Biomass Pyrolysis Kinetics Researching

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Abstract— **The biomass pyrolysis technology (carried out at moderate temperatures up to 1000˙C) allows improving of energy efficiency and workability of biomass utilization. The pyrolysis process controlling (with desired composition of products) is possible by changing the process parameters (temperature, pressure, heating rate, the biomass hold up time in pyrolysis reactor). Availability of kinetic equations linking technological parameters and vent of the pyrolysis products with biomass hold up time at preset temperature range is the necessary condition for pyrolysis process controlling. Obtaining of the pyrolysis kinetic parameters based on experimental data of the thermogravimetric analysis was the purpose of this study. Then, kinetic constants were obtained for various types of plant biomass, such as wood, corn straw, rice husk, and chicken litter, namely, the order of the pyrolysis process, the activation energy and pre-exponential factor. Obtained constants allow the reactor characteristics calculating for fixed products of pyrolysis process receiving.**

Keywords - biomass conversion; kinetic parametres; pellets; pyrolysis.

I. INTRODUCTION

Biomass thermochemical conversion in the power-producing purposes is subdivided into two technologies: gasification and pyrolysis. Gasification purpose is reception of gaseous fuel with the maximal degree of energy conversion (0,70-0,75) to the combustion heat of received fuel. The gasifier maximal temperature exceeds 1000 ˚C. Carbon of ash content is gasified to the limit by gasifying agents. However, gas thermotechnical characteristics do not satisfy to the modern power technologies with high intensity of heat and mass exchange: combustion heat does not exceed 10,5-10,9 MJ/nm^3, adiabatic combustion temperature is about 1400-1500 ˚C. The chemical compound of many kinds of biomass (crop residues, abilities to live, sewage sludge, etc.) limits the maximal temperature of conversion due to the formation of low-melting eutectics.

The biomass pyrolysis technology (carried out at moderate temperatures up to 1000˚C) allows to improve energy efficiency and workability of biomass utilization. In the pyrolysis process decomposition of organic compounds of the initial biomass is carried out with forming of non-condensable gases (CO, CO_2, H_2, CH_4, etc.), the solid residue, and vapors. The vapors are condensed under cooling in a mixture of high-molecular liquids (bio-oil) with a high energy density [1][2]. The pyrolysis process controlling (with desired composition of products) is possible by changing the process parameters (temperature, pressure, heating rate, the gas environment composition, the biomass hold up time in pyrolysis reactor). Availability of kinetic equations linking technological parameters and vent of the pyrolysis products with biomass hold up time at preset temperature range is the necessary condition for pyrolysis process controlling. Obtaining of the pyrolysis kinetic parameters based on experimental data of the thermogravimetric analysis was the purpose of this study. The authors studied many types of biomass, not only well-known, i.e., wood, but also those data which is under-explored: crop wastes and chicken litter [3].

This paper contains theoretical calculation of kinetic parameters, using experimental data, and experimental method description and obtained data. In conclusion, there is a discussion of legality of using this method to determine the kinetic parameters for different types of biomass.

II. THEORETICAL FOUNDATIONS

The physical-chemical basis of our method is [4]:

Biomass pyrolysis process is a simultaneous occurrence of many reactions. However, total reaction can be schematically represented by a single-component model as:

Initial sample => Volatile compounds + solid residue

Reaction rate can be written as a standard kinetic equation:

$$-\frac{dc}{d\tau} = kc^n. \tag{1}$$

c – sample current mass, n – the order of the reaction, k−rate constant of the total-reaction;

$$c = 1 - \frac{V_{T_f}}{V_k}$$

V_{T_f} – volatile matter loss at the temperature T_f, V_k-volatile matter loss at the end of the pyrolysis process.

We can finally get the formula for the rate constant using the Arrhenius equation:

$$-\frac{dc}{dT} = c^n \frac{Z}{\beta} e^{-\frac{E}{RT}} \tag{2}$$

β and Z – heating rate and pre-exponential factor, E – activation energy.

In (2), there are three unknowns: the activation energy E, pre-exponential factor Z, and the reaction order n.

Obtaining of a system of three equations is required to find these unknowns. The inflection point is the characteristic point of the kinetic curve. Exactly for this point required three equations could be found.

