Modeling and Analysis of the Kinetics of the Pyrolysis Process of Biomass with Influence Raw Material Composition on Comsol Multiphysics

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***Abstract*—In this article, the modeling and analysis of the kinetics of the pyrolysis process is carried out, which allows us to determine the rate of chemical reactions occurring during the decomposition of the material, as well as to identify key factors affecting the speed and efficiency of pyrolysis. The simulation was performed using Comsol Multiphysics software based on the kinetic mechanisms of the reaction of biomass of corn cob particles at a temperature of 500°C. The pyrolysis process of plant biomass was analyzed at a residence time of 0 to 10 minutes. The resulting models describe temperature changes well, especially in the center of the biomass. It was found that pyrolysis of corncob biomass occurred in the temperature range from 190 to 432 °C, at 190 °C mass loss began, which ended at 432 °C. The kinetic parameters were calculated using the Kissinger method, and the least squares method and correlation analysis were used to calculate the kinetic constants. The study results will be useful for optimizing the conditions of the biomass pyrolysis process in the future.**

Keywords: Kinetics of pyrolysis, Pyrolysis of biomass, Corn cob, Comsol multiphysics, Kissinger method

I. Introduction

For effective pyrolysis, it is crucial to understand its kinetics, which helps in the development of reactors and mathematical models to optimize the process. There are two main approaches to analyzing biomass kinetics: model-free methods and model-based methods. The model-free approach, such as the isoconversion method, is straightforward and does not require selecting a specific reaction model, reducing the risk of errors. However, it requires multiple measurements, which may introduce inaccuracies. On the other hand, model-based methods allow for more precise parameter selection and simplified calculations, but they have limitations in determining suitable models under non-isothermal conditions, making them less preferable in some cases.

In this paper, the rate of chemical reaction characteristics during material decomposition of corn cob biomass particles was studied in order to predict the efficiency of the pyrolysis process.. For the experiment, the biomass under consideration possessed certain thermophysical characteristics mentioned in the following table. The entire experiment was carried out in an isothermal condition in a furnace under an inert and stable atmosphere where the mass and temperature of pyrolytic samples could also be monitored. This paper uses the isoconversion method to decipher kinetic data and thereby estimate the activation energy. The pyrolysis rate was determined by an ability to change the mass and the temperature of the sample, activating the model in order to analyze the process.

When modeling the pyrolysis process of corn cob biomass using COMSOL Multiphysics at a heating temperature of 500°C over a period of 10 minutes, results on temperature and biomass mass changes were obtained. The surface temperature of the biomass peaked at 727 K after 460 seconds, while the center temperature reached 794 K after 433 seconds. The biomass mass showed a sharp decline, with 58% of the mass lost after 292 seconds. To calculate the kinetic parameters, the Kissinger method was used, yielding an activation energy of 51.53 kJ/mol and a frequency factor of 6.2×10^3 sec^{-1} for corn cob particles.

A kinetic analysis of the pyrolysis of corn cob biomass with a size of 0.02 m^2 was conducted using COMSOL Multiphysics software in the temperature range of 20–500°C over 10 minutes. The Kissinger method enabled the calculation of the kinetic parameters, which remained constant throughout the experiment. The data obtained, along with correlation analysis, will aid in optimizing the pyrolysis process conditions for biomass in the future.

Among all the types of thermochemical processing of biomass, pyrolysis is one of prominent processes. The enhanced feasibility of an energy project with the help of an industrial biomass pyrolysis plant will make the reduction of carbon emission possible to establish an energy project [1,2].

For modeling the behaviour of a material during pyrolysis, the kinetics of the processes are also determined. The information assists in selection of a suitable reactor and in building quantitative models for the improvement of the pyrolysis process. With regards to the thermal processing of hydrocarbon waste and biomass, issues such as pyrolysis kinetics; and influence of raw materials are deemed to be informative.

