

Statistical Description of Biomass Blends Devolatilization

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Biomass is widely used as a renewable energy source either as a raw material or as a form of pellets, which are very often produced of mixture of different sorts of biomass. This gives the opportunity to produce pellets which are characterized by desired properties. However there is a question of interactions between sorts of biomass which may occur during pyrolysis. The main scope of this paper is to investigate devolatilization of biomass mixture and to approximate amount of released volatiles as a function of biomass composition.

Five types of biomass has been selected for measurements: two types of wood – oak and pine, two types of agricultural wastes – rape straw and wheat straw and willow as popular energy crop. It has been assumed that the amount of volatiles released in a given temperature range can be expressed as a function of elemental composition of biomass mixture. Different forms of function have been tested and correlation coefficients as well as average and maximal approximation errors were examined as defining the quality of approximation. It has been found that linear form of a function gives the best quality of approximation characterized with high correlation coefficient and relatively small maximal approximation error.

1. Introduction

Limited resources of fossil fuels as well as problem of global climate changes are the motivation for increasing role of renewable energy sources. For many countries biomass is the only renewable energy source which may play a significant role. For example Poland has relatively low wind velocities at most of the territory, flat area and average solar radiation and thus wind turbines, hydro power plants and photovoltaic sources cannot play a significant role and the best option for increasing share of renewable energy sources is to energy utilization of biomass.

Biomass can be used either as a raw material such as straw, wood-chips etc. or in a processed form such as for example pellets and briquettes. In the second case during production of pellets and briquettes there is opportunity for selecting biomass mixture in a proper way in order to obtain pellets which are characterized by desired properties. When using mixtures of different kinds of biomasses there is a question of interactions which may occur during the thermal conversion of biomass.

On the other hand, some researchers (Wang, et al., 2011; Couhert, et al., 2009) have an opinion that pyrolysis of biomass cannot be predicted based on composition due to existing interactions. Giudicianni, et al. (2013) carried out steam pyrolysis of two-component mixtures and compared outcomes to results from calculations using additive law. Authors noticed differences in product distribution, gas composition as well as HHV of gas. The largest deviation was detected in case of xylan-lignin mixture, what is in accord with results from (Liu, et al., 2011). In another work (Hosoya, et al., 2007), pyrolysis of cellulose-hemicellulose and cellulose-lignin mixtures were investigated. Strong interactions between cellulose and lignin were observed, which led to product composition differences. These observations are on the contrary to work (Wang, et al., 2011), where only weak interaction in the mixture was noticed. Authors of work (Wang, et al., 2011) indicated that interactions in mixture of cellulose-hemicellulose were marginal, what is in good accordance with other researches (Giudicianni, et al., 2013; Hosoya, et al., 2007).

Inconsistency in interaction occurrence between major biomass organic components can be explained by hemicellulose and lignin different chemical forms presence in biomass, therefore products yield and interactions between them can be different.

The main objective of this paper is to search for the correlation between amount of volatiles released by the biomass mixture and properties of single biomasses which were used for mixture preparation.

2. Experimental investigation

Five different types of biomass have been selected for measurements, among them two wood biomass: oak and pine, two agricultural by-products: rape straw and wheat straw and one energy crop - willow. Elemental composition as well as proximate analysis of these biomasses is presented in Table 1 and ash composition in Table 2.

Table 1: Properties of biomasses used in experiments

parameter	unit	rape straw	wheat straw	willow	pine	oak
water	%,mass	2.3	5.1	2.8	3.0	1.3
ash	%,mass	4.0	5.7	2.3	0.4	0.2
volatiles	%,mass	76.8	71.5	77.7	82.0	80.7
LCV	MJ/kg	17.065	16.331	17.519	18.037	18.079
carbon	%, mass	46.64	43.92	47.69	49.11	49.13
hydrogen	%, mass	5.98	5.49	5.90	6.13	5.90
nitrogen	%, mass	0.66	0.99	0.34	0.01	0.04
sulfur	%, mass	0.16	0.14	0.04	0.02	0.03
chlorine	%, mass	0.046	0.129	0.004	0.003	0.005
fluorine	%, mass	0.004	0.004	0.000	0.001	0.004

Table 2: Biomass ash composition

	Si, %	Ca, %	Mg, %	S, %	P, %	K, %
wheat straw	29.29	9.32	3.95	4.80	7.55	33.0
rape straw	5.31	34.30	3.06	6.74	6.48	17.6
willow	2.14	39.40	3.45	2.53	6.12	14.10
pine	24.50	23.50	5.90	3.67	3.15	11.60
oak	6.64	17.30	3.12	3.82	3.97	34.40

For each of the pure components as well as for the mixture of biomasses in a proportion 30 %/ 70%, 50 %/50 % and 50 %/70 % TGA tests were done using Netsch thermo-balance, nitrogen as neutral atmosphere and heating rate 10 K/min as typical for fixed bed combustion. An example of a result of such measurement is shown in Figure 1.

