

NON-ISOTHERMAL KINETICS REACTION OF PYROLYSIS OF CASSAVA RHIZOME UTILIZING FLUE GAS

Karan Homchat^{2,*}, Thawan Sucharitakul¹, and Preecha Khantikomol²

Received date: May 01, 2014 Revised date: August 25, 2014 Accepted date: August 25, 2014

Abstract

The pyrolysis of a cylindrical cassava rhizome was studied to determine the kinetics parameters. The pyrolysis of the cassava rhizome under non-isothermal conditions at the heating rate of 17°C/min using flue gas in a metal kiln was investigated experimentally. In the present study, the dried cassava rhizome was examined. The temperatures inside the material and the kiln were measured. Moreover, the mass was weighed continuously during the pyrolysis process. Finally, the predicted fraction conversion was also considered and the kinetic parameters of the process were calculated using the method of Coats-Redfern. The results indicated that the mass loss started when the pyrolysis temperature was higher than 250°C and the pyrolysis process was completed at a temperature about 500°C. The obtained charcoal yield was 25.49% by weight at the pyrolysis temperature about 500°C. The result obtained from the simulation of the kinetics reaction equation, with the reaction order $n = 1.8$, and the predicted mass fraction conversion agreed well with the experiment only when the temperature was up to 420°C. However, in the case of the reaction order $n = 1.5$, the predicted fractional conversion agreed well with the experiment for a temperature higher than 420°C until the end of the process. At the end of the pyrolysis process the inside temperature of the examined material quickly increased due to the exothermic phenomena of the chemical reaction caused when the reaction order was decreased. The root mean square error of the mass fraction throughout the process was 2.4%.

Keywords: Pyrolysis, biomass, cassava rhizome, flue gas, kinetics reaction

Introduction

Some energy sources are of less interest due to a lot of smoke produced by direct combustion and stains from the tar gum sticking to equipment. Currently, the shortage of energy leads to increases in the cost of all kinds of fuel. Some products obtained from burning fossil fuel are

also a significant cause of the greenhouse effect which results in the global warming phenomenon. Agricultural and forestry residues, or biomass residues generally, can be used as raw materials to generate energy, chemicals, and activated carbon (Warb, 1983; Strub, 1984). In this way,

¹ Faculty of Engineering, Chiang Mai University, 239 Huay Kaew Road, Muang District, Chiang Mai, 50200, Thailand. Tel.: 081-669-4701, E-mail: kar_hom@yahoo.com

² Rajamangala University of Technology Isan, 744 Suranarai Road, Muang District, Nakon Ratchasima, 30000, Thailand.

* Corresponding author

thermochemical methods such as pyrolysis and gasification are the most appropriate, and also the most commercially used (Shafizadeh, 1982; Soltes, 1983). In order to solve the problem of energy, renewable and alternative energy sources are the most interesting; energy from agricultural waste or waste biomass i.e. rice husks, straw, corn cobs, cassava stems, cassava rhizomes or stems, sunflower seed shells, etc. especially should be considered. Obviously, biomass has been widely recognized as a source of renewable energy with an increasing potential to replace conventional fossil fuels in the energy market because it could contribute zero net carbon dioxide emission to the atmosphere.

In Thailand, the planted area of cassava is about 11840 km², was according to a survey by the Office of Agricultural Economics in year 2000. Each year, Thailand has a large amount of agricultural waste which is comparable to 1 million liters of petroleum (Biomass One-stop Clearing House, Energy for Environment Foundatio, 2006). Usually, most farmers burn the waste biomass in preparation for the new planting season leading to a lot of smoke and dust in the atmosphere. Biomass mainly consists of 3 components: 30–60% cellulose, 20–35% hemicellulose (polysaccharides), and 15–30% lignin (Zhang *et al.*, 2010).

