Biofuel from Rice Husk Pyrolysis: Effect of Temperature to Pyrolysis Oil and Its Kinetic Study

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ABSTRACT: *Rice husk is counted as an agricultural waste that results in environmental problems during its handling. In this work, rice husk was used as raw material for producing liquid biofuel (pyrolysis oil) via pyrolysis. The pyrolysis reaction was carried out at temperatures of 450, 500, and 550 °C for 1 hour. The pyrolysis oil was collected and weighted for every 10 minutes. The results showed that the increase in pyrolysis temperature caused the yield of pyrolysis oil to increase. The properties in the term of heating value also increased while viscosity and density of pyrolysis oil decreased. These properties were almost similar to diesel oil with a slightly lower heating value. The proposed model using the single reaction model and two stages model were fit to represent the mechanism of rice husk pyrolysis reaction in this study. However, the results of two stages model gave a lower error than those of the single reaction model. Furthermore, the rate of pyrolysis reaction at various temperatures could be determined using the kinetic data obtained from the developed model. This information would be useful for designing the pyrolysis reactor especially for producing biofuel (pyrolysis oil) from the rice husk.*

KEYWORDS: *Rice husk; Pyrolysis; Pyrolysis oil; Temperature; Kinetics.*

INTRODUCTION

The shortage of fossil fuel deposit has turned the attention to utilize renewable energy sources as the substitution of fossil fuel. One of the potential sources of renewable energy is biomass. Besides its abundant and sustainable sources, the utilization of biomass as biofuel performs zero net CO_2 emissions in the atmosphere so it does not contribute to the greenhouse effect [1].

Maize, rice and wheat are the world's three biggest food crops those provide more than 42% of all calories consumed by the total world population [2]. The world rice production in 2017 was 486.153 million tons and it significantly increased to 486.262 million tons in 2018 [3]. The growth of rice production was followed by the increase of the waste from the rice milling process. As reported in the previous research, the waste in the form of rice husk reached 23% of the total rice produced [4].

Biomass (including rice husk) that consist of carbon (C), hydrogen (H) and oxygen (O) compounds can be converted to biofuel via pyrolysis. Pyrolysis is a thermal decomposition of organic components in the biomass at high temperature in the conditions without oxygen to obtain products in the form of char (solid), pyrolysis oil (liquid) and gas [5,6]. Putun et al. [7] found that the yield and chemical composition of pyrolysis products were

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strongly influenced by the temperature, reactor configuration, type of biomass, catalyst and heating rate. The world biggest commercial plant was Dynamotive in Canada that processed 8 tons/h of lignocellulosic woody biomass into approximately 70-75% of it into pyrolysis oil [8].

Understanding the reaction mechanism during pyrolysis through the kinetic study will be useful for predicting biomass behavior, furthermore in designing appropiate reactor [9]. In many previous research, data from ThermoGravimetry Analysis (TGA) using TGA analyzer were used to determine the kinetics of biomass pyrolysis [9,10,11]. TGA method investigates the change in the weight of small sample of biomass with respect to the change in the temperature [12,13]. In other words, the TGA method records the biomass decomposition due to the increase of temperature. In comparison to the previous works those based on the TGA data, the present study was using the different data that was the formation rates of the pyrolysis products. In this study, the collected liquid product data resulted from the rice husk pyrolysis were used for measuring the kinetics. Moreover, its kinetic parameters were determined to understand about the rice husk pyrolysis mechanism. This result further would be advantageous in pyrolysis reactor design and its operating condition, especially for producing biofuel from the rice husk.

EXPERIMENTAL SECTION

Materials and Method

Rice husk was obtained from the local farmer at Tanjung Selor village, Banjar district, South Kalimantan, Indonesia. It was grinded and sieved to the size of 0.25-1 mm to homogenize the sample. The rice husk powder was dried in an oven. Then, this sample was characterized using proximate and ultimate analysis. The heating value of rice husk also be measured using bomb calorimeter. The rice husk characteristics are presented in Table 1.

Table 1: Characteristics of Rice Husk.

