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TG Characterization of Pyrolysis of Cassava Starch Residues Catalyzed by Ferric Sulfate

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Abstract

By using thermogravimetric analysis, the catalytic effect of ferric sulfate on the pyrolysis of residues from the cassava starch industry was studied. Thermogravimetric data were adjusted to the distributed activation energy model (DAEM) with two pseudo components. Calculated values for kinetic parameters of residues pyrolysis are into the reported range for other types of biomass. Ferric sulfate had a strong influence on the decomposition parameters of the second pseudocomponent of the DAEM, which is identified as lignin.

Keywords: Biomass pyrolysis, Cassava industrial waste, Ferric sulfate, Thermogravimetric analysis

1 Introduction

After rice, corn, and wheat, cassava is the most important agricultural product in the world, especially in tropical regions, where is an important food source for humans and animals. Also, the cassava starch is raw material for several food industry companies [19]. Considering global warming and world population growth, cassava can be used as an alternative for food security due to the high efficiency of the production [13]. A side effect, related to the increase of the cassava consumption is the growth of the waste generated in the industrial processing. The main residue is the cassava hull, with a production of fourteen millions of tons per year [1]. Several alternatives for the usage of this waste has been proposed, including animal feeding, adsorbent as a raw material of activated carbon production, energetic uses by a thermal process as pyrolysis, gasification and bioethanol production [13, 28]. Among those, pyrolysis is an excellent option due to the possibility of the production of liquid fuels [5, 10].

For the study of pyrolysis kinetics, thermogravimetric analysis (TGA) is one of the most widely used techniques. The behavior of several kinds of biomass by this method has been described extensively in previous studies due to TGA allows identifying the kinetic parameters of the pyrolysis process. Some studies of cassava industrial waste (CIW) pyrolysis has been made, including the use of fixed bed tubular reactors[10, 26], fluidized bed reactors [15, 17], free fall reactors [16] and TGA [25, 28].

The effect of the addition of metallic salts in the pyrolysis process also has been of interest for several scientific researchers: copper and iron salts as additives in wood pyrolysis [8], iron in fast pyrolysis of cellulose – wood mixtures [7] has been studied. Some others researchers studied the effect of some catalyst on the thermal treatment of biomass [29]. Nevertheless, the effect of iron salts on the products of pyrolysis of CIW has not been previously reported. In this study, pyrolysis of CIW using TGA at several heating rates and the effect of the presence of iron sulfate was studied. Determination of the kinetic parameters and the influence of the iron salt in pyrolysis were obtained.

2 Materials and methods

2.1 Materials

CIW was obtained from starch industries of the municipality of San Juan de Betulia, Sucre department, Colombia. Those were washed with tap water for dirt removal and then rinsed with distilled water. After the washing process, the CIW was dried at 378 K before grinding. Samples between 200 and 400 μm were separated and stored in a desiccator for further use. Ferric sulfate was supplied by Sigma- Aldrich with a purity of 75%.

2.2 Sample preparation

For the CIW impregnated with iron, an aqueous solution of ferric sulfate was prepared. The CIW was added to the solution and the suspension was stirred for two hours. After this time, the sample was dried at 80 C for two hours and additional two hours at 105 C. Two samples were prepared, CIW without catalyst and CIW+1%Fe, which has 1% of iron by mass.

2.3 Characterization

Proximate analysis of CIW was made using ASTM standards: ash content by ASTM D3172, volatile material with ASTM D3175, residual humidity under ASTM D3173 and heat capacity with ASTM 2015. For elemental analysis, ASTM D3177 was employed for sulfur, carbon, and hydrogen analysis with ASTM D3178, nitrogen under ASTM D3179. Oxygen was calculated by difference once carbon, hydrogen, nitrogen, and sulfur were obtained.

