Environmental characteristics of thermochemical conversion of agricultural residues

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Abstract. The main purpose of this study was to find optimal methods and conditions for the processing of plant biomass in regard to the energy parameters of the obtained combustible gases as well as to determine environmental indicators during the subsequent combustion of these gases. In the numerical assessment of biomass processing, a non-stoichiometric model was used. It was assumed that a chemically reacting multicomponent mixture is in a state of thermodynamic and chemical equilibrium. This state of the mixture corresponds to the minimum value of the isobaric-isothermal potential. Pyrolysis processes had low efficiency of the thermochemical conversion of biomass processing into a mixture of combustible gases. These processes are of practical importance in obtaining such target products, as tar, biocoal and ash. In addition to pyrolysis, two types of biomass gasification were studied: (A) gasification with internal heating of the reaction volume due to partial biomass combustion; and (B) gasification with the supply of water vapor and external heating of the reaction volume due to the combustion of a part of the generated gas. The energy and environmental characteristics of the synthetic gas obtained through the steam gasification (B) were significantly better than those of the gas obtained through the gasification type (A).

1 Introduction

Biomass energy is a renewable energy source that is neutral in terms of greenhouse gas emissions. Currently, pyrolysis, gasification and combustion are used as methods of thermochemical biomass conversion. The production of thermal and electrical energy by biomass burning has low efficiency and requires the use of complex systems for cleaning combustion products.

Pyrolysis makes it possible to obtain a mixture of high-molecular hydrocarbons (pyrolysis oil), pyrolysis gas and biochar. Obtaining these products has great potential for the further usage. Methods of optimization and management of pyrolysis processes, including the use of catalysts and joint pyrolysis of various types of raw materials, have

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been identified and studied [1, 2]. The processes of obtaining and prospects for the use of the pyrolysis gas have been investigated [3]. Much attention has been paid to the mathematical modeling of biomass pyrolysis [4, 5].

As opposed to pyrolysis, the main product in biomass gasification is the synthetic gas containing combustible gases (H_2, CO, CH_4, etc.). Gasification is one of the promising biomass processing technologies, e.g., in terms of energy supply, producing hydrogen and using the synthetic gas as a raw material in chemical technologies. Two methods of biomass gasification have been developed and used most often. The first method is based on burning a part of biomass with the air supply at low values of the equivalent ratio ER<<1 (hereinafter type A gasification). The thermal energy obtained this way is used to heat and gasify the remaining part of biomass. The gasifying agent in this case is combustion products, including molecular nitrogen N_2. The presence of nitrogen in the synthetic gas significantly reduces the heat of combustion and negatively influences the efficiency of the further usage of the synthetic gas to produce thermal energy during its combustion. The main factors influencing the biomass conversion rate are the equivalent ratio of ER, the elemental structure and the initial humidity of biomass. The second method is based on the external supply of thermal energy to biomass (hereinafter type B gasification). This thermal energy is obtained by burning a part of the generated synthetic gas. Often, heated water vapor is used as a gasifying agent. Here, the biomass conversion rate is determined by the following factors: the mass ratio of water vapor and biomass, the elemental structure and the initial humidity of the biomass. In addition, the efficiency of gasification processes is affected by the design of the gasifier, operating characteristics (such as temperature and pressure levels and performance) and other parameters.

When improving existing or creating new pyrolysis and gasification plants, it is highly important to increase the rate of biomass conversion into useful products, reduce the cost of implementing processes and minimize the negative impact on the environment. There are certain difficulties associated with using the results obtained from the operation of already created installations when creating new installations for other types of biomass and target products. To solve such problems, model and full-scale experiments are used, as well as the modeling of processes and their numerical assessment [6-10]. The assumption of thermodynamic equilibrium in a reacting system is often used to model processes. For such models, only the initial and final states of the reacting system itself are important. The main advantages of these models are the versatility for different types of biomass and parameters of the state of the final products, as well as independence from the gasifier design.