Analysis		Value
Proximate analysis (dry base,% weight)	Volatile matter	76.36
	Ash content	8.29
	Fixed carbon	15.35
Ultimate analysis (dry and ash free,% weight)	Carbon	34.40
	Hydrogen	5.07
	Nitrogen	0.35
	Oxygen	37.28
	Sulfur	0.04
	Ash	22.86
Heating value (MJ/kg)		15.48

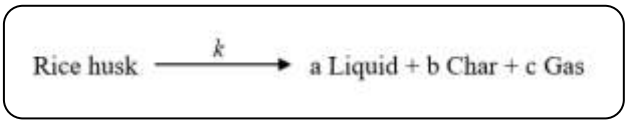

Fig. 1: Single Reaction Mechanism.

Pyrolysis Reaction

Pyrolysis reaction was investigated in a stainless steel tubular reactor with 16 cm of diameter and 25 cm of height. For every run, 500 gram of rice husk powder was used. This sample was heated up to 450, 500, and 550 °C at the heating rate of 8 ^{0}C/min and hold at that temperature for 1 hour. The vapor that produced from the reactor was flown through the connecting pipe and condensed through the condensor then the result was collected as pyrolysis oil in the flask that put on the balance for measuring the weight during the reaction. The weight was recorded for every 10 minutes. This data was used to determine the kinetics of pyrolysis reaction. When the reaction was completed (1 hour), the reactor was cooled down to room temperature so it could be opened to collect the char (solid product). The yields of product were obtained from the weight percentage of liquid, gas and char products to the total weight of rice husk used for every reaction. Furthermore, the pyrolysis oil was separated from its aqueous phase (contain much water) to get the organic phase that would be analyzed to measure its physical properties such as: heating value, viscosity and density.

Reaction Kinetics Model

The rice husk pyrolysis reaction kinetics model in this study was developed using a single reaction mechanism and a modification of a single reaction mechanism that called the two stages mechanism. The single reaction mechanism assumes the rice husk cracking will produce liquid, gas and solid products simultaneously, as can be seen in Fig. 1.

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{1}$$

$$0 - 0 - k.m_{rh} = \frac{dm_{rh}}{dt}$$

$$\frac{dm_{rh}}{dt} = -k.m_{rh}$$

Mass Balance of Liquid product (l):

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{2}$$

$$0 - 0 + a.k.m_{rh} = \frac{dm_l}{dt}$$

$$\frac{dm_l}{dt} = a.k.m_{rh}$$

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{3}$$

$$0 - 0 + b.k.m_{rh} = \frac{dm_s}{dt}$$

$$\frac{dm_s}{dt} = b.k.m_{rh}$$

Mass Balance of Gas product (g):

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{4}$$

$$0 - 0 + c.k.m_{rh} = \frac{dm_g}{dt}$$

$$\frac{dm_g}{dt} = c.k.m_{rh}$$

The two stages mechanism assumes the gas product will resulted from both, the rice husk decomposition to liquid and solid product and then followed by re-cracking of the liquid product into gas product [14]. In other words, during pyrolysis reaction, rice husk will decompose into liquid and solid (char) and then followed by gas production from the liquid product decomposition. The assumption used for this model is that the rice husk will decompose into liquid and solid with the reaction rate (k_1). Then the liquid will further decompose into gas with the other reaction rate (k_2) as presented in Fig. 2.

The rate of decomposition of rice husk and rate of formation of liquid, solid and gas was obtained by overall mass balance and each component.

Mass Balance of Rice Husk (rh):

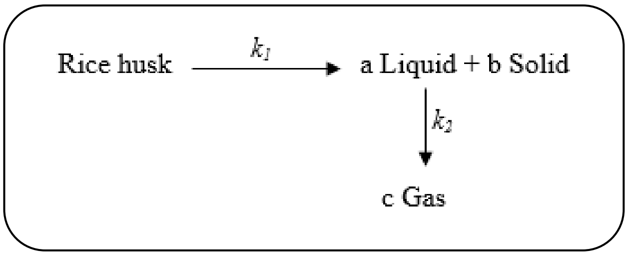

Fig. 2: Two Stages Mechanism.