Pyrolysis describes the process of anaerobic decomposition of solid fuel using only heat at an elevated temperature to produce gas, oil, and charcoal. Pyrolysis can be divided into 3 subclasses i.e. slow, flash, and fast pyrolysis. Slow pyrolysis occurs under a low heating rate which obtains more of a charcoal yield. Flash pyrolysis is a rapid heating rate process occurring at moderate temperatures (400–600°C) that obtains maximized volatile products at a short residence time. Fast pyrolysis occurs at high temperatures and longer residence times leading to increasing the biomass conversion and returning more of a gas product (Zabaniotou and Ioannidou, 2008). Demirbas, (2001) has studied the conversion of biomass to charcoal, liquid, and gaseous products using the carbonization process at different temperatures. He reported that the charcoal yield decreased

gradually with the increase of temperature but the gas yield increased with the increase of temperature. Larfeldt *et al.* (2000) investigated experimentally and numerically the heat transfer properties of dry wood and the pyrolysis mechanism on the pyrolysis of large wood particles. Measurements of the temperature distribution and mass loss were performed on cylindrical samples of dry birch wood during pyrolysis in an inert atmosphere at 700°C. The results indicated that the interior heating rate varies with the radial position in the measured samples and it was also found to influence the choice of the pyrolysis mechanism. Homchat and Sucharitakul (2011) investigated the pyrolysis of cassava rhizome utilizing the flue gas in a lab-scale metal kiln. The results showed that the charcoal yield for the dry cassava rhizome varied from 26% to 35% depending on the pyrolysis temperature and that the pyrolysis time was quite fast at only 19–38 min.

Vlaev *et al.* (2003) have represented the non-isothermal kinetics of pyrolysis of rice husk based on thermogravimetry curves and the kinetic parameters. The kinetic parameters of the process were calculated using the method of Coats–Redfern and 14 kinetic equations. They reported that the experimental data were best described by the equation of Ginstling–Brounshtein valid for diffusion-controlled reactions starting on the exterior of spherical particles with a uniform radius. Sharma and Rao (1999) also investigated the pyrolysis of rice husk in both grain and powder form. The experiment was done under isothermal and non-isothermal conditions to determine the pyrolysis rates at any heating rate. From analysis of both the isothermal and non-isothermal data, it was found that pyrolysis proceeds in 2 distinct temperature zones with a transition at 350°C. Furthermore, several kinetic models have also been reported in the literature for the pyrolysis of grainy biomass materials (Min *et al.*, 2007; Ebrahimi-Kahrizsangi and Abassi, 2008).

On the practicality of the pyrolysis of biomass for charcoal production, the heat source from flue gas was used more than that from electrical heating. Therefore, the objective of

this work is to study the pyrolysis of the one-piece cylindrical cassava rhizome in the lab scale metal kiln using flue gas. Slow pyrolysis at a moderate temperature was investigated under non-isothermal conditions to determine the kinetic parameters and to predict the pyrolysis rate.

Materials and Methods

Properties of Materials

A CHNS elemental analyzer and muffle furnaces calibrated to ASTM standards were used to carry out the ultimate and proximate analysis, respectively. The results of the proximate and ultimate analyses of the cassava rhizome are summarized in Table 1. The results show that there is a high amount of ash. Figure 1 shows the dimension and coordinate system of the examined material.

Properties of Flue Gas

The composition of the flue gas that is the product from the gas chromatograph burner used in the experiment and which was fitted with a molecular sieve 5A (GC-14B, Shimadzu Corp., Kyoto, Japan) is summarized in Table 2. The results show that the composition of the flue gas consists of a large amount of carbon dioxide while the amount of oxygen was much lower.

Experimental Setup

A metal kiln was constructed with circular steel pipe of 2 mm thickness, 150 mm diameter, and 300 mm length and covered with thermal insulation. Thirty-five mm diameter pipes were installed at 30 mm below the center of the kiln on both the front and rear of the kiln, which were

used as the supply pipe of the flue gas and the exhaust, respectively, as shown in Figure 2. The cassava rhizome was prepared with a 40 mm diameter and 120 mm in length as the sample material. The examined cassava rhizome was inserted into the type-K thermocouple to measure the radial temperature distribution, in radial positions at 0, 4, 8, 12, and 16 mm, respectively, and an axial position at 60 mm. The examined cassava rhizome was placed inside the kiln on 0.01g precision digital scales to measure the weight change during the experiment.