The main objectives of this study were (i) the determination of the component structures of pyrolysis products and two types of agricultural residues gasification; (ii) the determination of the lower heating value and the content of gaseous substances in gases after removal of water vapor, carbon particles and ash; (iii) the calculation of the emission factor CO_2 based on the carbon content in dry gases obtained during pyrolysis and biomass gasification; and (iv) the comparative assessment of CO_2 emissions from the combustion of the resulting purified gases.

2 Materials and methods

The initial raw materials were agricultural residues (for example, grain straw, sunflower husk, wood waste, etc.). Such types of biomass have approximately the same elemental composition. When modeling, it is accepted that conditional biomass is a mechanical mixture of organic and mineral parts with a certain moisture content. When performing the calculations, the average composition of the organic part in the dehydrated state was used, wt. %: C – 51.71; H – 5.25; O – 41.88; S – 0.12; N – 1.03. The ash included the following substances: K_2O, CaO, SiO_2, MgO. The ash structure was, wt. %: K – 9.12; Ca – 24.21; Si

– 22.47; Mg – 4.25; O – 39.94. The mass ash content in the biomass is assumed to be equal to 5%.

When modeling pyrolysis and gasification processes, a non-stoichiometric model was used [11]. A chemically reacting multicomponent mixture was in a state of thermodynamic and chemical balance. This state corresponds to the minimum value of the isobaric-isothermal potential. In the condensed phase, there are ash particles and a part of carbon may be present, which depends on the conditions of the processes.

The efficiency of thermochemical processes of biomass processing was evaluated using the following parameters:

M_p is the total mass of products including gaseous substances and condensed phase, kg;

M is the mass of dry ash-free gas obtained by processing 1 kg of biomass, kg gas/kg biomass;

h_p and h_b are specific mass enthalpy of products at pyrolysis or gasification temperature and biomass at an initial temperature of 293 K, MJ/kg, respectively;

LHV_b is the lower heating value of biomass, MJ/kg;

LHV_g is the lower heating value of dry ash-free gas, MJ/kg;

$m=M_p \cdot (h_p - h_b)/LHV_g$ is the mass of dry ash-free gas, the thermal energy of which is used to carry out thermochemical processes during the processing of 1 kg of biomass, kg gas /kg biomass ($m=0$ for A type gasification);

m_{H2O} is the mass of water vapor used in 1 kg of biomass gasification, kg H_2O/kg biomass;

$g_{H2O}=m_{H2O}/(1+m_{H2O})$ is the mass fraction of water vapor used for 1 kg of biomass gasification.

g_C is the mass fraction of condensed carbon in biomass processing products;

$Q=(M-m) \cdot LHV_g$ is the energy potential of the dry ash-free gas obtained by 1 kg of biomass processing , MJ;

$\eta=LHV_g \cdot (M-m) \cdot 100/LHV_b$ is the thermochemical efficiency of biomass conversion, %.

Indicators characterizing CO_2 emissions from various processing methods and process organization conditions:

G_C is the amount of carbon in dry ash-free gas, t C/t gas;

$W_C = G_C \cdot 10^3/LHV_g$ is the energy equivalent of carbon content, t C/TJ;

$EF_{CO2}=W_C \cdot 44/12$ is the carbon dioxide emission factor from gas combustion, t CO_2/TJ.

When performing calculations, the loss of thermal energy was not taken into account. Thus, the obtained estimates of the main indicators are close to their ideal theoretically achievable values.

3 Results and discussion

Calculations of the composition and parameters of the pyrolysis gas were carried out at the temperatures of 500, 600, and 700 °C and the pressure in the reaction volume p=0.101 MPa. Some of the results are given in Tables 1-3. The data are given for the dry, without ash condition of the pyrolysis gas.