2.4 Thermogravimetric analysis (TGA)

TGA was performed using a Thermogravimetric Analyzer TA instruments TGA 2920. Lower detection limit for TGA was 0.1 μg. Control and acquisition of experimental data were made by Universal Analysis software. Linear ramps of 10 and 100 K/min were employed. Purge of the gases was made with helium 5.0.

2.5 Distributed Activation Energy Model

In this model, the mass rate conversion is represented by several numbers of reactions that share the same frequency factor (A_j) with an activation energy distributed in Gaussian form. A media activation energy E_{0j} and a standard deviation of the activation energy represented by σ_j are part of the model represented by Equation 1 [22]:

$$Y^{calc}(t) = -\sum_{j=1}^{M} c_j \frac{dx_j}{dt} \quad (1)$$

where Y^{calc} represents the conversion rate of the sample; M is the number of reactions or pseudo components of the sample; c_j is a proportionality constant, and dx_j/dt is the rate of production or consumption of j [20, 21, 23], which can be calculated as:

$$\frac{dx_j}{dt}(t) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[{\mu_j}^2] \exp[0{,}75{\mu_j}^2] \frac{dX_j(t,\mu_j)}{dt} d\mu_j \quad (2)$$

Where $\mu_j = 2(E - E_{0j})/(\sqrt{2}\,\sigma_j)$, and $X_j(t, \mu_j)$ is the solution for dx_j/dt at time t, and the value of the energy of activation is E. Solution of equation (2) was made using Matlab software as described previously [2].

3 Results

Proximate and ultimate analysis of CIW is shown in Table 1. Obtained data agree with previous studies for cassava waste [24, 28], including heat power [26, 28].

Table 1. Proximate and ultimate analysis of CIW.

Proximate analysis		**Ultimate Analysis**	
Property	**Value**	**Element**	**Value** (%)
Residual humidity (%)	13.74	C	43.21
Ash (% Dry basis)	2.53	H	6.01
Volatile matter (%)	87.48	N	no detected
Fixed carbon (%)	9.99	S	0.06
Heat power (BTU/lb)	7403	O	50.72

3.1 Thermogravimetric analysis

Thermograms of the samples of CIW and CIW+1%Fe at 10 and 100 K/min are showed in figure 1a and the derivate of temperature in the figure 1b. Two main events are present; the first one at temperatures below 453 K, that correspond to the loss of residual humidity of the samples. The second one is present between 473K and 873 K, that belongs to the pyrolysis process. Characteristics of the second event are shown in table 2. For CIW and CIW+1%Fe, an increasing of the heat rate is related with an increase of the weight loss of the samples in the onset and DTG peak temperatures. This behavior is characteristic of a chemical process. In another way, the presence of iron sulfate leads to an increase in the weight loss, a reduction of the onset temperature and an increase of the DTG peak temperature. This behavior suggests that there is a catalytic effect of the iron sulfate represented by the onset temperature reduction, but also causes a retarding effect of the pyrolytic process.

Table 2. Thermal characteristics for the pyrolysis process of CIW

	Pyrolysis weight loss (% dry basis)		Onset Temperature[b] (K)		Peak Temperature[c] (K)	
Heating rate (K/min)	10	100	10	100	10	100
Cassava industrial wastes	72.13	77.91	543.7	564.9	584.4	609.1
Cassava industrial wastes + 1% Fe	74.83	81.45	533.6	558.8	593.7	619.7

[a] Maximum standard deviation 1%; [b] Maximum standard deviation 4 K; [c] Maximum standard deviation 3 K.