Table 1. Physical properties of the dried cassava rhizome (Obtained from the experiment)

Proximate analysis (% by weight, dry basis)	
Moisture content	0.00
Volatile matter	76.20
Ash	3.72
Fix carbon	20.08
Ultimate analysis (% by weight, dry ash-free basis)	
Carbon	52.33
Hydrogen	5.95
Nitrogen	1.02
Total sulphur	0.08
Oxygen	40.62
H/C molar ratio	1.36
O/C molar ratio	0.58
Empirical formula	$\text{CH}_{1.36}\text{O}_{0.58}$

Table 2. Composition of the flue gas

Composition of the flue gas (% by volume)	
Oxygen	0.280
Nitrogen	3.674
Carbon monoxide	0.143
Carbon dioxide	95.900

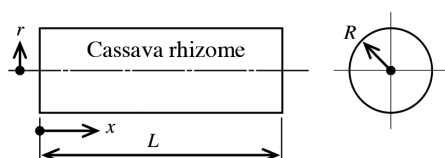


Figure 1. The coordinate system of the examined material

The experiment was conducted in stagnant air to prevent the effect of air flow. The experimental procedures were as follows: to start, 1 piece of cylindrical cassava rhizome was weighed before being placed in the metal kiln; then, the type-K thermocouples were inserted inside the examined cassava rhizome and the metal kiln to measure the temperatures; then, the digital data logger was used to record the temperatures, which were recorded every second; then, the experiment was started by controlling the pressure of the liquefied petroleum gas, the volume flow rate, and the flame of the burner; then, the flue gas was fed into the kiln, the weight change of the material during the experiment was measured with the precision digital scales and was recorded by photography every minute; then, the smoke from the chimney was monitored until it faded and then the experiment was stopped; after that, the gas supply to the burner was shut off, the inlet and exit ports of the kiln were closed in order to prevent the air from leaking; finally, we waited until the decreasing temperature reached room temperature. The charcoal yield and other results were weighed. The temperatures and the weight of the biomass were recorded continuously during the pyrolysis process.

Rate of Mass Loss

The pyrolysis process is represented by the following reaction scheme.



The rate of mass loss for a decomposition reaction is described as

$$\frac{dX}{dt} = K(1 - X)^n, \quad (2)$$

$$X = \frac{(W_0 - W_t)}{W_0 - W_f}, \quad (3)$$

where X is the degree of pyrolysis, and W_0 , W_t , and W_f are the initial, actual, and final weight of the sample, respectively.

The temperature dependence of the rate constant is usually described by the Arrhenius equation:

$$X = A \exp\left(\frac{-E}{RT}\right). \quad (4)$$

where A is the pre-exponential or frequency factor (s^{-1}), E is the activation energy, T is the absolute temperature (K), and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). By combination, the above expressions give the general non-isothermal kinetic equation:

$$\frac{dX}{dt} = A \exp\left(\frac{-E}{RT}\right)(1 - X)^n. \quad (5)$$

For the constant heating rate q :

$$\frac{dT}{dt} = q = \text{Constant}. \quad (6)$$

Then, equation (5) can be rewritten as

$$\int_0^X \frac{dX}{(1 - X)^n} = \frac{A}{q} \int_0^T \exp\left(\frac{-E}{RT}\right) dT. \quad (7)$$