The first equation is obtained by applying (2) for the inflection point. The maximum of decomposition rate with certainty is obtained from the experimental derivative thermogravimetric analysis (DTG) curve:

$$\left(\frac{dc}{dT}\right)_{T=T_f} = W_{max} = -Z \frac{e^{\frac{-E}{RT_f \ast C_f^n}}}{\beta} \tag{3.1}$$

The second one could be found by equating the second derivative at this point to zero:

$$-\frac{Z}{\beta}e^{\frac{-E}{RT_f}}*C_f^{n-1}\left(\frac{dc}{dT}\right)_{T=T_f}-\frac{Z}{\beta}e^{\frac{-E}{RT_f}}*C_f^n\frac{E}{RT_f^2}=0$$

Solving this equation for E may be received:

$$E=-nRT_f^2\frac{W_{max}}{C_f} \tag{3.2}$$

The third equation is obtained by integrating the basic equation (2): the left part in the range from 1 to C_f, the right one in the range from T_0 to T_f :

$$\int_1^{c=c_f}\frac{dc}{c^n}=-\frac{Z}{\beta}\int_{T_0}^{T=T_f}e^{\frac{-E}{RT}}dT=-\frac{ZE}{\beta R}(\frac{e^{-X}}{X}-\int_X^\infty\frac{e^{-u}}{u}du)=-\frac{ZEe^{-X}}{\beta R\ X^2}\left(X-X^2e^X\int_X^\infty\frac{e^{-u}}{u}du\right),$$

$$X=\frac{E}{RT}.$$

Expression for $\frac{e^{-X}}{X^2}$ can be obtained by dividing both sides of (3.2) at RT and T and substituting as substituting the value $\frac{dc}{dT}$ from (3.1):

$$\frac{E}{RT}*\frac{RX}{E}=-\frac{n}{c_f}(-\frac{Z}{\beta}e^{\frac{-E}{RT_f}}*C_f^n)$$

Or

$$\frac{X^2R}{E}=\frac{nZe^{-X}c_f^{n-1}}{\beta}$$

As a result, we obtain:

$$\frac{e^{-X}}{X^2}=\frac{R\beta}{EnZc_f^{n-1}}$$

$$\int_1^{c=c_f}\frac{dc}{c^n}=-\frac{1}{nc_f^{n-1}}(X-X^2e^X\int_X^\infty\frac{e^{-u}}{u}du)$$

For $n\neq 1$:

$$\frac{n}{n-1}(1-c_f^{n-1})=X-X^2e^X\int_X^\infty\frac{e^{-u}}{u}du$$

Transforming, we obtain:

$$nc_f^{n-1}=1+(n-1)[1-X+X^2e^X\int_X^\infty\frac{e^{-u}}{u}du]$$

Denoting the expression in parentheses as P(X):

$$nC_f^{n-1}=1+(n-1)P(X) \tag{3.3}$$

The system of (3.1), (3.2), and (3.3) the subscript f refers to the parameter values at the inflection point.

$$P(X)=1-X+X^2e^X\int_X^\infty\frac{e^{-u}}{u}du, \tag{4}$$

$$X=\frac{E}{RT_f}.$$

Definite integral in (4) cannot be expressed in terms of elementary functions. It is the exponential integral function whose values are given in the special mathematical tables.

In this paper, for (4), we obtained the regression equation with a correlation coefficient of 0.996 for the entire relevant range of values of the pyrolysis process X:

$$P(X)=1,132X^{-0,858}-6,968\times10^{-4} \tag{5}$$

Solving (3.1-3.3) and (4) with using of TGA data kinetic parameters n, E и Z can be obtained as follows:

1) Determine the coordinates of the inflection point on the experimental curve and the following parameters for this point: share decomposed substance, decomposition rate and temperature.

2) Solve system (3).

$$\begin{cases}(\frac{dc}{dT})_{T=T_f}=W_{max}=-Z\frac{e^{\frac{-E}{RT_f*C_f^n}}}{\beta}\\ E=-nRT_f^2\frac{W_{max}}{C_f}\\ nC_f^{n-1}=1+(n-1)P(X)\end{cases} \tag{3}$$

3) Plot the calculated curve of thermal decomposition of biomass samples according to the equation:

$$V_T=V_K(1-C_T), \tag{6}$$

$$C_T=\exp(\frac{1}{1-n}\ln(1-\frac{ZE}{\beta R}\frac{(1-n)(1-P(X))}{e^XX^2})).$$

A solution of (3) together with (5) and (6) was obtained by using MathCad 14.