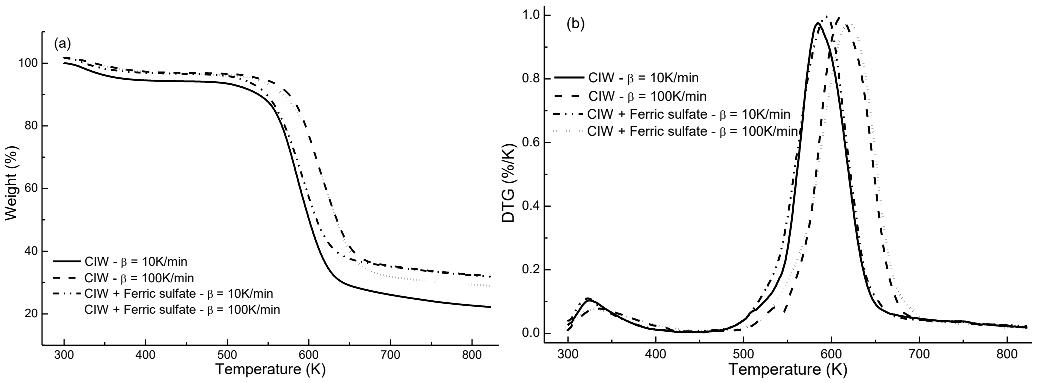

Figure 1. a) TG and b) DTG thermograms of CIW and CIW + 1%Fe heated at 10 and 100 K/min.

Fitting to DAEM model.

Table 3 shows the fitting of the data of conversion rate to the DAEM model with one, two and three pseudo components for the pyrolysis of the CIW with and without iron sulfate. In Figure 2 the fitting with 1 and 3 pseudo components is presented for a heating rate of 10 K/min. Figure 3 shows the fitting using 2 pseudo components in the presence and absence of catalyst at 10 and 100 K/min. In a general way, the DAEM model with two pseudo components represents the data in a proper way and there is no major improvement of the fitting with three pseudo components like in previous studies [4]. For this reason, the DAEM model with two pseudo components was selected for the representation of the experimental data as shown in Figure 3.

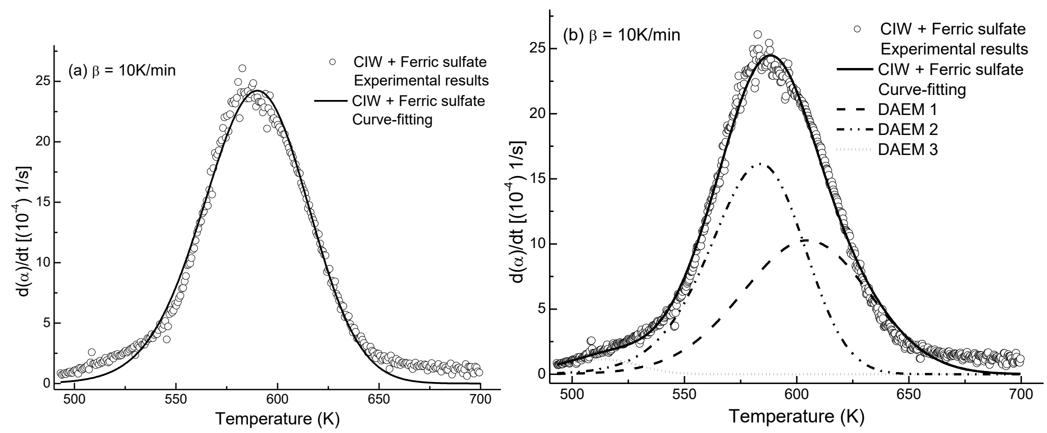

Figure 2. DAEM fitting with a) 1 and b) 3 pseudo components of the pyrolysis of CIW heated at 10 K/min.

Table 3. DAEM parameters with 1, 2, and 3 pseudo components for CIW and CIW + 1% Fe heated at 10 and 100 K/min.