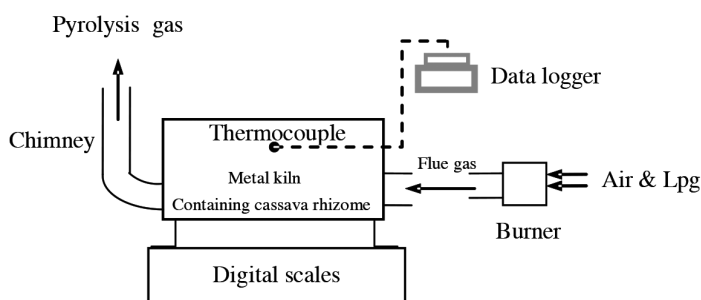


Figure 2. Schematic diagram of the equipment and the laboratory scale metal kiln

Integration of equation (7) according to the Coats and Redfern (1964) method, gives the following equation:

$$\ln[F(X)] = -\frac{E}{RT} + \ln\left[\left(\frac{AR}{qE}\right)\left(1 - \frac{2RT}{E}\right)\right]. \quad (8)$$

The activation energy E is a very high value, thus the term of $2RT/E$ can be neglected. Since $2RT/E \ll 1$, hence

$$\ln[F(X)] = -\frac{E}{RT} + \ln\left(\frac{AR}{qE}\right), \quad (9)$$

where,

$$F(X) = \begin{cases} \ln \frac{(1-X)}{T^2}, & \text{for } n=1 \\ \frac{1-(1-X)^{1-n}}{(1-n)T^2}. & \text{for } n \neq 1 \end{cases} \quad (10)$$

Here, n is the reaction order.

Results and Discussion

The pyrolysis of the cylindrical cassava rhizome using flue gas has been investigated experimentally

and numerically under non-isothermal conditions. Figure 3 illustrates the relationship between the temperatures and the pyrolysis time within a dried cassava rhizome with a 40 mm diameter, 120 mm length, and 62.15 g weight where the kiln temperature is up to 500°C, (the temperature is a dependent variable depending on the gas flow rate), and the heating rate is 17°C/min, (obtained from the experiment, as revealed in Figure 3). The effect of the temperature on the mass loss during pyrolysis of the cylindrical cassava rhizome at 17°C/min of heating rate is revealed in Figure 4. The drying process occurs when the temperature is lower than 423K so that the mass loss is slightly decreased. After that, pyrolysis would occur from the surface to the center of the cylindrical cassava rhizome leading to a smooth decrease of the mass loss. The completed pyrolysis process could be considered when the examined material's weight is constant. The remaining mass that is the charcoal yield was 25.49% by weight with the kiln temperature up to 500°C.

The fractional conversions (X) corresponding to the volatile content released from the biomass sample could be calculated

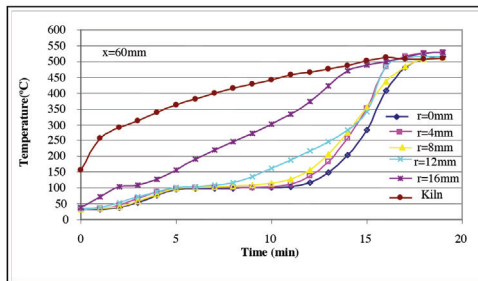


Figure 3. The temperatures and the pyrolysis time of a cassava rhizome where the kiln temperature is up to 500°C

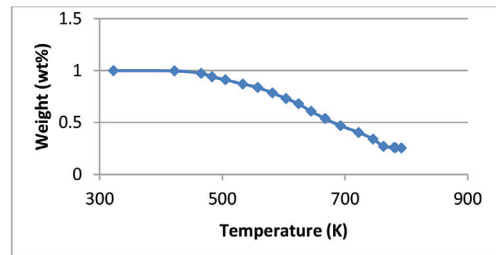


Figure 4. Effect of temperature on the percentage of residue mass (W_t / W_o) during pyrolysis of cylindrical cassava rhizome at 17°C/min heating rate

Table 3. Kinetic parameters of cassava rhizome pyrolysis under non-isothermal conditions using flue gas