III. EXPERIMENTAL STUDIES

Thermogravimetric data were obtained on a modern thermoanalyzer SDT Q600 firm "TA Instruments" (USA). It is a high-precision instrument with a wide range of opportunities. Thermogravimetric analysis (TGA) and DTG curves can be received with different heating rates in an artificially created gas atmosphere during pyrolysis process at the different final temperatures, etc. The pyrolysis process parameters for all kinds of biomass have a decisive influence on the kinetic regularities of this process.

At the studies first stage, namely, a thermal analysis of all types of biomass was carried out in a nitrogen atmosphere with a heating rate of 10 K/min. TGA and DTG measurements were performed simultaneously. The DTG curve could precisely determine undecomposed biomass content, rate of decomposition and temperature at the inflection point. All these values correspond to the maximum on the DTG curve. This method allows receiving the correct input data for solving the system of equations (3).

Sample weight was measured by comparing the mass microbalance empty cup and cup with sample.

Low sample weight (less than 100 mg) and size suggest pyrolysis proceeding in the kinetic mode without internal and external diffusion limitations.

Sample weight was measured by comparing the mass microbalance empty cup and cup with sample. Table I shows sample weight data.

TABLE I. SAMPLE WEIGHTS

Type of biomass	Weight, mg
Wood	30.47
Rice husk	55.8
Corn straw	62.3
Chicken litter	69.39

A typical recording of the thermal degradation of biomass is shown in Fig.1. According to graph, we can find initial data at the inflection point for determining kinetic parameters (in this case, for wood):

- Temperature, T_f= 639 K;
- Undecomposed biomass content, Cper = 0.466;

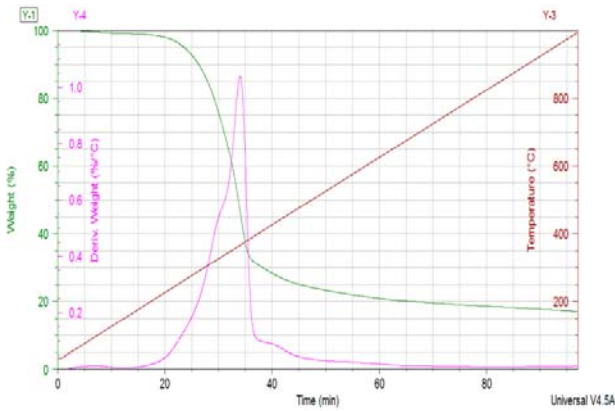- Rate of decomposition, Wmax = -0.0104 1/K

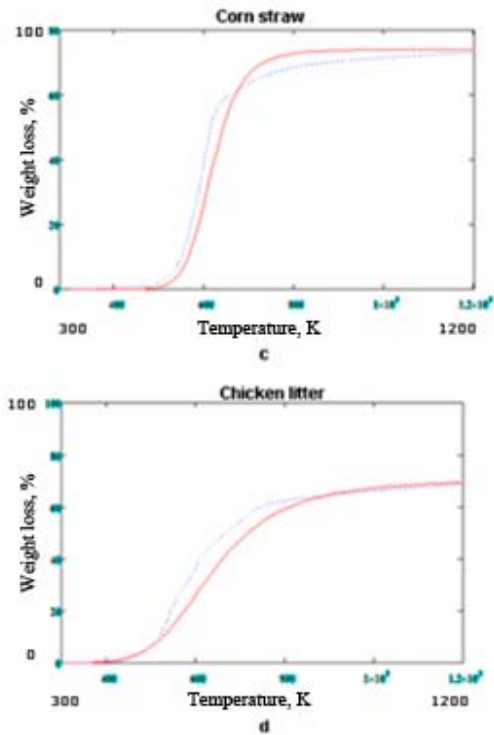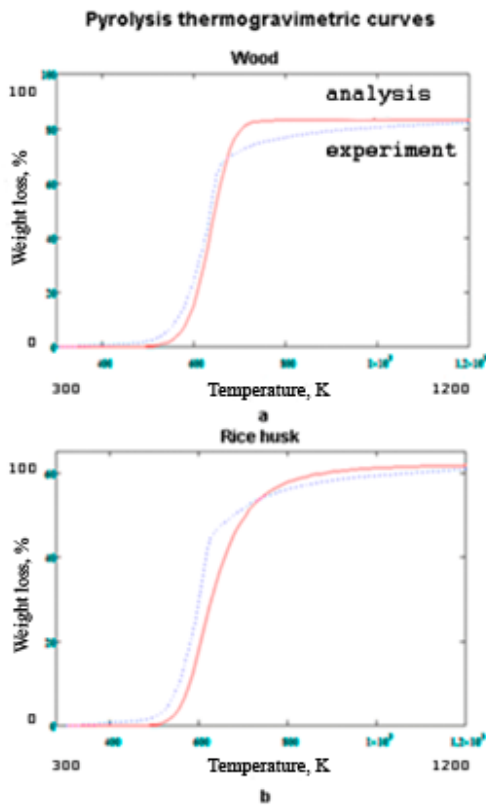Figure 1. The characteristic curve of the biomass pyrolysis process