For different temperature conditions of pyrolysis organization, as well as at different humidity values (W) of the feedstock, it was found that the maximum amount of produced condensed carbon can reach 28 wt. % at T=500 °C and W=10 wt. %. With an increase in the humidity of the feedstock and an increase in the pyrolysis temperature, the amount of condensed of carbon decreased. For example, about 10 wt. % at T=700 °C and W=30 wt. %. Accordingly, the amount of gaseous pyrolysis products and the energy potential of the dry ash-free gas increased.

Table 1. The composition and parameters of the gas at the humidity of the feedstock 10 wt. %.

Composition and parameters pyrolysis gas	Pyrolysis temperature T, °C		
	500	600	700
CO, vol. %	1.806	7.233	18.627
H_2, vol. %	16.772	28.91	38.787
CH_4, vol. %	35.711	25.479	15.429
H_2S, vol. %	0.199	0.161	0.123
CO_2, vol. %	43.622	36.691	25.871
N_2, vol. %	1.889	1.526	1.163
LHV_g, MJ/kg	12.632	12.664	13.380
Q, MJ	3.129	3.481	4.324
g_C	0.280	0.271	0.248
G_C, t C/t gas	0.369	0.357	0.356
W_C, t C/TJ	29.241	28.202	26.578
EF_{CO2}, t CO_2/TJ	107.22	103.41	97.45

Table 2. The composition and parameters of the gas at the humidity of the feedstock 20 wt. %.

Composition and parameters pyrolysis gas	Pyrolysis temperature T, °C		
	500	600	700
CO, vol. %	1.822	7.155	18.733
H_2, vol. %	16.882	28.876	38.942
CH_4, vol. %	35.869	25.719	15.448
H_2S, vol. %	0.160	0.129	0.098
CO_2, vol. %	43.749	36.891	25.846
N_2, vol. %	1.517	1.228	0.932
LHV_g, MJ/kg	12.698	12.722	13.447
Q, MJ	3.727	4.062	4.943
g_C	0.213	0.203	0.177
G_C, t C/t gas	0.371	0.359	0.357
W_C, t C/TJ	29.231	28.097	26.553
EF_{CO2}, t CO_2/TJ	107.18	103.02	97.36

Table 3. The composition and parameters of the gas at the humidity of the feedstock 30 wt. %.

Composition and parameters pyrolysis gas	Pyrolysis temperature T, °C		
	500	600	700
CO, vol. %	1.843	7.215	18.821
H_2, vol. %	17.005	29.025	39.076
CH_4, vol. %	35.975	25.757	15.460
H_2S, vol. %	0.128	0.103	0.078
CO_2, vol. %	43.839	36.920	25.823
N_2, vol. %	1.209	0.978	0.742
LHV_g, MJ/kg	12.753	12.774	13.502
Q, MJ	4.331	4.655	5.563
g_C	0.146	0.135	0.107
G_C, t C/t gas	0.372	0.360	0.358
W_C, t C/TJ	29.217	28.192	26.532
EF_{CO2}, t CO_2/TJ	107.13	103.37	97.28

The main results of predicting the composition and parameters of gas during type A gasification are given in Table 4. The composition, specific heat of combustion and mass of the resulting gas are given for the dry without ash condition.

Table 4. Composition and parameters of the gas at different values of the equivalent ratio (ER).

Composition and parameters gas	Equivalent ratio (ER)		
	0.31	0.32	0.33
CO, vol. %	25.7151	26.0377	25.9304
H_2, vol. %	20.6933	20.4186	20.2896
CH_4, vol. %	0.6970	0.59852	0.29611
H_2S, vol. %	0.0331	0.0323	0.0318
CO_2, vol. %	9.7049	9.4008	9.2654
N_2, vol. %	42.8697	43.2188	43.885
LHV_g, MJ/kg	5.325	5.295	5.158
Q, MJ	13.449	13.711	13.590
G_C, t C/t gas	0.18051	0.17986	0.1768
W_C, t C/TJ	33.898	33.968	34.278
EF_{CO2}, t CO_2/TJ	124.29	124.55	125.68

Changes in concentrations of gaseous substances and the main parameters of the generator gas correspond to the known patterns. The maximal concentration of CO was detected at ER≈0.32. With an increased ER, the concentration of H_2 decreased, and the concentration of N_2 increased. As ER decreased, the amount of condensed carbon in biomass processing products increased. The maximum values of the energy potential (Q) of the generator gas and the thermochemical efficiency (η≈84 %) of gasification processes were observed at ER≈0.32.