Heating rate (K/min)	10		100	
Sample	Cassava	Cassava + 1 %Fe	Cassava	Cassava + 1 %Fe
1 pseudocomponent				
c_1	1.86E+00	1.91E+00	1.87E+00	1.83E+00
A_1 (1/s)	3.86E+15	3.86E+15	3.86E+15	3.86E+15
E_{01} (kJ/mol)	2.00E+05	2.00E+05	1.97E+05	1.98E+05
σ_1 (kJ/mol)	1.43E+04	1.65E+04	1.43E+04	1.63E+04
SE*	1.00E-04	7.39E-05	6.61E-04	5.70E-04
2 pseudo components				
c_1	1.61E+00	1.41E+00	1.75E+00	1.46E+00
A_1 (1/s)	5.10E+14	5.10E+14	5.10E+14	5.10E+14
E_{01} (kJ/mol)	1.89E+05	1.90E+05	1.87E+05	1.89E+05
σ_1 (kJ/mol)	1.15E+04	1.23E+04	1.23E+04	1.20E+04
c_2	3.96E-01	5.44E-01	2.22E-01	4.60E-01
A_2 (1/s)	4.24E+13	4.24E+13	4.24E+13	4.24E+13
E_{02} (kJ/mol)	1.92E+05	1.79E+05	1.90E+05	1.70E+05
σ_2 (kJ/mol)	3.56E+04	2.74E+04	4.48E+04	3.50E+04
SE*	8.34E-05	4.39E-05	5.17E-04	5.27E-04
3 pseudo components				
c_1	8.66E-01	6.05E-01	1.63E-01	1.30E-01
A_1 (1/s)	2.60E+15	2.60E+15	2.60E+15	2.60E+15
E_{01} (kJ/mol)	2.03E+05	1.99E+05	2.16E+05	2.32E+05
σ_1 (kJ/mol)	1.60E+04	2.68E+04	2.88E+04	3.31E+04
c_2	1.02E+00	1.33E+00	1.79E+00	1.71E+00
A_2 (1/s)	1.87E+14	1.87E+14	1.87E+14	1.87E+14
E_{02} (kJ/mol)	1.83E+05	1.85E+05	1.82E+05	1.84E+05
σ_2 (kJ/mol)	8.63E+03	1.16E+04	1.18E+04	1.23E+04
c_3	4.81E-02	2.55E-02	2.44E-02	1.27E-01
A_3 (1/s)	4.19E+13	4.19E+13	4.19E+13	4.19E+13
E_{03} (kJ/mol)	1.54E+05	1.56E+05	1.46E+05	1.55E+05
σ_3 (kJ/mol)	5.51E+03	9.35E+03	6.67E+03	9.43E+03
SE*	7.51E-05	4.34E-05	5.36E-04	2.20E-04

* Standard error of the adjustment

Values of the activation energy and frequency factor obtained in this work are in the same size order of various biomass previously studied by using DAEM model [3, 4, 6]. For the specific case of cassava, the values of those parameters are in the same order of size compared with other different models [25, 28].

DAEM model results show that the presence of iron sulfate affects mainly the second pseudo component, identified as lignin A, according to the termogram. In the same way, the pseudo first component can be related to cellulose. The presence of iron sulfate reduces the activation energy and the standard deviation of this parameter for the second pseudo component. Previous studies have reported catalytic effects of the ferrous sulfate in the decomposition of lignin in wood pyrolysis[8]. This effect could explain the reduction of the onset temperature for the pyrolytic process of CIW, because the reduction of the activation energy influences the increase of the decomposition rate of this component, making that the pyrolytic process starts at lower temperatures. In another hand, the reduction of the standard deviation of the activation energy of the second pseudo component has an effect that the pyrolytic process of this component has a narrow temperature range, making the effect of the conversion rate for this pseudo component more significant in the temperature range of the main pyrolytic event. The presence of ferric sulfate is related to an increase of the DTG peak of the cellulose because the peak of the second pseudo component in the pyrolytic process is higher than the cellulose for the CIW. This explains the observed behavior of the onset temperature and the DTG peak in presence of the catalyst.