Figure 2. Pyrolysis thermogravimetric curves

Various kinds of biomass pyrolysis curves (analysis and experimental) are shown in the graphs in Fig.2: a – wood pellets; b – rice-husk pellets; c – corn-straw pellets; d – chicken litter pellets.

The results of different kinds of biomass pyrolysis exploration are shown in Table II.

TABLE II.   INITIAL AND CALCULATED DATA FOR EACH BIOMASS SORT

Kind of biomass	Initial data (in the inflection point)		
	Decomposition rate, Wmax, 1/K	*Temperature, T_f, K*	*Undecomposed biomass content, C_f*
Wood	-0.0104	639	0.466
Corn straw	-0.008	609	0.571
Rice husk	-0.00698	609	0.651
Chicken litter	-0.0042	604	0.624
Kind of biomass	**Kinetic parameters**		
	Order of the process, n	*Pre-exponential factor, Z, s*	*Activation energy , E, kJ/moll*
Wood	1,371	$1.55*10^6$	103.94
Corn straw	2.268	$1.25*10^6$	98.16
Rice husk	3.526	$5.29*10^7$	116.59
Chicken litter	2.23	2.87	34.47

Kind of biomass	The maximum discrepancy between experiment and calculation, %
Wood	3.6
Corn straw	2.4
Rice husk	7
Chicken litter	7

Based on these results, we can conclude that the pyrolysis process is a sum of the parallel-serial reactions (because the order of the process is not an integer number).

IV. DISCUSSION

The obtained data indicate the correctness of using this method to determine the kinetic parameters for different types of biomass. The largest discrepancy between calculated and experimental curve is 7%, which can be considered as acceptable. The obtained data can be used for pyrolysis reactor characteristics calculations. Explored phytogenic kinds of biomass (wood, corn straw, rice husk, chicken litter) have only one inflection point at TGA curve and one extreme at DTG curve. The main components of these biomass types are lignin, cellulose and hemicellulose which determine the thermal decomposition kinetics of the thermochemical degradation. The complex nature of the thermal decomposition and differed kinetic parameters of chicken litter due to its structure: biomass, which contains the minimum amount of lignin and cellulose (chicken manure) and phytogenic biomass (litter). On the DTA curve there are several clear-cut inflection points, in which the rate of decomposition passes through an extreme.

V. CONCLUSION AND FUTURE WORK

Based on the proposed method, the following kinetic constants were obtained: the order of the pyrolysis process, the activation energy and pre-exponential factor - for various types of plant biomass: wood, corn straw, rice husk, chicken litter.

Obtained constants allow calculating the reactor characteristics for fixed products of pyrolysis process receiving.

Waste made of biomass utilization is of considerable interest from both an ecological and power-engineering point of view.

Some further research directions:
- the kinetics constants for different heating rates determination;
- the pyrolysis kinetics in various gas atmospheres exploration;
- study the effect of internal thermal effects (exothermic) on the kinetics of pyrolysis.

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