Comparison of thermal conversion methods of different biomass types into gaseous fuel

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Abstract. Thermal conversion methods of different biomass types into gaseous fuel are considered. The comparison of the gas mixtures characteristics (volume yield, composition and calorific value) that can be produced from the main biomass types by gasification and pyrolysis is presented. The merits and demerits of these methods are discussed. It is shown that the two-stage pyrolysis technology, which consists of the biomass pyrolysis and the consequent high-temperature conversion of pyrolysis gases and vapors into synthesis gas by filtration through a porous carbon medium, allows to achieve both a high degree of biomass conversion into gaseous fuel and a high energy efficiency.

1. Introduction

Progress and adoption of distributed energy resource systems and increased attention to the environmental issues associated with the use of fossil hydrocarbon fuel gave rise to the increased interest in the development of modern technologies of using renewable hydrocarbon resources for energy purposes. Biomass is quite universal type of the energy raw material that can be used either as a solid fuel for direct combustion, or as a raw material for production of liquid and gaseous fuels [1]. Thermal methods of biomass conversion into gaseous fuel depending on the ways of generating the heat, required for processing, and the technique of putting the heat into feedstock can be divided into autothermal and allothermic. The former include the different schemes of gasification in which heat is produced by the partial combustion of raw material in controlled oxidizing atmosphere and the conversion of raw material into gaseous state occurs in the flow of combustion products. The latter include the pyrolysis methods in which heating of the feedstock is carried out in oxygen free environment. As a result, gas, liquid and solid products whose composition and mass depend on the final temperature and the heating rate are obtained. Increase of the yield of gaseous products can be achieved by subsequent thermal conversion of liquid pyrolysis products into the gaseous state [2–4]. In the present paper the comparison of characteristics (volatile content, ash content, elemental composition and calorific value) of different types of organic feedstock and characteristics (volume, composition and calorific value) of the product gas mixtures is carried out. The main attention is given to pyrolytic treatment methods. Discussion of gasification methods is based on the familiar literature data. When the pyrolysis conversion methods are considered both new and previously obtained experimental data on volume yield and properties of the gas mixtures that can be produced from different types of biomass are used.

Table 1. Properties of initial raw materials (data on elemental composition of sunflower husk were taken from [5]).

Raw material		Wood	Peat	Straw husk	Sunflower litter	Chicken sludge	Sewage
Moisture content (wt %)	W	8.0	8.0	6.0	7.4	16	2.7
Volatile matter on daf basis (wt %)	M_{vp}	83.6	64.1	79.4	79.1	82.6	89.1
Ash content on dry basis (wt %)	A	0.8	3.3	6.8	6.4	13.8	22.7
Elemental composition on daf basis (wt %)	C	50.3	55.7	47.8	51.7	48.0	56.5
	H	6.0	6.9	6.2	6.3	6.4	7.5
	N	0.4	1.7	0.6		5.9	8.5
	O	43.3	35.7	45.4	42.0	39.0	26.0
	S	< 0.05	< 0.05	< 0.05		0.7	1.5
Higher calorific value on daf basis (MJ/kg)	Q_h^{exp}	20.6	21.9	19.6	21.4	20.4	25.0
	Q_h^{cal}	19.8	23.6	19.0	20.8	20.1	25.9

2. Experimental procedure

The six types of biomass that present the main categories of organic wastes were used as a raw material for processing into gaseous fuel, namely: sawdust, straw, sunflower husk, chicken litter, sewage sludge and peat that is related to the youngest fossil fuel and at the same time is renewable energy raw material. All samples of biomass excepting samples from sewage sludge were used in the form of pellets. It had no effect on the obtained results, but allowed to unify the experiment, because the pellets from different types of biomass produced industrially had the same geometric sizes. The results of proximate and elemental analyses of the samples of initial raw material are shown in table 1. The moisture, volatile content and ash content were measured by method of thermogravimetric analysis (TGA) with SDT Q600 thermal analyzer. The moisture and volatile content were determined from thermogravimetric curves measured in nitrogen. The ash content was determined from thermogravimetric curves measured in air.