Currently, several techniques are used to analysis of kinetic data of biomass and they are categorized as either non-parametric or parametric. The model-free method is also called the iso-conversion method for which the test is conducted at varying heating rates, and calculations are done at the similar conversion rates. From this, the activation energy for a particular conversion point is determined. However, in model-based methods, the genetic parameters are identified using a fitting function for a whole set of parameters which provide a predicted data set. It is the variation between the actual data and the predicted data concerning any set of model parameters. In the case of the kinetic analysis, the best chosen values of the parameters are those that reduce this difference [3,4,5]. Thus, the method has several disadvantages, firstly, it is impossible to determine a suitable reaction model for non-isothermal mode. This method is usually likely to provide higher values of the kinetic constant that is why it was mostly substituted by iso-conversional methods. The main strength of the model free method is that the procedure is conceptually simple and no errors arise from choosing a specific kinetic rate model. These methods seek to determine the activation energy, EEE, for a particular transformation. The disadvantage of this method is that it necessary to obtain a series of measurements of the sample mass at different heating rates and different inert gas flow, and these measurements can contain errors [6,7,14].

II. MATERIALS AND METHODS

Due to their high calorific value and bio-oil yield [8,9,10,15], corn cobs were selected as the biomass for this research. The corn cob biomass, with a particle size of 0.02 m² and thermophysical properties listed in Table I, was analyzed using COMSOL Multiphysics software.

Concerning the experiments, an experimental system was established for the series of experiments including isothermal furnace in an inert atmosphere comprised of tubular reactor. The thermocouples TP were used in order to maintain constant furnace temperature, while the nitrogen purging through the furnace chamber provided the inert atmosphere. Five grams of sample was conditioned in the isothermal furnace and during each experiment, 1 kg of biomass was used with the temperature and mass of the sample measured during pyrolysis.

In this work, the pyrolysis rate in the tubular reactor was obtained to examine the kinetic of the pyrolysis process of corn cob biomass. Parameters that yielded information in this kind of reactor include rate of pyrolysis, temperature, pressure and the rate of heating.

The pyrolysis rate in a tubular reactor was quantified by weight loss technique and also using temperature probes identified in COMSOL Multiphysics. The weight method is one of the methods that are used to quantify dynamics of biomass mass in the reactor. The rate at which pyrolysis occurs can then be found using data obtained from the mass loss after pyrolysis had taken place. Because pyrolysis is generally associated with heat generation, temperature probes were used to measure reactor temperature fluctuations with time. These measurements brought extra information which help estimate the pyrolysis rate with respect the to thermal parameter.

Table I: Thermophysical Properties of Corn Cob Waste [8,9,10]

	Indicators	Values
1	Density, kg/m^3	282,38
2	Humidity, %	5-6,5
3	Dimensions, mm	10x20
4	Coefficient of thermal conductivity, W/m·°C	0,096
5	Porosity	0.4
6	Pore size	5E-5 m
7	Emissivity	0.95
8	Effective thermal conductivity in the transverse direction of the fibers, W/(m•K)	1,32
9	Effective thermal conductivity in the direction of the fibers, W/(m•K)	3,7

To conduct the experiment, the experimental conditions were set up in the Comsol Multiphysics software, which are shown in Table II.

Table II: Experimental Conditions for the Analysi

	Indicators	Values
1	The initial temperature of the biomass, K	293
2	Furnace temperature, K	820
3	The temperature of the gas in the reactor, K	773

For investigating the kinetics of biomass pyrolysis, the thermophysical properties for corn cobs were subsequently introduced into COMSOL Multiphysics. In this case, the initial weight of the biomass sample was set to 1kg:0 with a BOD value of 500mg/l. Since TGA mass loss is relative to the initial mass of the sample, this initial value was employed for measuring the mass change of the sample during pyrolysis.

During the pyrolysis the needed experimental conditions, for example the temperature and the pressure, were set by the help of the COMSOL Multiphysics software. To maintain accuracy the weight of the sample was weighed using the built in software functions every now and then.

As the pyrolysis progressed, the sample's mass decreased, and this change was recorded continuously during the experiment.

