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STUDY ON THE KINETICS OF BIOMASS BLENDS DEWATERING AS A STAGE OF THERMAL DEGRADATION

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Abstract: *Solid biomass co-combustion with coal in industrial furnaces, including those of power plants, looks promising in terms of fuel base diversification and also presents a way to reduce significantly the emission of air harmful pollutants, particularly carbon dioxide. CO_2 resulting from biomass burning is environmentally neutral, since the same amount of carbon dioxide will be consumed at the next cycle of biomass photosynthesis. In case of the Ukrainian low reactive anthracite schtib used in such technology, the radical differences in the kinetic characteristics of co-fired fuels become critical issues. A significant difference in the attainable degree of fuel milling fineness due to the prohibitively high expense for solid biomass milling makes the problem more complicated. The values of biomass particle fineness are approximately 5…15 mm; whereas the fineness of pulverized coal reaches as low as 30...50 mkm. The moisture and volatiles content for the fuel mentioned also differ noticeably. Therefore, the stages of these fuels burn out will be extremely complex in terms of various time scales of subsequent stages and their positioning in the furnace. The case becomes even more aggravated insofar the kinetic characteristic of the stages of biomass combustion are not known yet in details. The present work is dedicated to the research into the kinetics of biomass blends demoisturization and aimed at the deriving of the Arrhenius type equations, allowing to develop submodels of the demoisturization as an individual stage of biomass burn out for 3-D models.*

Keywords: *Biomass, gravimetry, activation energy, moisture,*

1. Introduction

The release of moisture from the heated solid fuel which undergoes combustion usually happens quickly, if compared to the total time of fuel burn out. This generally holds when the moisture content of the fuel is negligibly low, approx. 3-5%, which is typical for coal. In case of burning solid biomass, one deals with the moisture content of 30…40% and in some cases as high as 70% for sugar pulp, for example. Keeping in mind that a typical particle size of solid biomass prepared for pulverized combustion falls between 5…25mm, one should expect an extended duration of the demoisturization stage along with the significant heat consumption for moisture evaporation. Extensive emission of vapor will also contribute to the formation of the concentration field of flue gases components. To correctly simulate the process of pulverized co-firing of coal and solid biomass it is necessary to have precise kinetic characteristics of biomass demoisturisation as an individual fuel, and as blends of various types of biomass.
The kinetic characteristics of individual stages of biomass thermal degradation are being determined using thermogravimetric methods [1-7].

The essence of the method of dynamic thermal gravimetrical analysis (TGA) [1-7] consists in the continuous measurement during the experiment of temperature and weight of a sample and comparison them with those of the standard, which does not participate in the reaction. The sample and the standard are both heated with a certain constant speed. Thus, registering the time of each measurement, weights and temperatures continuously, it becomes possible to determine the time derivative (dm/dt) for the sample along with the thermal effect of the process. The time change in the degree of conversion in a process can mathematically be described using the respective physical constants and corresponding model functions by the equation [4-12]:

$$\frac{d\alpha}{d\tau} = -k \cdot f(\alpha) \qquad (1)$$

where α - the degree of conversion; τ - time; *k* - constant of the reaction rate; *f(α)* - a function that describes a particular reaction model.

The degree of conversion within a demoisturization process is determined using the continuous data of the sample weight measurements as follows:

$$\alpha = (m_0 - m_\tau)/(m_0 - m_\infty) \qquad (2)$$

where m_o - initial mass of the sample; m_∞ - sample mass at the end of the process. moisture release; m_τ -is the sample mass at a time **τ**.

Thus, the degree of conversion characterizes the current proportion of moisture which evaporates to the instant τ to the initial mass of moisture in the sample.

The constant of the reaction rate is given in the form of the Arrhenius equation [1-10]

$$k = A \cdot \exp(-E/RT),$$

where A - frequency factor, 1/s; E - activation energy, J/mole; R - universal gas constant – 8.314 J/(mole K); T - temperature, K.