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{5}$$

$$0 - 0 - k_1.m_{rh} = \frac{dm_{rh}}{dt}$$

$$\frac{dm_{rh}}{dt} = -k_1.m_{rh}$$

Mass Balance of Liquid product (l):

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{6}$$

$$0 - 0 + a.k_1.m_{rh} - \frac{c}{a}k_2.m_l$$

$$\frac{dm_l}{dt} = a.k_1.m_{rh} - \frac{c}{a}k_2.m_l$$

Mass Balance of Solid product (s):

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{7}$$

$$0 - 0 + b.k_1.m_{rh} = \frac{dm_s}{dt}$$

$$\frac{dm_s}{dt} = b.k_1.m_{rh}$$

Mass Balance of Gas product (g):

$$R_{input} - R_{output} - R_{reaction} = R_{accumulation} \tag{8}$$

$$0 - 0 + \frac{c}{a}k_2.m_l = \frac{dm_g}{dt}$$

$$\frac{dm_g}{dt} = \frac{c}{a}k_2.m_l$$

The values of k, k_1, k_2, a, b and c were evaluated by trial and error method using Matlab software until a minimum Sum of Square Error (SSE) is obtained:

$$SSE = \sum\left(m_{l_{calc}} - m_{l_{exp}}\right)^2 \tag{9}$$

To validate the values obtained, the following equation was applied.

$$\%\text{Error} = \sum\left|\frac{m_{l_{exp}} - m_{l_{calc}}}{m_{l_{exp}}}\right| \qquad (10)$$

Where calc = calculation (simulation) and exp = experiment

RESULTS AND DISCUSSION

Effect of Temperature on The Product Yield

This work presents the pyrolysis of rice husk produced three products (i.e. solids (char), liquid (pyrolysis oil) and gas those are presented in the form of their yields . The composition of each product was vary depends on the temperature, the same trend also observed by *Heo et al.* [15]. Among the pyrolysis products, pyrolysis oil is the main product desired. Effect of the temperature on the liquid yield can be seen in Fig. 3. It can be seen that the increase of pyrolysis temperature, resulted in the increase of liquid product as also discovered by *Shah et al.* [16]. In contrast, the solid (char) product was decline by the increasing of pyrolysis temperature. The previous research [17-19] also showed the same results.

This result implies that the decomposition of rice husk is much more occurred at high temperatures. At low temperatures the decomposition of rice husk could not be completely occured, so that the yields of char were high. On the other hand, at higher temperature, more rice husk being converted into liquid then gas and secondary decomposition of char also possibly occured [20], so that the char will decrease.

Effect of Temperature on Pyrolysis Oil Properties

Table 2 presents the increase of temperature resulted in lowering density and viscosity. This implies that the decomposition reaction during pyrolysis tends to produce more water via dehydration and cracking reaction. The dehydration reaction released water as the product while cracking reaction broke the heavy compounds in the rice husk into the lighter ones these contributed to lowering density and viscosity of the liquid products. Bakar and Titiloye [21] who measured the water content of pyrolysis liquid products confirmed these study results. Furthermore, the heating value increased significantly as the temperature increased. This result indicates that more hydrocarbon compounds (C and H compounds) those were formed during biomass (C, H, and O compounds) decomposition were produced in the liquid product. In addition, during pyrolysis reaction, it is possible that oxygen in rice husk was released in the form of water (H_2O) and gas (CO_2, CO), that also contributed to the rise of the heating value, as the oxygen content reduce the heating value [8].

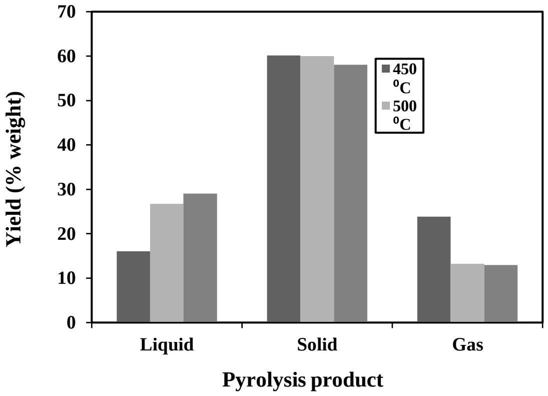

Fig. 3: The composition of rice husk pyrolysis product at different temperature.

Table 2 also indicates that the properties of pyrolysis oil from rice husk pyrolysis in this study comparable to diesel oil, however, the heating value slighly lower than gasoline possibly due to oxygen compounds those still contained in the pyrolysis oil as concluded by *Bridgwater* [8].