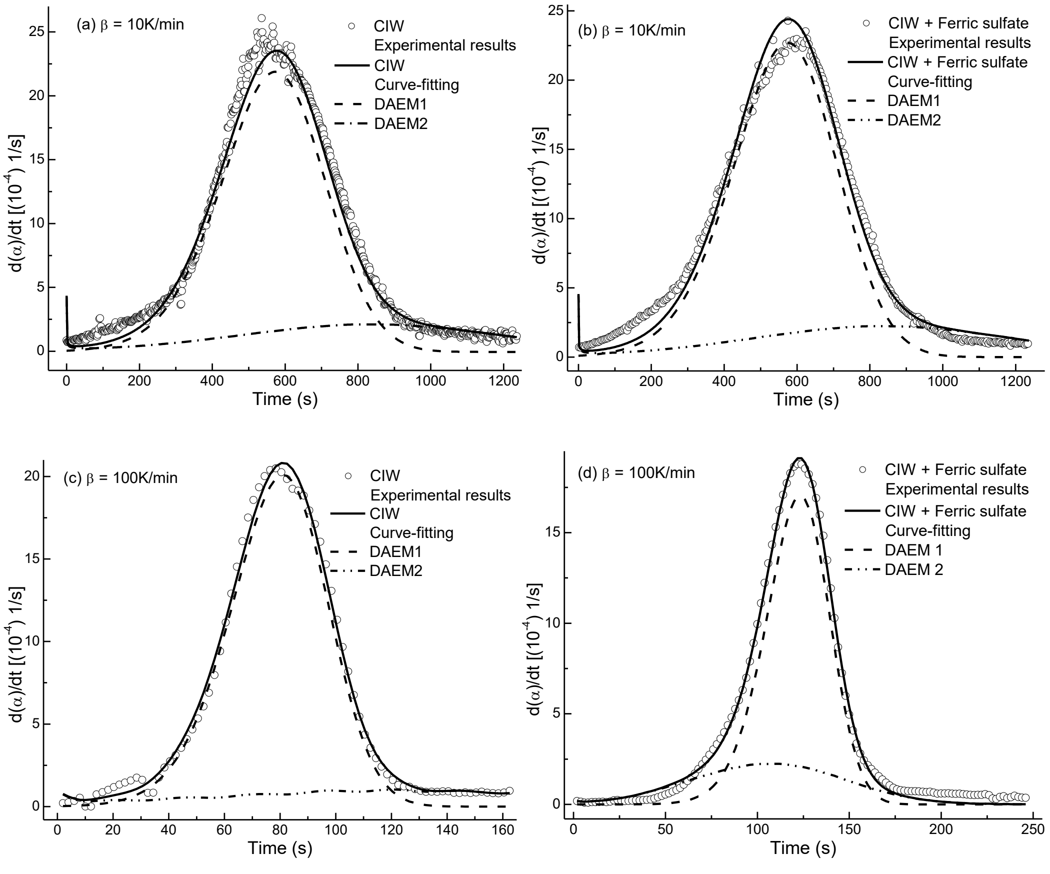

Figure 3. Fitting of DAEM with 2 pseudo components of a) CIW heated at 10 K/min; b) CIW + 1% Fe heated at 10 K/min; c) CIW heated at 100 K/min; and d) CIW + 1% Fe heated at 100 K/min.

4. Conclusions

The effect of the ferric sulfate over the pyrolysis process of CIW using TGA was made. Kinetic analysis was performed using the DAEM model using two pseudo components for the data of TG data. Fitting parameters shows that the catalyst employed affect mainly the lignin pyrolysis of the CIW.

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References

[1] A. Adekunle, V. Orsat, V. Raghavan, Lignocellulosic bioethanol: A review and design conceptualization study of production from cassava peels, *Renew. Sustain. Energy Rev.,* **64** (2016), 518-530. https://doi.org/10.1016/j.rser.2016.06.064

[2] A. Albis, E. Ortiz, A. Suárez, I. Piñeres, TG/MS study of the thermal devolatization of Copoazú peels (Theobroma grandiflorum), *J. Therm. Anal. Calorim.,* **115** (2013), 275-283. https://doi.org/10.1007/s10973-013-3227-8