Upon completion, the recorded mass change data were analyzed. These data were then used to determine the heating rate over time and as a function of temperature.

For the analysis of activation energy at conversion points in both isothermal and non-isothermal experiments, the model-free approach is represented by the isoconversion method [11]. The application of this method is consistent, allowing for the extraction of standard kinetic data from non-isothermal experiments. A model-free equation for three different methods is provided below [12,13,16].

To study the kinetics of pyrolysis of biomass particles by corn cob, the Kissinger method was used in the study:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m}$$

where E - the activation energy (kJ/mol), T - the absolute temperature (K), T_m - the peak temperature (K), A - the frequency coefficient (min^{-1}), β - the heating rate (°C/min), R - the gas constant (kJ/mol*K).

III. RESULTS AND DISCUSSION

When modeling the pyrolysis process of biomass, such as corn cobs, using COMSOL Multiphysics software, in the time range of 0–10 minutes, with a heating temperature of 500°C, the following results were obtained (Fig. 1–3).

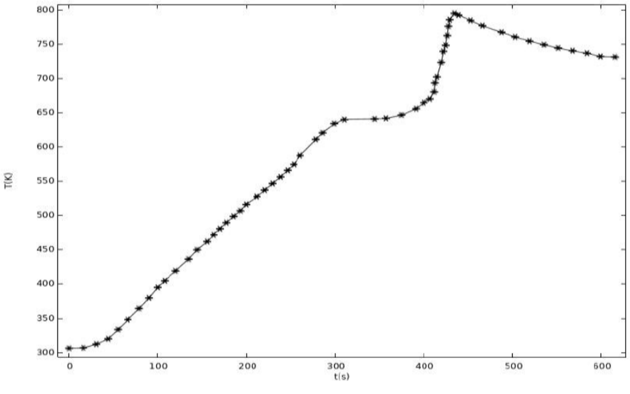

Fig. 1: Temperature Change During Pyrolysis at the Center of the Biomass

During the modeling of the pyrolysis process for corn cob biomass using COMSOL Multiphysics, temperature sensors were positioned both on the surface and at the center of the biomass to monitor temperature changes. The temperature variation over time is shown in Fig. 1. The resulting models describe the temperature trends well, especially in the center of the biomass. Both the time and absolute peak temperature values at each position are lower than those observed in experiments. Fig. 1 shows that the surface temperature of the biomass reaches a peak of 727 K after 460 seconds, while the temperature at the center reaches 794 K after 433 seconds.

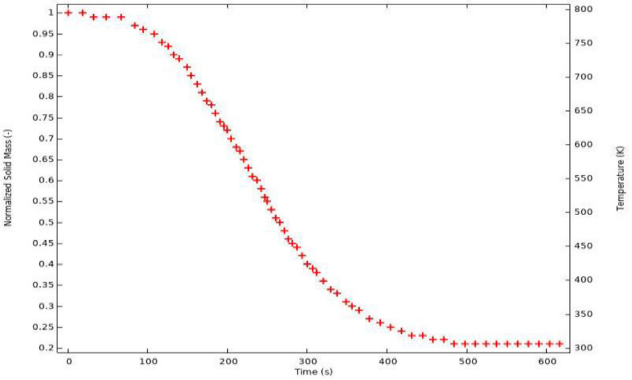

Fig. 2: Change in Biomass Mass as a Function of Time

The mass loss of the biomass over time is presented in Fig. 2. Starting at 112 seconds, the corn cob particle rapidly begins to lose mass. In about 292 seconds, the particle loses 58% of its mass. By the end of the process, the corn cob biomass is fully transformed, with most of the material converted into char.

Based on the temperature data obtained from the sensors, we calculated the heating rate (Fig. 3). This was determined by taking the arithmetic mean of the surface temperature and the temperature at the center of the biomass.