Obviously, it is critical to determine the exact instants of the beginning and end of the process and register respective values m_o, m_∞. It is also important to determine with the maximum accuracy the time instants and corresponding values of m_τ and sample temperatures. In the practical conditions determining of the certain process" start and finish does not look an easy problem, since there might be a superimposition of various processes at one temperature range, which leads to the change in the sample mass. For example, in case of demoisturization process, the moisture removal ending coincides with the beginning of devolatilization, which significantly hampers the precise determination of the dewatering process limits. Therefore, for dewatering, the point where the second derivative of the mass change function passes through a zero value in the range of 170...200°C and the local reaction rate acquires minimum value that corresponds to the practically complete removal of moisture usualy is considered the process ending.

Given the Arrhenius equation, the Eq. (1) acquires the form:

$$\frac{d\alpha}{d\tau} = A \cdot \exp(-E/RT) f(\alpha) \qquad (3)$$

If the sample is heated at a constant rate, the time – temperature function will be [4-10]:

$$T = \beta\tau + C \qquad (4)$$

where β- the rate of heating.

Combining Eq. (3) and (4), we obtain:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\cdot f(\alpha) \qquad (5)$$

Typically, f (α) is used extensively for the description of heterogeneous reactions of devolatilization in the form of power or special functions [5,7].

Common in the processing of TGA data is the assumption of the first order of reaction. By grouping variables and taking logarithms of Eq.(5) we obtain:

$$ln\left(\frac{1}{1-\alpha}\frac{d\alpha}{dT}\right)=-\frac{E}{RT}+lnA \qquad (6)$$

Equation (6) forms the methodological basis of the differential approach to the determination of kinetic constants on the basis of TG studies. A detailed analysis of data processing specifics and interpretation based on the application of Eq. (6) is given in [5,7,12,13]. Despite its visibility and simplicity, this approach has significant drawbacks, related to the need to calculate the left-hand side of Eq. (6). It contains the conversion rates and their time derivative which is a varying mass change function, and has to be taken at the precisely same time instants. In this case, the value of the temperature in the right side of Eq. (6) must correspond to the same moment. The critical point of this methodology is also the need to scale the value of the derivative, based on the actual curve m_τ [3,7,12,13].

In accordance with the integral approach, which has become widely used [2-7,11-13] in recent years, equation (6) is integrated to the form:

$$\int_0^\alpha \frac{1}{(1-\alpha)^n}d\alpha=\int_0^T \exp\left(-\frac{A}{RT}\right)dT \qquad (7)$$

If the integration of the expression on the left side does not cause complications at any choice of the reaction model, then the expression on the right side could be represented as an approximating asymptotic series, and, upon the integration, yields [7,12,13,14-21]:

$$\int_0^T \exp\left(-\frac{E}{RT}\right)dT=\frac{ART^2}{\beta E}\left(1-2\frac{RT}{E}\right)e^{-\frac{E}{RT}} \qquad (8)$$

This method, called the integral one is transformed depending on the accepted model of the reaction. For the first-order reaction at n=1 we obtain from Eq. (8):

$$\ln(1-\alpha)=\frac{ART^2}{\beta E}\left(1-2\frac{RT}{E}\right)\exp\left(-\frac{E}{RT}\right) \qquad (9)$$

which after taking logarithms yields:

$$\ln\left[\frac{-\ln(1-\alpha)\beta}{T^2(1-2\frac{RT}{E})}\right]=\left(-\frac{E}{R}\frac{1}{T}\right)+\ln\frac{AR}{E} \qquad (10)$$

2. Matherials and methods

The kinetic characteristics of the samples of ground solid biomass blends were determined based on the differential thermal gravimetry curves obtained derivatigraph **Q-1500 D (Paulik-Erdey).**

All measured data were recorded in analogue format with a six channel recorder with measurement limits for each channel from 50 μV to 5 mV / 250 mm.

The parameters of the derivatograph operation corresponded to the following values: medium - oxidizing (air), weight of weight gain - 50±4 mg (error±1%), heating rate - 20°C/min, inert material Al_2O_3, crucible - platinum, size particles - polyfractional. The sample was heated from room temperature (25±3°C) to 900°C. Samples of the biomass from which mixtures were formed, are shown in figure

1 and the results of the biomass technical analysis are presented in Table 1.

Fig. 1 Biomass samples

a-beet sugar pulp, b-wheat straw, c- pinewood sawdust, d-sunflower husk

Table 1.