The higher calorific values Q_h^{exp} were measured with the help of a combustion calorimeter and were converted to dry ash-free state. The elemental composition of raw material was determined with the help of CHN analyzer. Calculation of the higher calorific values Q_h^{cal} (MJ/kg) according to Mendeleev's formula was carried out on the basis of data on the elemental composition:

$$Q_h^{cal} = 4.18 \times 10^{-3}(81C_C + 300C_H + 26(C_S - C_O)),$$

where C_C, C_H, C_S, C_O—carbon, hydrogen, sulfur and oxygen content (wt %) in initial raw material. From comparison of Q_h^{exp} and Q_h^{cal} listed in table 1 it is seen that the maximum difference between the experimental and calculated calorific values (on a dry ash-free state) does not exceed 7%.

From table 1 one can see that the elemental compositions of all initial raw materials are similar. At the same time it should be noted that the highest carbon content in comparison with other biomass types is observed in peat and sewage sludge. In addition, the organic mass of sewage sludge has a relatively low oxygen content that, as will be seen later, affects the

composition of gas mixtures obtained from sewage sludge by pyrolytic methods. Talking about proximate composition, the wood pellets have the lowest ash content, while the chicken litter and sewage sludge have the highest ash content. The lowest amount of volatile products and, therefore, the highest amount of fixed carbon are contained in the combustible mass of peat.

The experiments on pyrolysis conversion of biomass were carried out at a setup described in [6]. Thermochemical reactor consisted of two sections. The temperature of each section could be regulated independently. The first section (the section of pyrolysis of initial raw material) was filled with feedstock. The second section (section of cracking of volatile pyrolysis products) was filled with charcoal or carbon residue obtained by pyrolysis of initial raw material. The thermochemical reactor was purged by argon before experiments. The vapor-gas products of the thermal decomposition of feedstock, formed in the first section, due to overpressure entered the second section which was previously heated up to a fixed temperature. The gas mixture at the exit of reactor was cooled to room temperature. During experiments the volume of gas mixture $V(t)$ formed to this point of time t was measured by eudiometric methods. Gas sampling and subsequent chromatographic analysis allowed to determine the current composition of the gas mixture at the exit of reactor $C_i(t)$ ($i =$ H$_2$, CO, CO$_2$, N$_2$ and C$_n$H$_m$). On the base of the obtained experimental data the final composition of the gas mixture formed during the pyrolysis treatment of initial raw material was calculated.

The feedstock in pyrolysis section was heated up to 1000 °C. The heating rate was equal to 10 °C/min. From experiment results presented in [3] it follows that when the temperature of the second section is equal to 1000 °C and the residence time of the vapor-gas products of pyrolysis within it is not less than $\tau = 4$ s, a liquid fraction is absent in final products at the exit of reactor. This gives evidence of complete thermal destruction of high-molecular organic compounds that are formed during biomass pyrolysis and condensed under normal conditions as a liquid fraction. Thus obtained gas mixture is a synthesis gas with hydrogen and carbon monoxide as the main combustible components. Besides, methane amounts the main fraction among the gaseous hydrocarbons C$_n$H$_m$. In present paper all experimental investigations as to two-stage pyrolysis conversion were fulfilled under such conditions. To obtain the data on the composition and volume yield of the gas mixtures corresponding to the conventional process of biomass pyrolysis similar investigations were carried out at the same experimental setup in the absence of the carbon residue in the second section of the reactor and at the temperature 100 °C. Temperature in the second section of reactor at the level of 100 °C has been insufficient for thermal decomposition of the pyrolysis gases and vapors but did not allow them to condense.