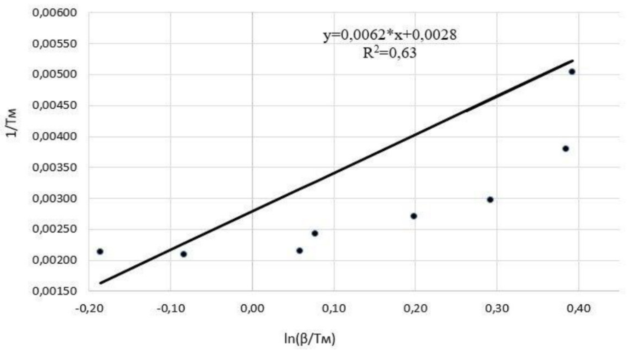

Fig. 3: Kissinger Graph for a Corncob Particle

Table III: Kinetic Parameters of the Corn Cob Determined by the Kissinger Method

Biomass	Heating Speed (˚C/Sec)	$T_{мах}$ (˚C)	E (kJ/mol)	A (sec^{-1})	R^2
A particle of corn cob	1,30	95,38	51,53	6,2*10^3	0,63
	1,48	198,54			
	1,47	263,54			
	1,34	336,38			
	1,22	368,38			
	1,08	411,86			
	1,06	464,59			
	0,92	478,49			
	0,83	467,37			

To apply the peak temperature in the Kissinger method, the maximum temperature was selected based on the arithmetic mean of the temperatures at the surface and center of the biomass particle. This value remained constant at different heating rates. A linear line, obtained using the Kissinger method, is shown in Fig. 3, from which the kinetic constants were calculated. These constants were determined using the least squares method.

The activation energy and frequency factor were derived from the slope and intercept of the linear regression line, as presented in Table III. For a corn cob particle, the activation energy and frequency factor were found to be 51.53 kJ/mol and 6.2×10^3 sec^{-1}, respectively.

IV. Conclusions

In this study, a kinetic analysis of biomass pyrolysis for a corn cob particle with a surface area of 0.02 m^2 was conducted using COMSOL Multiphysics software. The temperature range was 20–500°C, and the experiment lasted for 10 minutes. The software allowed us to monitor temperature changes at both the surface and center of the biomass, as well as track mass loss over time. Using the obtained data, and through mathematical calculations, weight analysis, and the least squares method, we created Kissinger plots, which provided kinetic constants essential for studying the pyrolysis process of corn cob particles.

From the data obtained, the following conclusions can be drawn:

- The temperature at the surface of the biomass particle rapidly increased to 684 K within 200 seconds, then rose to 717 K over 400 seconds, eventually stabilizing at 773 K inside the reactor.
- The temperature at the center of the biomass particle reached 684 K in 374 seconds, with a peak of 794 K at 433 seconds, after which it slowly decreased to 615 K.
- Biomass degradation began after 108 seconds and ended after 483 seconds, during which the mass loss reached 79%, leaving a charred mass of 21% or 210 grams.
- The maximum weight loss of the corn cob, 58%, was observed within the temperature range of 180–360°C.

It was concluded that the pyrolysis process for the corn cob biomass occurred within the temperature range of 190–432°C. Biomass began losing mass at 190°C, with the process concluding at 432°C. The kinetic parameters were calculated using the Kissinger method, and both the least squares method and correlation analysis were used to determine the kinetic constants. These results are expected to be useful in optimizing future biomass pyrolysis processes. In the Kissinger method, the kinetic parameters remained consistent throughout the pyrolysis process, and the correlation coefficient between temperature and heating rate in the model was found to be 0.79.

References

[1] C. Jaroenkhasemmeesuk, N. Tippayawong, Thermal degradation kinetics of sawdust at intermediate heating rates, Appl. Therm. Eng., 103 (2016), pp. 170-176.

[2] Uzakov G., Mamatkulova S., Ergashev, S.: Thermal mode of the condenser of a pyrolysis bioenergy plant with recuperation of secondary thermal energy. E3S Web of Conferences, 411, 01021, (2023).

[3] Haykiri-Acma, H.,Yaman, S. and Kucukbayrak, S., "Effect of heating rate on the pyrolysis yields of rapeseed", Renewable Energy, Vol. 31, (2006), 803-810. (http://dx.doi.org/10.1016/j.renene.2005.03.013).