The Kinetic Study of Rice Husk Pyrolysis

The suitability of the kinetic model with the experimental data was tested using the Matlab software, by minimizing the value of the Sum of Square Error (SSE) to get the kinetic parameter (i.e the reaction rate constant (k)). As mentioned in the methodology section, the kinetic models used were a single reaction model and a two stages model. The mass of liquid product collected from the pyrolysis experiments at various time was compared to the mass of liquid product calculated from the model. The mass of model was calculated using the kinetic parameters those have been previously obtained. The relation of liquid mass (experiment and model) with respect to the time at temperatures of 450℃, 500℃ and 550℃ is shown in Fig. 4.

In general, a single reaction model was used to represent the simple pyrolysis mechanism [22]. In this present study a single reaction model and a two stages model were applied. Furthermore, the suitability of the model was determined by using Eq.(10) in the methodology section and the results are listed in Table 3.

Table 2: The Physical Properties of Pyrolysis Oil.

Temperature (°C)	Density (20°C) (g/cm^3)	Kinematic viscosity (40°) (mm^2/s)	Heating value (MJ/kg)
450	0.96	6.05	38.84
500	0.90	5.61	39.39
550	0.89	3.42	39.94
Fossil fuel			
Gasoline	0.75	0.75	42.84
Diesel oil	0.83	2.5-3.5	45.50

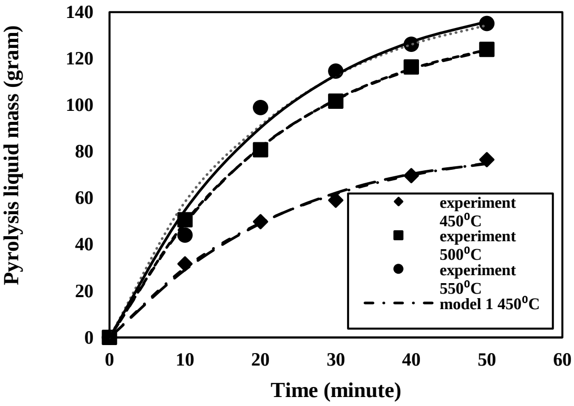

Fig. 4: The Comparison of Liquid Mass Product (Experiment and Model) at 450 ℃, 500 ℃, 550 ℃

From Fig. 4 and Table 3, it can be seen that the calculation data (model) for both model have a trend that approach experimental data with the total average error of single reaction model and two stages model were 4.1569 and 3.9463 %, respectively. From this result, it can be concluded that the proposed model is suitable and appropiate with the real pyrolysis reaction. Thus the single reaction model and two-stages model were fit to represent the mechanism of rice husk pyrolysis reaction in this study. However, the two stages model resulted lower error than that of the single reaction model. Furthermore, the rate of pyrolysis reaction at various temperature can be determined using the reaction rate constant (k) at 450 °C, 500°C and 550°C obtained from the two-stages model.

To determine the kinetic equation in the pyrolysis of rice husk, the reaction rate constants were assumed to follow the Arrhenius equation [23]:

$$k = A.e^{-\frac{E}{RT}} \qquad (11)$$

The kinetics parameters of the pre-exponential factor (A) and activation energy (E) were resulted from the linearization of the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \qquad (12)$$

The plotting of ln k versus 1/T for each reaction can be seen in Fig. 5.

The second stages model involves 2 reaction rate constants, k_1 which is the rate constant of the formation of liquid and solid from the rice husk decomposition and k_2 which is the rate constant of the gas formation reaction from the liquid formed (see Fig. 2). From the linearization of equation in Fig. 5, the value of A was obtained by the calculation of the intercept and the value of E is obtained by the calculation of the slope. The values of A for k_1 and k_2 were 8582,667 min^{-1} and 3,5131 min^{-1}, respectively. Whereas the E values obtained were 81.8281 kJ/mol and 13.7746 kJ/mol for k_1 and k_2, respectively. Thus, the reaction rate constant (k) can be formulated as follows:

$$k_1 = 8582,667 e^{-\frac{81,8281}{RT}} \quad ; \quad k_2 = 3,5131 e^{-\frac{13,7746}{RT}}$$

with T in Kelvin and R is ideal gas constant.

From these results, it is revealed that the activation energy of liquid and solid formation from the rice husk decomposition is greater than that of gas formation from the liquid product. It indicates that the decomposition of liquid into gas (with k_2) is easier to occur than decomposition of rice husk into liquid and solid (k_1). All material has energy stored in its molecular structures and those molecules are linked by bonds with a specific energy that holds them together. When the temperature increased, the dissociation energy for breaking the bonds also increased, this is in agreement with *Zadgaonkar* [24]. Moreover, the molecular chain bonds of rice husk (solid)

Table 3: The Calculated Error of Experimental Data and Model Data for Single Reaction Model and Two Stages Model.

