it possible to suggest that the development and the efficiency of the processes of thermo-chemical conversion when co-combusting straw with crashed coal are highly influenced by the variations of the straw-to-coal mass ratio. The thermal decomposition of the mixtures and the formation of volatiles are influenced by the thermal interaction between the components at a mass load of straw up to 30 %, thus enhancing the release of the volatiles and improving the combustion conditions with the positive effect on the main combustion characteristics (heat output from the device and products composition). At higher straw mass loads, the thermal decomposition of the mixture and the formation of volatiles predominately are influenced by the linear decrease of the mixture HHV, hydrogen and carbon content with the correlating linear decrease of the biomass weight loss rate, volume fraction of volatiles at the combustor inlet determining thus the negative effect of straw on the coal combustion characteristics.

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