[4] Islam, M.A., Auta, M., Kabir, G. and Hameed, B.H., "A thermogravimetric analysis of the combustion kinetics of karanja (Pongamiapinnata) fruit hulls char", Bioresource Technology, Vol. 200, (2016), 335-341. (http://dx.doi.org/10.1016/j.biortech.2015.09.057).

[5] G. Uzakov, S. Mamatkulova, Sh. Ergashev and el. Modeling of heat exchange processes in a condenser of a pyrolysis bioenergy plant. BIO Web Conf., 71 02021. DOI: https://doi.org/10.1051/bioconf/20237102021, (2023).

[6] Ather, D., Chaudhary, N., Singh, G., Beig, T., & Kler, R. (2023, December). Enhancing Used Automobile Valuations: A Data-Cleaning and Linear Regression Approach for Predicting Prices In Competitive Market. In 2023 4th International Conference on Computation, Automation and Knowledge Management (ICCAKM) (pp. 1-5). IEEE.

[7] Chaudhary, N., Singh, G., Ather, D., Kler, R., & Bhandwal, M. (2023, December). Arduino-Based Monitoring of Microclimatic Variables for Precision Agriculture in Sugarcane Cultivation. In 2023 4th International Conference on Computation, Automation and Knowledge Management (ICCAKM) (pp. 1-6). IEEE.

[8] Kler, R., Ather, D., Singh, G., Chaudhary, N., & Arora, M. (2023, December). Predicting Agricultural Growth in Jizzax Region Using Advanced Machine Learning Techniques: An ARIMA-Based Approach. In 2023 4th International Conference on Computation, Automation and Knowledge Management (ICCAKM) (pp. 1-5). IEEE.

[9] Mishra, G., Kumar, J. and Bhaskar, T., "Kinetic studies on the pyrolysis of pinewood", Bioresource Technology, Vol. 182, (2015), 282-288. (http://dx.doi.org/10.1016/j.biortech.2015.01.087)

[10] Mamatkulova S. G. and Uzakov G. N.: Modeling and calculation of the thermal balance of a pyrolysis plant for the production of alternative fuels from biomass. IOP Conference Series: Earth and Environmental Science T 1070 1**, (**2022)

[11] Damartzis, Th., Vamvuka, D., Sfakiotakis, S. and Zabaniotou, A., "Thermal degradation studies and kinetic modeling of cardoon (Cynaracardunculus) pyrolysis using thermogravimetric analysis (TGA)", Bioresource Technology, Vol. 102, (2011), 6230-6238. (http://dx.doi.org/10.1016/j.biortech.2011.02.060).

[12] T. Onsari et al. Pyrolysis of corn residues: Kinetic analysis using a discrete distributed activation energy model, IOP. Ser Conference. The environment of the Earth. Sciences. (2018).

[13] Z. Kaczor, Z. Buliński, S. Werle: Modelling approaches to waste biomass pyrolysis: a review, Renewable Energy, 2020, Volume 159, Pages 427-443, ISSN 0960-1481, https://doi.org/10.1016/j.renene.2020.05.110.

[14] Heydari, M., Rahman, M. and Gupta, R., "Kinetic study and thermal decomposition behavior of lignite coal", International Journal of Chemical Engineering, Vol. 2015, (2015), 1-9. (http://dx.doi.org/10.1155/2015/481739).

[15] Uzakov, G., Mamatkulova, S., Ergashev, S., Qodirov, F., & Turayev, A. (2023). Modeling of heat exchange processes in a condenser of a pyrolysis bioenergy plant. In BIO Web of Conferences (Vol. 71, p. 02021). EDP Sciences.

[16] Uzakov, G., Mamatkulova, S., Qodirov, F., & Sojida, O. Simulation of a Tubular Pyrolysis Reactor Using Comsol Multiphysics Software. In International Scientific and Practical Conference Digital and Information Technologies in Economics and Management 2024, (pp. 131-142). Cham: Springer Nature Switzerland.