Temperature (ºC)	The mass of pyrolisis liquid data (gram)	The mass of pyrolisis liquid for single reaction model (gram)	The mass of pyrolisis liquid for two stages model (gram)	The error of single reaction model (%)	The error of two stages model (%)
450	31.74	29.9445	29.0732	5.6569	8.4020
	49.77	49.2823	49.0346	0.9799	1.4776
	59.03	61.7703	62.1998	4.6422	5.3698
	69.62	69.8349	70.328	0.3087	1.0169
	76.46	75.043	74.7533	1.8533	2.2321
Average error (%)				2.6882	3.6997
500	50.68	48.9536	50.68	3.4065	2.2214
	80.77	81.8536	80.77	1.3416	1.1406
	101.71	102.225	101.71	0.5063	0.6696
	116.42	115.2341	116.42	1.0186	0.7210
	123.94	123.5417	123.94	0.3214	0.0804
Average error (%)				1.3189	0.9666
550	44.07	58.3103	54.7361	32.3129	24.2026
	98.87	91.165	90.202	7.7931	8.7671
	114.59	112.7394	112.9227	1.5892	1.4550
	126.17	126.0936	127.2168	0.0606	0.8297
	135.12	134.3597	135.9428	0.5627	0.6089
Average error (%)				8.4637	7.1727
The total average error (%)				4.1569	3.9463

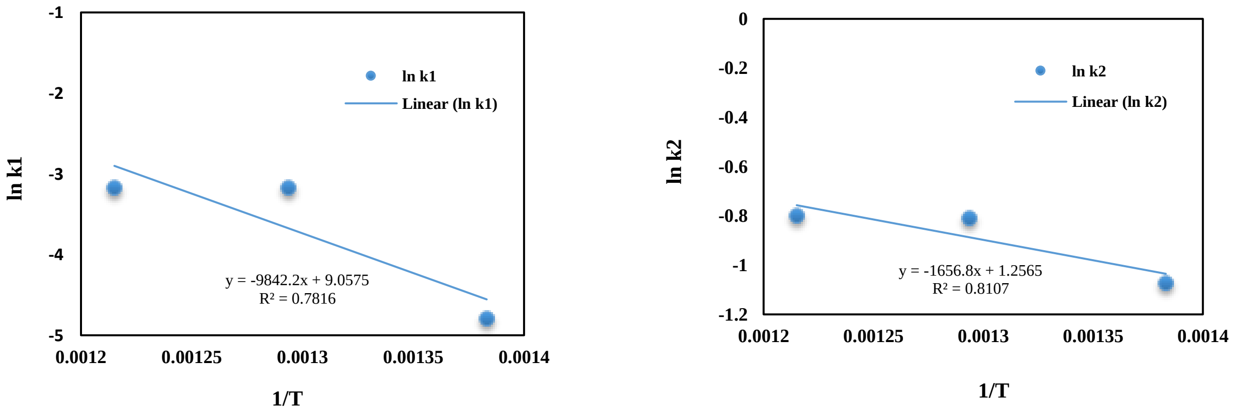

Fig. 5: The Plotting of ln k_1 and ln k_2 vs 1/T.

were stronger than that of liquid, as a result, they required more energy to break them [25]. On the other hand, the chain bonds of fluid are weaker than solid so they were more easily decomposed into small molecules including gas.

The result from the previous research on rice husk pyrolysis [6,9,11,26,27] were in the range of 32 – 222 kJ/mol. They are higher than this study results. *Antal* [28] suggested that the variation in the literatures reflects

Table 4: The Thermodynamic Data of Rice Husk Pyrolysis.

T(K)	k (min^{-1})		ΔH (J/mol)	ΔS (J/K.mol)	ΔG (J/mol)
723	k_1	0.0083	75817.0290	-187.2468	211196.43
	k_2	0.3425	7763.6132	-250.4450	188835.33
773	k_1	0.0420	75401.3290	-181.6430	215811.37
	k_2	0.4452	7347.9132	-250.0529	200638.81
823	k_1	0.0420	74985.6290	-188.5953	230199.57
	k_2	0.4502	6932.2132	-251.5638	213969.19

the complexity of pyrolysis mechanism which cannot be adequately simulated by a simple rate law. It indicates that a number of parameters are involved in the determination of kinetic data of biomass pyrolysis, which should be considered. These parameters include the physical form of the sample, the trace of metal content, and the reactor configuration, including the exact measurement of the sample temperature [10].