Biomass technical analysis data

Biomass	Volatiles, V^d %	Ash, A^d %	Moisture, W^r_t %
Beet sugar pulp	80.5	2.0	10
Wheat straw	76.0	16.7	10
Pinewood sawdust	85.0	1.75	10
Sunflower husk	77.1	15.8	7

Special samples of biomass blends were prepared with the weight of 40...50 mg of individual components in a 1: 1 proportion to be used in the experimental studies of the stages of thermal destruction kinetics. The blends sawdust-straw, pulp-straw, pulp-husk, pulp-sawdust were studied.

Experimental samples of individual biomass were pre-dried in a muffle furnace SNOL 24/200 at a temperature of 105...110°C, ground and sifted through sieves to have a nearly mono-dispersed structure with particle size of 1...3 mm and mixed in a given proportion. The calculated moisture was added to get the initial moisture content of the sample mixture at 10%. The bulk weight of a sample was 50±4 mg and was selected from the condition that in the process of thermal decomposition the fuel would covere the bead of the thermocouple at the bottom of the platinum crucible and also to reduce the temperature gradient between the center and the sample surface. The samples were heated from room temperature (25 ± 3°C) to 900°C at a constant speed of 6.6...7.2°C/min. (0.11...0.12 K/s) to ensure maximum proximity to isothermal conditions in the oxidizing medium (air). As an inert material, Al_2O_3 was used. Experiments were carried out under the same conditions in order to obtain comparable results for various mixtures of biofuels.

3. Results and discussion

The processing of the obtained data and their interpretation were performed on the basis of the non-isothermal integral method based on the Coates-Retfern model [6,7,11-14,16-22]. The data were presented as a dependence of Y = f(1/T), where:

$$\mathrm{Y} = Ln\left[-Ln(1-\alpha)\beta / T^2\left(1-2\frac{RT}{E}\right)\right] \qquad (11)$$

As can be seen from the structure of the equation for Y, its application is possible by the method of successive approximations, that is, the complex Y is calculated preliminarily, on the basis of processing the graphs Y = f(1/T).

$$Y_1 = Ln\left[-Ln(1-\alpha)\beta/T^2\right] \qquad (12)$$

Values E_1 and A_1 are determined as the first approximation, for which the correction factor is calculated. Obtained thus initial values E_1 and A_1 allow calculating the correction multiplier:

$$\left[\left(1-2\frac{RT}{E_1}\right)\right],$$

which, in turn, allows calculating Y_2, followed by the definition of a new pair of values E_2 and A_2. As a rule, a one-time iteration provides a deviation of E_2 and A_2 from the pair of E_1 and A_1 to values of less than 2...3%. The obtained data in the form Y = f(1/T) with the serial iterations of E and A are shown in Figure 2.

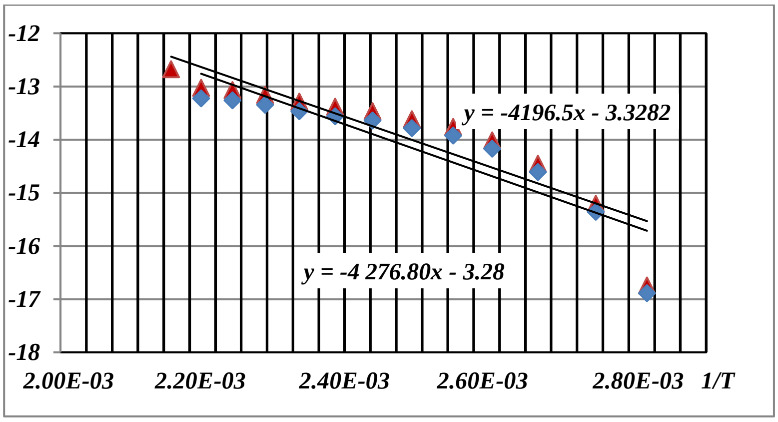
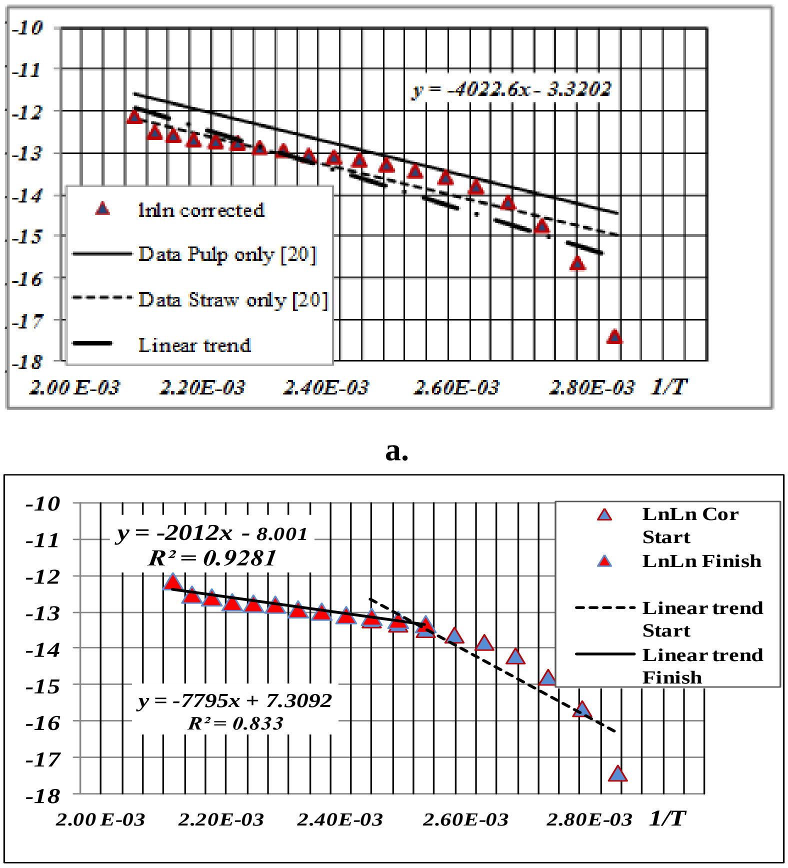