3. Results and discussion
3.1. Pyrolysis
The data on volume V (per 1 kg of raw material) and characteristics of gas mixtures produced by conventional pyrolysis of different biomass types are presented in table 2. The higher calorific value of the product gas is in the range of 7.8–13.2 MJ/m^3 and it is the more, than more content of methane. From the results of the chromatographic investigations it follows that gaseous hydrocarbons are evolved at the temperatures above 350 °C and hydrogen–at the temperatures above 450 °C. The main gaseous components at the lower temperatures are carbon dioxide and carbon monoxide. The volume of the product gas increases monotonically with an approximately constant velocity (figure 1) with increasing of the feedstock temperature in the range from 200 to 1000 °C. From energy point of view an efficiency of biomass conversion into the gaseous state η can be characterized by the ratio of the higher calorific value of product gas produced from one kg organic mass of feedstock to the higher calorific value of the feedstock on a dry ash-free state. From the data presented in table 2 it is seen that η for the conventional process of biomass pyrolysis does not exceed 0.18.
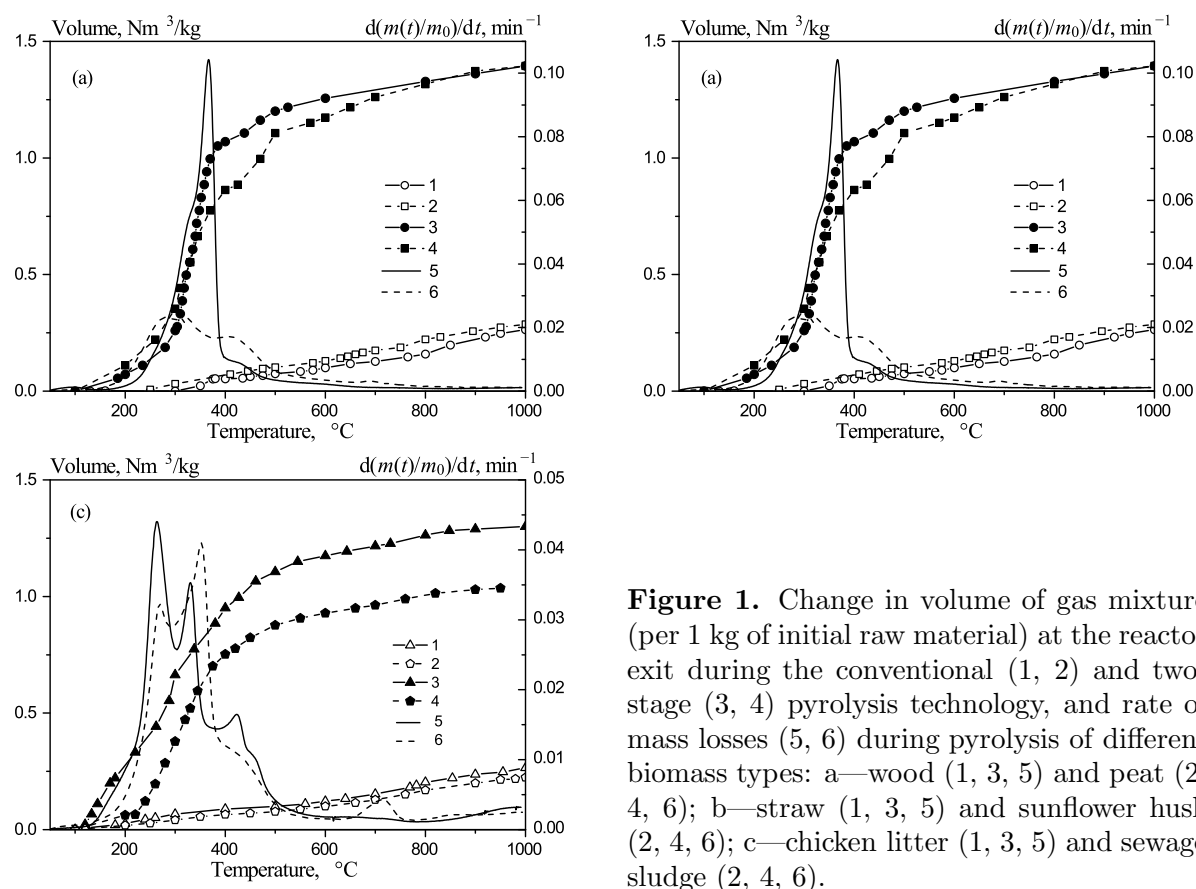
Figure 1. Change in volume of gas mixture (per 1 kg of initial raw material) at the reactor exit during the conventional (1, 2) and two-stage (3, 4) pyrolysis technology, and rate of mass losses (5, 6) during pyrolysis of different biomass types: a—wood (1, 3, 5) and peat (2, 4, 6); b—straw (1, 3, 5) and sunflower husk (2, 4, 6); c—chicken litter (1, 3, 5) and sewage sludge (2, 4, 6).