In the study of type B gasification processes, based on preliminary calculations, temperature ranges (T=700…850 °C) and the amount of water vapor (g_{H2O}=0.19…0.31) were established, at which a sufficiently high gasification efficiency was achieved, estimated by the highest values of the energy potential of the generator gas and the thermochemical efficiency of the biomass conversion. The main results of forecasting the composition and parameters of the generator gas are given in Table 5.

Table 5. Gas composition and parameters at different gasification temperatures.

Composition and parameters gas	Gasification temperature T, °C		
	727	777	827
CO, vol. %	40.067	44.708	45.477
H_2, vol. %	49.973	49.543	50.473
CH_4, vol. %	2.183	1.371	0.487
H_2S, vol. %	0.048	0.045	0.044
CO_2, vol. %	7.261	3.904	3.098
N_2, vol. %	0.464	0.428	0.419
LHV_g, MJ/kg	15.820	16.511	16.622
Q, MJ	11.974	13.237	13.093
G_C, t C/t gas	0.373	0.385	0.384
W_C, t C/TJ	23.594	23.302	23.113
EF_{CO2}, t CO_2/TJ	86.51	85.44	84.75

The analysis of the obtained results made it possible to determine the optimal modes of steam gasification processes corresponding to the maximum calculated values of the energy potential of the generator gas and the thermochemical efficiency of the biomass conversion (η≈82 %): temperature range T=750-850 °C; the amount of steam supplied was 0.28 kg H_2O/kg biomass. To ensure this temperature level, a supply of thermal energy is required by burning about 37% of the generated gas.

At gasification temperatures below 700 °C, the content of condensed carbon in products increased (> 3 wt. %), and the thermochemical efficiency decreased (η≤73 %). With an

increase in the amount of steam supplied, the content of condensed carbon in the gasification products decreased. It follows from the calculation results: the heat of combustion of the gas obtained by steam gasification and external supply of thermal energy was significantly higher than the heat of combustion of the gas obtained by the internal supply of thermal energy. However, the values of energy potential and thermochemical efficiency were approximately same for both types of gasification.

The analysis of the calculated data given in Tables 1-5 shows that in regard to the energy potential of dry ash-free gases and CO_2 emissions during the subsequent combustion of these gases to produce thermal energy, the steam gasification of biomass is the most effective with the external heat supply (type B gasification).

4 Conclusion

Optimal conditions for the organization of biomass processing were determined, contributing to an increase in the degree of conversion of raw materials into the generator gas.

From the studied methods for processing biomass in regard to the beneficial use of the generated gas, its pyrolysis is the least effective. The carbon dioxide emission factor reached $EF_{CO2} \approx 107$ t CO_2/TJ.

With the internal supply of thermal energy for gasification, the maximum calculated values of the energy potential of the dry ash-free gas and the thermochemical efficiency were obtained with an equivalent ratio of 0.32. The carbon dioxide emission factor reached $EF_{CO2} \approx 125$ t CO_2/TJ.

Compared to the previous methods of biomass processing, the method based on the external supply of thermal energy obtained by burning part of the synthesis gas was more effective in terms of the energy value of the generated gas. The gas obtained by this method has less negative impact on the environment during its subsequent combustion. The carbon dioxide emission factor reached $EF_{CO2} \approx 85$ t CO_2/TJ.

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