Fig. 2. Dependence Y=f (1/T) for the mixture of pulp-husk in the zone of dehydration
▲ - with correction multiplier, ◆ - no correction

The analysis of the data obtained in conjunction with the data [12,13] for pure biomass shows that at small values of α, less than 0.05 and at values α, greater than 0.95, there is a significant deviation from the approximating lines. This particular circumstance is noticeable in the process of moisture release. The results of studies into the drying process indicate that the initial free moisture release (constant speed drying) and the subsequent period of the release of chemically bound moisture [12] are essentially different. Therefore, the representation of the demoisturization process by the first order reaction looks somewhat arbitrary. From the data shown in Figure 3 (a) and (b) follows that it is expedient to approximate them by two lines on the abscissa sections 0.0032...0.0026 and 0.0026...0.0022 separately.



a.

b

Fig. 3. Dependence Y = f(1/T) for the mixture of pulp-wheat straw in the zone of dehydration.

a - approximated within a whole range of reverse temperatures; b - approximated in sections of 1/T range

It should be noted that in [12,13] data were generalized, starting with α>0,05. When involving the generalization of the lower values of α, the need to generalize the process of moisture release on the two segments of 1/T axis becomes apparent. In figure 2 (a) shows the obtained data for a mixture of wheat straw- pulp. For the comparison, here are given the lines calculated as recommended in [12,13] for the pure components of the mixture, as well as the approximation line for the whole range of the process. The data clearly prove that the kinetics of the blend demoisturization corresponds with the kinetics of the individual components of the mixture, since the data for the mixture lay closely to and within the lines for the components. It should be marked that the equation of the approximating line is strongly dependent upon the 1/T range of approximation. The lower (and equally the higher) the values of α are to be included into the approximation the bigger the deviation of the experimental points from the approximating line should be expected. This proves distinctly the necessity to introduce the two section approximation of the experimental data aimed at the increasing accuracy of the calculations, which is shown in Figure 2. Kinetic constants thus obtained are shown in Table 2 and 3.