Table 2. Characteristics of gas mixtures, which were obtained by method of conventional pyrolysis from different types of biomass (data on composition and volume of gas mixtures obtained by treatment of wood, peat and straw pellets were taken from [2, 3]).

Raw material		Wood	Peat	Straw husk	Sunflower litter	Chicken sludge	Sewage
Volume, V	initial	0.26	0.29	0.26	0.38	0.26	0.22
($N\,m^3$/kg)	daf	0.28	0.33	0.30	0.44	0.36	0.29
Volume fraction	H_2	0.28	0.23	0.20	0.18	0.20	0.24
of combustible	CO	0.26	0.19	0.17	0.16	0.23	0.07
components	C_nH_m	0.16	0.13	0.11	0.09	0.06	0.18
Calorific value	Q_h	13.2	10.5	9.1	7.9	7.8	11.1
(MJ/kg)	Q_l	12.0	9.5	8.2	7.2	7.2	9.9
Degree of energy conversion	η	0.18	0.16	0.14	0.16	0.14	0.13
Adiabatic temperature of combustion (°C)	T_{ad}	1860	1730	1720	1640	1710	1770

3.2. Pyrolysis and cracking

As mentioned above, the possibility to increase the degree of biomass conversion into gas associated with the processing of liquid pyrolysis products. The experimental data on the volume V of the gas mixtures (per 1 kg of initial raw material) formed during the pyrolysis of different biomass types and subsequent thermal processing of the pyrolysis vapor-gas products are shown in figure 1. In contrast to the conventional pyrolysis in two-stage pyrolysis the main gas generation occurs in the temperature range 100–600 °C. Shift of the beginning of intensive gas generation towards lower temperatures (curves 3, 4 and 1, 2 should be compared) is due to water-gas reaction ($C + H_2O = CO + H_2$), which proceeds in section of cracking in two-stage pyrolysis. In turn, the thermal decomposition of high-molecular hydrocarbon compounds forming the liquid fraction under normal conditions leads to increase of the product gas volume several times for all types of biomass. The Boudouard's reaction ($CO_2 + C = 2CO$) does the same. Simultaneously, heterogeneous pyrolysis of gaseous hydrocarbons C_nH_m occurs, resulting in a decrease of their content in the product gas and a decrease of its heat of combustion, accordingly.

The differential thermogravimetric (DTG) curves measured with the thermal analyzer at the heating rate of 10 °C/min are also shown in figure 1. DTG curves describe the rate of thermal decomposition of different biomass types in pyrolysis. A comparison of the volume change V during heating and DTG curves confirms that gas evolution in the two-stage pyrolysis is the most intensive in the temperature range corresponding to the thermal decomposition range of organic biomass component.

Summary data on the characteristics of the gas mixtures produced in the two-stage pyrolysis process of different biomass types are shown in table 3. From a comparison of the experimental values of the gas mixture volumes it is seen that the lowest values are produced during the sewage sludge and chicken litter processing. However, it should be taken into account the difference in the moisture and ash content of initial raw materials. The experimental values recalculated on a dry ash-free state for all investigated biomass types are different by no more than 10% (table 3). It should be noted that during recalculation of experimental values V on a dry state the volume of synthesis gas produced by the water-gas conversion of carbon material placed in the second section of reactor $V_{add} = 2.49 \times 10^{-2} W$ m^3/kg (W—moisture content of raw material, wt %) was subtracted from the measured volume values. The volume of synthesis gas, calculated on the basis of elemental feedstock composition assuming that entire inner oxygen is converted to CO and hydrogen and nitrogen are evolved as H_2 and N_2 in two-stage pyrolysis, are also shown in table 3.