[3] J. Cai and L. Ji, Pattern search method for determination of DAEM kinetic parameters from nonisothermal TGA data of biomass, *J. Math. Chem.,* **42** (2007), 547-553. https://doi.org/10.1007/s10910-006-9130-9

[4] J. Cai, W. Wu, R. Liu, An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass, *Renew. Sustain. Energy Rev.,* **36** (2014), 236-246. https://doi.org/10.1016/j.rser.2014.04.052

[5] J. Corton, I.S. Donnison, M. Patel, L. Bühle, E. Hodgson, M. Wachendorf, A. Bridgwater, G. Allison, M.D. Fraser, Expanding the biomass resource: sustainable oil production via fast pyrolysis of low input high diversity biomass and the potential integration of thermochemical and biological conversion routes, *Applied Energy,* **177** (2016), 852-862. https://doi.org/10.1016/j.apenergy.2016.05.088

[6] T. Chen, J. Zhang, J. Wu, Kinetic and energy production analysis of pyrolysis of lignocellulosic biomass using a three-parallel Gaussian reaction model, *Bioresour. Technol.,* **211** (2016), 502-508. https://doi.org/10.1016/j.biortech.2016.03.091

[7] G. Dobele, G. Rossinskaja, T. Dizhbite, G. Telysheva, D. Meier, O. Faix, Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis, J. *Anal. Appl. Pyrolysis,* **74** (2005), 401-405. https://doi.org/10.1016/j.jaap.2004.11.031

[8] L. Edye, G. N. Richards, G. Zheng, Transition metals as catalysts for pyro-

lysis and gasification of biomass, in *ACS Symposium Series*, Vol. 515, ACS Publications, 1992. https://doi.org/10.1021/bk-1992-0515.ch008

[9] K. Jayaraman, M. Kok, I. Gokalp, Combustion properties and kinetics of different biomass samples using TG–MS technique, *J. Therm. Anal. Calorim.*, **127** (2017), 1361-1370. https://doi.org/10.1007/s10973-016-6042-1

[10] O. L. Ki, A. Kurniawan, C. Lin, Yi-Hsu Ju, S. Ismadji, Bio-oil from cassava peel: a potential renewable energy source, *Bioresour. Technol.,* **145** (2013), 157-161. https://doi.org/10.1016/j.biortech.2013.01.122

[11] A. Malika, N. Jacques, El Fallah Jaafar, B. Fatima, A. Mohammed, Pyrolysis investigation of food wastes by TG-MS-DSC technique, *Biomass Conversion and Biorefinery*, **6** (2016), 161-172. https://doi.org/10.1007/s13399-015-0171-9

[12] A. Meng, H. Zhou, L. Qin, Y. Zhang, Q. Li, Quantitative and kinetic TG-FTIR investigation on three kinds of biomass pyrolysis, *J. Anal. Appl. Pyrolysis*, **104** (2013), 28-37. https://doi.org/10.1016/j.jaap.2013.09.013

[13] S. Mombo, C. Dumat, M. Shahid, E. Schreck, A socio-scientific analysis of the environmental and health benefits as well as potential risks of cassava production and consumption, *Environmental Science and Pollution Research*, **24** (2016), 1-15. https://doi.org/10.1007/s11356-016-8190-z

[14] G. Özsin and A. E. Pütün, Kinetics and evolved gas analysis for pyrolysis of food processing wastes using TGA/MS/FT-IR, *Waste Management,* **64** (2017), 315-326. https://doi.org/10.1016/j.wasman.2017.03.020

[15] A. Pattiya, James O. Titiloye and Anthony V. Bridgwater, Fast pyrolysis of agricultural residues from cassava plantation for bio-oil production, *Carbon,* **51** (2009), 51.59.