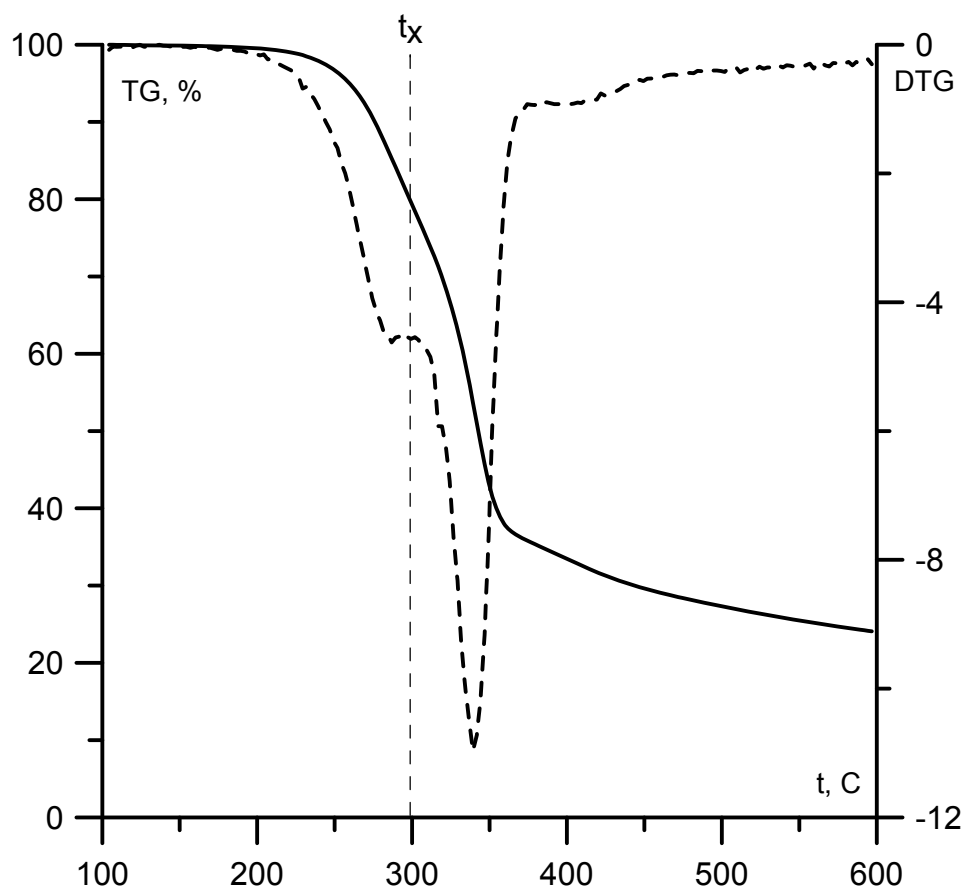


Figure 1: Example TG and DTG as a function of temperature for sample – oak, atmosphere-nitrogen, heating rate 10 K/min

In the Figure 1 it is shown characteristic temperature $t=300\text{ }^{\circ}\text{C}$ which is a temperature for which most of the hemicellulose is already decomposed while cellulose and lignin still not. In total 49 different mixtures were investigated.

Approximation of results

It was assumed that the total amount of volatiles v should be a function of elemental composition of an organic part of mixture:

$$v = f(c, h, o) \quad (1)$$

where c, h, o denote mass fraction of respectively carbon, hydrogen and oxygen in a organic matter.

Since in organic matter $c + h + o \approx 1$ it can be written that:

$$v = f(c, h) \quad (2)$$

It has been also assumed that the function should be polynomial of the order no greater than 2. Under such conditions eight functions can be written which are presented in Table 3.

For each of the functions least square procedure was applied obtain the coefficients and next it was calculated average error of approximation, maximal error of approximation and correlation coefficient of measurement values with values calculated using tested functions. Results are shown in Table 4.