The maximum difference between the experimental and calculated values of V (7%) is observed in case of sunflower husk pellets for which elemental composition was not measured in this study and was taken from [5]. The validity of such estimations is also confirmed by the good agreement between the experimentally and calculated magnitudes of ratio of the volume content of H_2 to volume content of CO in the gas mixtures produced from different raw materials. In particular, for wood pellets and sewage sludge the measured ratios V_{H_2}/V_{CO} are 1.0 and 2.0 and calculated ratios are 1.1 and 2.3 consequently. The ability to predict the composition of the synthesis gas, which can be produced from different organic raw materials, based on such simple estimations is an important in terms of its possible use in chemical industry.

3.3. Gasification

There is a wide variety of gasification schemes. They can be classified by type of used gasifying agent (air, oxygen, steam) and by gas-solid contacting reactor (moving-bed, fluidized-bed and entrained-flow). The analogy between the two-stage scheme of biomass pyrolysis and scheme of the downdraft moving-bed gasifier is that in downdraft moving-bed gasifier the pyrolysis and combustion products moves also over and through the remaining hot char, where gasification

Table 3. Characteristics of gas mixtures, which were obtained by method of two-stage pyrolysis from different types of biomass (at the temperature in second section equal to 1000 °C; experimental data on composition and volume of gas mixtures obtained by treatment of wood, peat and straw pellets were taken from [2,3]).

Raw material			Wood	Peat	Straw	Sunflower husk	Chicken litter	Sewage sludge
Volume,	measured	initial	1.39	1.39	1.35	1.39	1.3	1.04
V	measured	daf	1.3	1.34	1.37	1.39	1.25	1.29
$(\mathrm{N\,m^3/kg})$	calculated	daf	1.28	1.29	1.33	1.29	1.31	1.27
Volume fraction		H_2	0.46	0.49	0.4	0.43	0.46	0.53
of the combustible		CO	0.46	0.41	0.38	0.37	0.37	0.27
components		C_nH_m	0	0.01	0	0	0.01	0.05
Calorific value		Q_h	11.7	11.8	9.9	10.2	10.9	12.2
(MJ/kg)		Q_l	10.8	10.8	9.1	9.3	10	10.9
Degree of energy conversion		η	0.74	0.72	0.69	0.66	0.67	0.63
Adiabatic temperature of combustion (°C)		T_{ad}	2040	2030	2000	2010	2020	1970
Filling agent of cracking section			Wood char	Peat char	Straw char	Sunflower husk char	Wood char	Wood char

takes place. Usage of such gasification scheme results in production of tar-free gas mixtures. By this indicator only the entrained-flow gasifier can compete with the downdraft moving-bed gasifier [1]. The choice of gasifying agent significantly affects the calorific value of product gas. Thus, when air is used as the gasifying agent the calorific value of product gas is in the range of 4–7 MJ/m^3, when steam is used—in the range of 10–18 MJ/m^3 and when oxygen is used—in the range of 12–28 MJ/m^3 [1]. The relatively low calorific value when air is used as the gasifying agent associated with a high content of nitrogen in the product gas (up to 50 vol %). At the same time, the using of oxygen or steam requires presence of unit of an air separation or a steam generator in gasification flowsheet, which leads to a significant increase in the cost of the final product.

4. Conclusion
The comparison of different thermal methods of biomass conversion into gaseous fuel was carried out. The experimental data on volume yield and composition of gas mixtures that can be produced by both conventional and two-stage pyrolysis from different biomass types are presented. From submitted results it follows that the method of two-stage pyrolysis consisted of the pyrolysis of the feedstock and the subsequent high temperature conversion of the pyrolysis gases and vapors into the synthesis gas by filtering through a porous carbon medium allows to obtain the gas mixture with a higher calorific value of 10–12 MJ/m^3. Depending on the biomass type the ratio between the volume content of hydrogen and carbon monoxide in the obtained synthesis gas can range from 1 to 2. The volume and composition of the produced synthesis gas can be estimated based on the elemental composition of the organic part of raw material. The absence of the liquid fraction in final processing products at the reactor outlet indicating

the complete thermal decomposition of high-molecular volatile products of pyrolysis, on the one hand, leads to increase the efficiency of conversion of the initial raw material into gas and, on the other hand, solves the problem of environmentally friendly disposal of liquid pyrolysis products.

Acknowledgments

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