Furthermore, the kinetic model can be used to determine the rate of decomposition of rice husk and the rate of formation of pyrolysis products, i.e liquid, solid and gas. Also through this model, the mass of the product as well as the mass of raw materials reduced at a certain temperature and time can be calculated. Thus, the appropriate operating conditions can be designed to obtain the desired of products before carrying out the pyrolysis of rice husks with the same equipment.

The Thermodynamic of Rice Husk Pyrolysis

The thermodynamic properties can be used to determine the characteristics of the pyrolysis reaction. These can be obtained from the relationship between the values of enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) those respect to temperatures. The results are shown in Table 4.

From Table 4, the enthalpy changes are positive, that means the pyrolysis reaction of rice husk was endothermic reaction. Endothermic reactions indicate that heat is needed to perform the reaction. The entropy changes with a negative value indicate a change in particle structures from less to more regular. The changes in Gibbs free energy which were positive shows that the pyrolysis reaction did not take place spontaneously. In general, the reaction takes place spontaneously if the value of ΔG is less than 0. From this thermodynamic results, the characteristic of the pyrolysis of rice husk needs the supply of energy (at high temperature) so that the cracking reaction can occurred, which is indicated by the positive value of enthalpy changes (endothermic reaction) and also the positive value of Gibbs free energy changes (non-spontaneous reaction).

CONCLUSIONS

This work reveals that the yield of pyrolysis oil increased and their properties were improve as the temperature rose. It also indicates that the decomposition of pyrolysis liquid product into gas is easier to occur than the decomposition of rice husk into liquid product and solid product (char).The kinetic data in this study suggest that the single reaction model and two stages model were fit to represent the mechanism of rice husk pyrolysis reaction. However, the error of the two stages model results was lower than that of the single reaction model. Further research for reducing oxygen compounds should be conducted to improve the properties of pyrolysis oil resulted.

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REFERENCES

[1] Ji-Lu Z., Bio-Oil From Fast Pyrolysis of Rice Husk: Yields And Related Properties and Improvement of The Pyrolysis System, *Pyrolysis*, **80**: 30-35 (2007).

[2] Ricepedia, The global staple, http://ricepedia.org/rice-as-food/the-global-staple-rice-consumers. Accessed 28 January (2019).

[3] United State Department of Agriculture (USDA) Economic Research Service, World Rice Supply and Utilization, https://www.ers.usda.gov/data-products/rice-yearbook/rice-yearbook/#World%20Supply,%20Utilization,%20and%20Trade. Accessed on 28 January (2019).

[4] Prasara J., Grant T., "Environmental Impacts of Alternative Uses of Rice Husks for Thailand, Proceeding", *The 6th International Conference on LCA in the Agri-Food Sector*, Zurich, 12-14 November (2008).

[5] Yaman S., Pyrolysis of Biomass to Produce Fuels and Chemical Feedstocks, *Energy Convers. Manage*, **45**: 651-671 (2004).

[6] Braga R.M., Melo D.M.A., Aquino F.M., Freitas J.C.O., Melo M.A.F., Barros J.M.F., and Fontes M.S.B., Characterization and Comparative Study of Pyrolysis Kinetics of The Rice Husk and the Elephant Grass, *J. Therm. Anal. Calorim*, **155**: 1915-1920 (2014).

[7] Pütün E., Uzun B.B., and Pütün A.E., Fixed-Bed Catalytic Pyrolysis of Cotton-Seed Cake: Effects of Pyrolysis Temperature, Natural Zeolite Content and Sweeping Gas Flow Rate, *Bioresour. Technol*, **97**: 701-710 (2006).

[8] Bridgwater A.V., Review of Fast Pyrolysis of Biomass and Product Upgrading, *Biomass Bioenergy*, **38**: 68-94 (2012).

[9] Sonobe T. and Worasuwannarak N., Kinetic Analysis of Biomass Pyrolysis Using the Distributed Activation Energy Model, *Fuel*, **87**: 414-421 (2008).

[10] Williams P.T., Besler S., The Pyrolysis of Rice Husks in a Thermogravimetric Analyser and Static Batch Reactor, *Fuel*, **72**: 151-159 (1993).