Table 3: Formulas for approximation functions which were tested

Number of function	Number of coefficients	Formula
1	3	$a_1 + a_2c + a_3h$
2	4	$a_1 + a_2c + a_3h + a_4c^2$
3	4	$a_1 + a_2c + a_3h + a_4h^2$
4	4	$a_1 + a_2c + a_3h + a_4ch$
5	5	$a_1 + a_2c + a_3h + a_4h^2 + a_5c^2$
6	5	$a_1 + a_2c + a_3h + a_4h^2 + a_5ch$
7	5	$a_1 + a_2c + a_3h + a_4c^2 + a_5ch$
8	6	$a_1 + a_2c + a_3h + a_4c^2 + a_5h^2 + a_6ch$

Table 4: Average error, maximal error and correlation coefficient of tested functions

1. Function	Avg error, %	Max error, %	Correlation
1	0.83	2.02	0.947
2	0.80	2.30	0.958
3	0.82	2.28	0.957
4	0.83	2.23	0.958
5	0.77	2.30	0.958
6	0.75	2.22	0.957
7	0.76	2.28	0.958
8	0.67	2.27	0.958

It can be noticed that with increasing number of coefficients in a function average error decreases which is a rule for approximation problems. However, at the same time maximal error increases with increasing number of coefficients, while correlation coefficient remains almost constant. Dependence of the maximal and average errors and correlation coefficient on the number of coefficients in a function is shown in Figure 2.

Basing on this consideration it can be concluded that the best function of all tested is the one which has a form:

$$v = a_1 + a_2c + a_3h \quad (3)$$

or, for a given set of biomasses:

$$v = -14,2917 + 116,44c + 538,74h \quad (4)$$

Similar considerations were repeated for the amount of volatiles released in a temperature range up to 300 °C. Also in this case the best function was the one having only linear expression. For the amount of volatiles released in the temperature range up to 300 °C function has following form:

$$v_{300} = 153,8 - 0,7585c - 16,122h \quad (5)$$

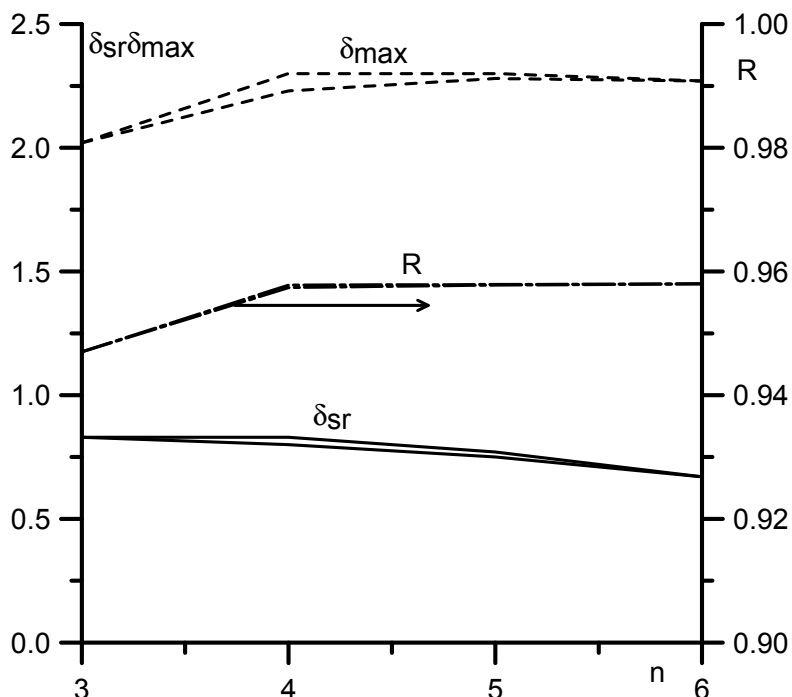


Figure 2: Maximal and average error as well as correlation coefficient R as a function of number of functions coefficients n

3. Summary

In the paper, it is shown how different forms of approximation function can describe amount of volatiles releases from the biomass mixture. It has been assumed that amount of volatiles can be expressed as a function of elemental composition of organic matter of a biomass mixture. Eight different forms of function were tested and finally the simplest one was concluded to be the best one having relatively small maximal error of approximation and good enough correlation coefficient.

Consideration was done separately for total amount of volatiles as well for the amount of volatiles released in the temperature range up to 300 °C. The form of the best fitting function was the same in both cases while the coefficients in both functions were different.

Obtained results show the possibility of using approximation functions for proper selection of biomass types which should be used to obtain the mixture of desired properties. This can be used for example for pellets production.

4. Acknowledgments

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