Temperature (K)	E (J/mole-K)	A (s ⁻¹)	Reaction order n
T < 693	41939	505.909	1.8
T ≥ 693	189742	6.093 × 10 ¹³	1.5

from the experimental data (Figure 4). From a linear regression analysis, the obtained reaction orders are 1.8 and 1.5 at the lower and higher temperature zone, respectively, and are the best fit criteria for pyrolysis of cylindrical cassava rhizome in flue gas at a heating rate of 17°C/min. Figure 5 shows the relation of $\ln[F(X)]$ and $1/T$, which was evaluated by replacing X and the reaction order n in the equation (10). Obviously, the reaction orders 1.8 and 1.5 correspond to the temperature range $T < 693\text{K}$ and $T \geq 693\text{K}$, respectively. Furthermore, the calculated kinetic parameters for the pyrolysis under non-isothermal conditions are also given in Table 3. Then, the predicted fraction conversion (X) could be evaluated from the Equations (9) and (10) by employing the parameters from Table 3.

In the case of using the reaction order $n = 1.8$ for all the range of temperature, the predicted fraction conversion agrees well only when the temperature is lower than 693K, as shown in Figure 5. However, the tendency of the fractional conversion (X) is asymptotic to unity. Indeed, the asymptotic fractional conversion occurred at about 780K. Obviously, we should use the reaction orders 1.8 and 1.5 to predict the fractional conversion for the temperature range $T < 420^\circ\text{C}$ and $T \geq 420^\circ\text{C}$, respectively, as presented in Figure 7. At the end of the pyrolysis process the inside temperature of the examined material quickly increased due to the exothermic phenomena of the chemical reaction caused when the reaction order was decreased. From this Figure, the root mean square error (RMSE) of the prediction is 0.024.

Conclusions

The pyrolysis of the cylindrical cassava rhizome using flue gas under a non-isothermal condition in the lab-scale metal kiln was conducted. It can be concluded that the important finding of the study is that the cylindrical cassava rhizome was a good material to be an alternative energy source. From the pyrolysis process, the mass loss slightly decreases when the temperature is lower than 150°C, which is the drying process. Then, the mass loss started when the pyrolysis

temperature was higher than 250°C. After that, the temperature was rapidly increased leading to a dramatic increase in the mass loss until the end of mass loss when the pyrolysis process was completed at a temperature about 500°C. The obtained charcoal yield was 25.49% by weight

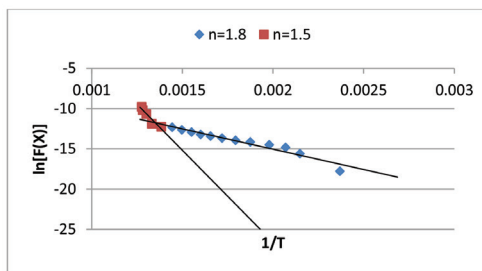


Figure 5. Relation of $\ln[F(X)]$ and $1/T$ for cassava rhizome at 14°C/min heating rate

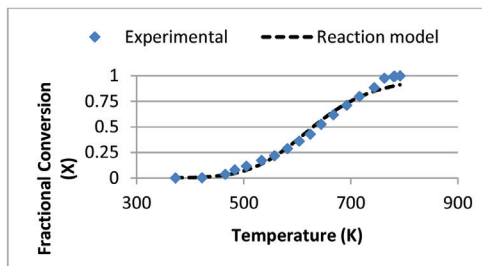


Figure 6. Comparison of experimental and predicted fractional conversions for pyrolysis of cassava rhizome using flue gas: reaction order $n = 1.8$

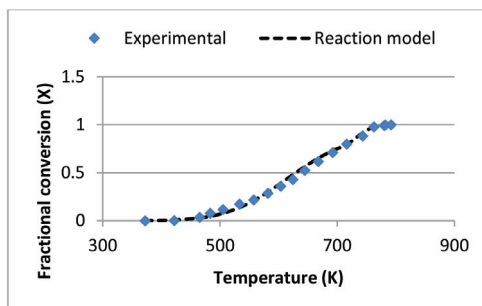


Figure 7. Comparison of experimental and predicted fractional conversions for pyrolysis of cassava rhizome using flue gas: reaction order $n = 1.8$ ($T < 693\text{ K}$) and $n = 1.5$ ($T \geq 693\text{ K}$)

at the pyrolysis temperature of about 500°C. From the experimental data, the obtained reaction orders of the cylindrical cassava rhizome were 1.8 and 1.5 for $T < 420^{\circ}\text{C}$ and $T \geq 420^{\circ}\text{C}$, respectively. Therefore, the fraction conversion (X) could be predicted by the RMSE of the prediction and experiment which was less than 0.024.