[11] Zhang S., Dong Q., Zhang L., Xiong Y., Effects of Water Washing and Torrefaction on the Pyrolysis Behavior and Kinetic of Rice Husk Through TGA and Py-GC/MS, *Bioresour. Technol.*, **199**: 352-361 (2016).

[12] Balasundram V., Ibrahim N., Samsudin M.D.H., Kasmani R.Md., Hamid M.K.A., Isha R., Hasbullah H., Thermogravimetric Studies on the Catalytic Pyrolysis of Rice Husk, *Chemical Engineering Transactions*, **56**: 427-432 (2017).

[13] Gul H., Shah A.A., Gul S., Arjomandi J., and Bilal S., Study on the Thermal Decomposition Kinetics and Calculation of Activation Energy of Degradation of Poly(*O*-Toluidine) Using Thermogravimetric Analysis, *Iranian Journal of Chemistry and Chemical Engineering*, **37**(1): 193-204 (2018).

[14] Prakash N. and Karunanithi T., Kinetic Modeling in Biomass Pyrolysis – A Review, *J. Appl. Sci. Res*, **4**: 1627-1636 (2008).

[15] Heo H.S., Park H.J., Park Y.K., Ryu C., Suh D.J., Suh Y.W., Yim J.H., Kim S.S., Bio-Oil Production from Fast Pyrolysis of Waste Furniture Sawdust in a Fluidized Bed, *Bioresour. Technol.*, **101**: S91-S96 (2010).

[16] Shah J., Jan M.R., and Mabood F., Catalytic Pyrolysis of Waste Tyre Rubber into Hydrocarbons Via Base Catalysts, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **27(2)**: 103-109 (2008).

[17] Marco I., Caballero B.M., Cabrero M.A., Laresgoiti M.F., Torres A., Chomon M.J., Recycling of Automobile Shredder Residues by Means of Pyrolysis, *J. Anal. Appl. Pyrol*, **79**: 403-408 (2007).

[18] Korkmaz A., Yanik J., Brebu M., and Vasile C., Pyrolysis of Tetra Pak, *Waste Manage.*, **29**: 2836-2841 (2009).

[19] Undri A., Rosi L., Frediani M., and Frediani P., Fuel from Microwave Assisted Pyrolysis of Waste Multilayer Packaging Beverage, *J. Fuel*, **133**: 7-16 (2014).

[20] Zhou L., Yang H., Wu H., Wang M. , and Cheng D., Catalytic Pyrolysis of Rice Husk By Mixing with Zinc Oxide: Characterization of Bio-Oil and Its Rheological Behavior, *Fuel Process. Technol.*, **106**: 385-391 (2013).

[21] Bakar M.S.A. Titiloye J.O., Catalytic Pyrolysis of Rice Husk for Bio-Oil Production, *J. Anal. Appl. Pyrol.*, **103**: 362-368 (2013).

[22] Fadhillah F., "Synthesis of Bio Crude Oil by Pyrolysis of Salak Midribs in Fixed-Bed Reactor", Thesis, Faculty of Engineering, Gadjah Mada University, Yogyakarta (2005).

[23] Aboulkas A., El Harfi K., El Bouadili A., Ben Chanâa M., Mokhlisse A., Pyrolysis Kinetics of Polypropylene: Morocco Oil Shale and Their Mixture, *J. Therm. Anal. Calorim.*, **89**: 203–209 (2007).

[24] Zadgaonkar A., "Process and Equipment for Conversions of Waste Plastics into Fuels", In: John Scheirs, (Editor), "Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels", John Wiley & Sons, Ltd, UK (2006).

[25] Callister Jr W.D., "Materials Science and Engineering An Introduction", John Wiley & Sons, Ltd, UK (2004).

[26] Williams P.T., Nugranad N., Comparison of Products from the Pyrolysis and Catalytic Pyrolysis of Rice Husks, *Energy*, **25**: 493-513 (2000).

[27] Hu S., Jess A., and Xu M., Kinetic Study of Chinese Biomass Slow Pyrolysis: Comparison of Different Kinetic Models. *Fuel*, **86**: 2778–2788 (2007).

[28] Antal J.M., "Biomass Pyrolysis: a Review of the Literature. Part I-Carbohydrate Pyrolysis", In: "Advances Solar Energy", Springer, New York (1983).