[16] A. Pattiya, S. Sukkasi, V. Goodwin, Fast pyrolysis of sugarcane and cassava residues in a free-fall reactor, *Energy*, **44** (2012), 1067-1077. https://doi.org/10.1016/j.energy.2012.04.035

[17] A. Pattiya and S. Suttibak, Production of bio-oil via fast pyrolysis of agricultural residues from cassava plantations in a fluidised-bed reactor with a hot vapour filtration unit, *J. Anal. Appl. Pyrolysis,* **95** (2012), 227-235. https://doi.org/10.1016/j.jaap.2012.02.010

[18] S. Polat, Esin Apaydin-Varol, Ayşe Eren Pütün, Thermal decomposition behavior of tobacco stem Part I: TGA–FTIR–MS analysis, *Energy Sources,*

Part A: Recovery, Utilization, and Environmental Effects, **38** (2016), 3065-3072. https://doi.org/10.1080/15567036.2015.1129373

[19] N. J. Tonukari, Cassava and the future of starch, *Electronic Journal of Biotechnology,* **7** (2004), 5-8. https://doi.org/10.2225/vol7-issue1-fulltext-9

[20] G. Varhegyi, M. Antal, E. Jakab, P. Szabó, Kinetic modeling of biomass pyrolysis, *J. Anal. Appl. Pyrolysis,* **42** (1997), 73-87. https://doi.org/10.1016/s0165-2370(96)00971-0

[21] G. Várhegyi, P. Szabó, F. Till, B. Zelei, M. Antal, X. Dai, TG, TG-MS, and FTIR characterization of high-yield biomass charcoals, *Energy & Fuels,* **12** (1998), 969-974. https://doi.org/10.1021/ef9800359

[22] G. Várhegyi, P. Szabó, M. Antal, Kinetics of charcoal devolatilization, *Energy & Fuels,* **16** (2002), 724-731. https://doi.org/10.1021/ef010227v

[23] G. Várhegyi, Z. Czégény, E. Jakab, K. McAdam, C. Liu, Tobacco pyrolysis. Kinetic evaluation of thermogravimetric–mass spectrometric experiments, *J. Anal. Appl. Pyrolysis,* **86** (2009), 310-322. https://doi.org/10.1016/j.jaap.2009.08.008

[24] J. P. S. Veiga, T. Valle, J. Feltran, W. Bizzo, Characterization and productivity of cassava waste and its use as an energy source, *Renew. Energy,* **93** (2016), 691-699. https://doi.org/10.1016/j.renene.2016.02.078

[25] P. Weerachanchai, C. Tangsathitkulchai, M. Tangsathitkulchai, Comparison of pyrolysis kinetic models for thermogravimetric analysis of biomass, *Suranaree Journal of Science & Technology,* **17** (2010), 387-400.

[26] P. Weerachanchai, C. Tangsathitkulchai, M. Tangsathitkulchai, Characterization of products from slow pyrolysis of palm kernel cake and cassava pulp residue, *Korean Journal of Chemical Engineering,* **28** (2011), 2262-2274. https://doi.org/10.1007/s11814-011-0116-3

[27] X. Yao, K. Xu, Yu Liang, Analytical Pyrolysis Study of Peanut Shells using TG-MS Technique and Characterization for the Waste Peanut Shell Ash, *Journal of Residuals Science & Technology,* **13** (2016), 295-305. https://doi.org/10.12783/issn.1544-8053/13/4/7

[28] E. R. Zanatta, T. Reinehr, J. Awadallak, S. Kleinübing, J. dos Santos, R. Bariccatti, P. Arroyo, E. da Silva, Kinetic studies of thermal decomposition of sugarcane bagasse and cassava bagasse, *J. Therm. Anal. Calorim.,* **125** (2016), 437-445. https://doi.org/10.1007/s10973-016-5378-x

[29] C.-H. Zhou, Xi Xia, Chun-Xiang Lin, Dong-Shen Tong, Jorge Beltramini, Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, *Chem. Soc. Rev.*, **40** (2011), 5588-5617. https://doi.org/10.1039/c1cs15124j

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