Acknowledgements

The authors would like to deeply acknowledge the National Science and Technology Development Agency (NSTDA) for the scholarship. Especially, the authors wish to thank the Department of Mechanical Engineering, Faculty of Engineering and Architecture, Rajamangala University of Technology Isan, Nakhon Ratchasima for support with tools and equipment.

References

- Biomass One-stop Clearing House, Energy for Environment Foundation. (2006). Biomass. Q Print Management Co. Ltd., Bangkok, Thailand.
- Coats, A.W. and Redfern, J.P. (1964). Kinetic parameters from thermogravimetric data. *Nature*, 201:68-69.
- Demirbas, A. (2001). Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energ. Convers. Manage.*, 42:1229-1238.
- Ebrahimi-Kahrizsangi, R. and Abbasi, M.H. (2008). Evaluation of reliability of Coats-Redfern method for kinetic analysis of non-isothermal TGA. *Trans. Nonferrous Met. Soc. China*, 18:217-221.
- Homchat, K. and Sucharitakul, T. (2011). The experimental study on pyrolysis of cassava rhizome utilizing flue gas. *Energy Procedia*, 9:264-273.
- Larfeldt, J., Leckner, B., and Melaaen, M.C. (2000). Modelling and measurements of the pyrolysis of large wood particles. *Fuel*, 79:1,637-1,643.
- Min, F., Zhang, M., and Chen, Q. (2007). Non-isothermal kinetics of pyrolysis of three kinds of fresh biomass. *Journal of China University of Mining & Technology*, 17:105-111.
- Office of Agricultural Economics. Available from: <http://oae.go.th/yearbook/2000-01>. Accessed date :
- Shafizadeh, F. (1982). Chemistry of pyrolysis and combustion of wood. In: *Progress in Biomass Conversion*, Vol. 3. Sarkanen, K.V., Tillman, D.A., and Jahns, E.C., (eds). Academic Press, London, UK, p. 51-76.
- Sharma, A. and Rao, T.R. (1999). Kinetics of pyrolysis of rice husk. *Bioresource Technol.*, 67:53-59.
- Soltes, E.J. (1983). Thermochemical routes to chemicals, fuels and energy from forestry and agricultural residues. In: *Biomass Utilization*. Cote, W.A. (ed.). Nato ASI Series A:67, Plenum Press, NY, USA, p. 537-552.
- Strub, A. (1984). The commission of the European Communities R and D programme 'Energy from biomass'. In: *Thermochemical Processing Biomass*. Bridgwater, A.V., (ed.). Butterworth, London, UK, p. 1-10.
- Vlaev, L.T., Markovska, I.G., and Lyubchev, L.A. (2003). Non-isothermal kinetics of pyrolysis of rice husk. *Thermochim. Acta*, 406:1-7.
- Warb, R.F. (1983). Food, chemical feedstocks and energy from biomass. In: *Biomass Utilization*. Cote, W.A. (ed.). Nato ASI Series A:67, Plenum Press, NY, USA, p. 23-49.
- Zabaniotou, A. and Ioannidou, O. (2008). Evaluation of utilization of corn stalks for energy and carbon material production by using rapid pyrolysis at high temperature. *Fuel*, 87:834-843.
- Zhang, L., Xu, C., and Champagne, P. (2010). Overview of recent advances in thermo-chemical conversion of biomass. *Energ. Convers. Manage.*, 51:969-982.