Table 2

Kinetic constants for the whole range and sections

Blend	Constants					
	Average		1 section		2 section	
	A, 1/s	E, KJ/mole	A, 1/c	E, KJ/mole	A, 1/s	E, KJ/mole
Pulp-straw	145.4	33.44	1.16e07	64.8	0.675	16.73
Pulp-husk	154.9	34.92	8.9e08	82.72	0.70	18.26
Pulp-sawdust	1603	39.96	10.4e12	106.37	12.325	24.85
Straw-sawdust	522	39.2	9.4e09	87.65	3.28	23.25

Table 3

Approximating equations

Blend	**Line Equation**		
	average	1 section	2 section
Pulp-straw	-4023x-3.2	-7798x+7.3	-2012x-8.0
Pulp-husk	-4200x-3.3	-9552x+11.4	-2196x-8.1
Pulp-sawdust	-4806x-1.1	-12794x+20.5	-2989x-5.5
Straw sawdust	-4712x-2.2	-10542x+13.7	-2797x-6.75

Data on the degree of conversion calculated by the basic equation (3) and by using the data given in Table 2 and Tabl3 in MathCad are presented in Figures 4 and 5

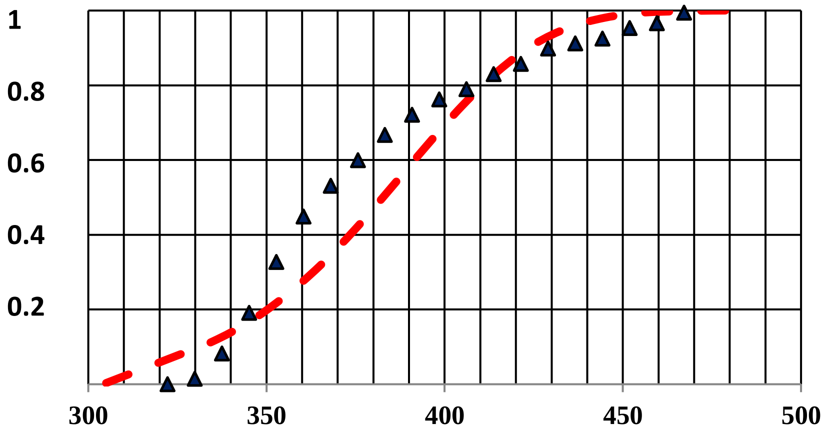


Fig. 4 . Degree of moisture conversion at heating within 300…500 K of wheat straw-pulp blend approximated within a whole region

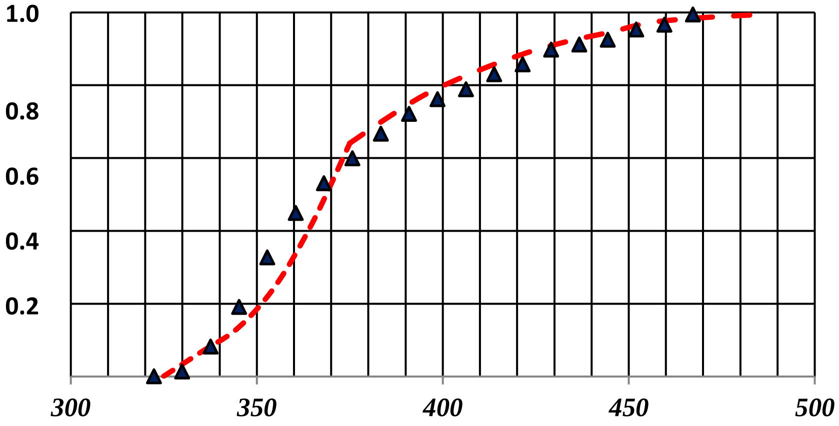


Fig. 5 . Degree of moisture conversion at heating within 300…500 K of wheat straw-pulp blend approximated in two sections

As it can be clearly seen, the approximation within the two sections of the temperature range of the demoisturization section allows obtaining much more accurate correspondence of the experimental data to those calculated, which, in turn, allows precise determination of the target product yield.

4. Conclusion

The kinetics of the dewatering stage within a whole process of thermal degradation of the set of ground solid biomass blends was determined by means of the dynamic thermogravimetry analysis.

Data processing and determination of process kinetic constants were done within the modified Coats-Redfern method.

It has been shown that the process of demoisturization can hardly be distinguished on the TGA curves, since the first derivative of mass never reaches zero because the process of dewatering at its end coincides with the next process of devolatilization.

The accuracy of data generalization which leads to the determination of kinetic constants depends strongly on the marked limits of the process.

The method of the approximation data on two sections within the process temperature range has been proposed. The method allows much closer match of the experimental data to the results of calculations.

Proposed kinetic constants may be used at calculations of the demoisturisatrion stage of biomass blends during their thermal degradation and at deriving 3-D sub models of biomass combustion.

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