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Valorisation of Napier grass and agricultural residues via pyrolysis – A kinetic study

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Thermal pyrolysis of Thai Napier grass, cassava stalk and rice straw were studied thermogravimetrically, which was followed by a kinetic analysis assuming multiple kinetic schemes and a distributed activation energy model (DAEM) with reaction order *n* = 1 and *n* ≠ 1. The results showed that the DAEM described well the experimental data. The assumption of multiple kinetic schemes appeared more reasonable than that of similar studies reported in the literature assuming a single kinetic scheme. Consequently, the kinetic parameters extracted from the present study are more realistic and within reasonable ranges. Overall, the activation energies are within 31.6–223.53 kJ mol-1. The reaction orders are within 1.02–1.32 for the assumption of *n* ≠ 1.

**1. Introduction**

According to a report of the National Science Technology and Innovation Policy Office of Thailand, the total of agricultural residues in Thailand in 2013 was equivalent to 9.20 Mtoe, of which cassava stalk accounted for 0.50 Mtoe. On the other hand, approx. 8-14 Mt of rice straw becomes byproduct after paddy harvesting annually (Suramaythangkoor and Gheewala 2008). Lately, the Thai government has promoted a project of electricity production from energy crops with an emphasis on Napier grass and biogas production from Napier grass by anaerobic digestion (AD). However, AD is not capable of digesting the lignin component of grasses, which normally account for one thirds of the energy content of energy crops. The digestate can be used as fertilizer or solid fuel for heat and power generation via thermochemical conversion processes. In general, the digestate, Napier grass, cassava stalk and rice straw can be converted to thermal energy through combustion, of which the devolatilization (pyrolysis) is a fundamental step ( Biagini et al. 2008). Therefore, it is important to study the thermal behaviour of these biomass materials during devolatilization. However, past studies on non-catalytic pyrolysis of Napier grass (Phuakpunk et al. 2020) and cassava stalk (Zhang et al. 2020; Jia et al. 2014) available in the literature were very limited. In addition, these studies assumed single lump kinetic schemes, which are less relevant for pyrolysis of complex lignocellulosic materials (Tran et al. 2014). For these reasons, the present study was carried out for better understandings of pyrolysis behaviour and kinetics of Napier grass and cassava stalk. Rice straw was included in this study for comparison, co-considering the seasonal variation of biomass and the consistence need of an energy alternate. The pyrolysis was studied by means of thermo-gravimetric analysis (TGA), associated with a kinetic modelling assuming multiple kinetic schemes followed with a non-linear regression analysis.

**2. Material and experimental methods**

Three biomass samples of Napier grass, cassava stalk and rice straw from Thailand were collected for this work. The samples were carefully washed with distillated water to eliminate contaminants. After that, the samples were dried at 378 K for 24 h, followed by grounding and sieving to obtain sample powders with particles sizes smaller than 125 μm. The use of these particle sizes is to ensure a kinetic control regime for the TGA experiments. The obtained powder was stored in plastic bags and kept at room temperature.

*Table 1. Characterization of three biomass samples*

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| --- | --- | --- |
| Sample | Proximate analysis (wt%) | Ultimate analysis (wt%) |
|  | M VM FC Ash | C H N O |
| Cassava stalk  Napier grass  Rice Straw | 3.12 80.77 10.36 5.75  3.56 64.45 14.54 17.45  3.20 69.23 9.36 18.21 | 38.60 7.22 1.00 53.18  35.50 6.10 1.80 56.60  34.33 5.96 0.96 58.75 |

M = Moisture; VM= volatile matter; FC= fixed carbon.

Fuel properties of the biomass materials under investigation are shown in Table 1, which include the data of ultimate analysis and proximate analysis. The content of carbon, hydrogen and nitrogen was determined by an elemental analyzer LECO Truspec CHN, whereas the oxygen content was calculated by difference. The proximate analysis was determined by using a thermogravimetric analyzer (NETZSCH STA 449F3). The proximate analysis procedure is as followings: first the samples were heated from room temperature to 383 K at a heating rate of 10oC min-1 with a hold-up time of 10 min to obtain the weight loss associated with the moisture content; Subsequently, the temperature was ramped at 20oC min-1 to 1173 K, at which the samples were held for 10 min to determine the weight loss associated with the volatile matters. Oxygen was then introduced into the furnace chamber to oxidize the formed charcoals. The weight loss during this period was attributed to the fixed carbon. The remaining material after combustion was regarded as the ash content (Jeguirim et al. 2014). Another thermogravimetric analyzer Pyris 1 (TGA), Perkin Elmer, was used to study the non-isothermal pyrolysis of the biomass samples in Nitrogen. For each TGA run, approximately 6-8 mg of a dried sample was loaded into a crucible located in the furnace of the TGA. Before heating, the furnace was purged with Nitrogen for 20 min to eliminate any possible air content. The furnace was then heated from room temperature to 873 K at a constant heating rate of 10oC min-1 and a Nitrogen gas flow rate of 80 ml min-1.

**2.1 Kinetic modelling assuming distributed activation energy model**

Thermal pyrolysis of biomass may be defined as the process of thermal treatment of the material at elevated temperatures in an inert environment. It is a common practice to describe the process by the global scheme of Eq. 1 (Tran et al. 2014).

Solid biomass -- > Char + volatiles (1)

The fundamental kinetic equation for the above scheme is represented by Eq. (2)

where *f*(*α*) is the conversion function of conversion degree, *α*, which is determined as the mass fraction of the decomposed solid (mass loss) or released volatiles of samples. The conversion degree *α* is defined by Eq. (3)

where *m*0, *m*f , and *m*t are the initial mass, final mass, and the mass of the sample at time *t*, respectively. The conversion function *f*(*α*) is dependent on the reaction mechanism and its different forms can be found in the literature (Criado et al. 1989; Vlaev et al. 2003)

Various methods for estimating the kinetic parameters have been proposed and can be classified into three main groups based on the solution approaches: 1) simple algebraic models; 2) analytical model; and 3) integral model. The details of many different models have been intensively reviewed by several researchers (Di Blasi 1993; Moghtaderi 2006). Among others, the distributed activation energy model (DAEM) is believed to be the most accurate model. This model assumes that thermal pyrolysis consists of numerous independent parallel reactions with their own activation energy and pre-exponential coefficient. If it is simplified that all reactions share the same pre-exponential coefficient and the number of reactions is large enough so that the activation energy is then represented by a continuous distribution function *f*(*E*) (Anthony and Howard 1976). Several forms of *f*(*E*) can be applied to DAEM model including Gaussian, Gamma, Weibull and Logistic distribution (Cai and Liu 2008; Cai et al. 2011; De Caprariis et al. 2012). Among these, Gaussian function (Eq. 4) is most widely used following the popularization (Anthony et al. 1975).

where *E*0 and *σ* are the mean activation energy and its standard deviation, respectively.

For the single DAEM model with the reaction order that equals to unity, *n* = 1 (Eq. 4a), or differs from unity, *n*≠1 (Eq. 4b), the conversion degree can be described as below (Anthony and Howard 1976):

In general, lignocellulosic biomass materials are mainly composed of three components including hemicellulose, cellulose and lignin. The chemical structure of hemicellulose is more complicated than that of cellulose and it undergoes the thermal degradation in the temperature range of 473- 623 K (Jensen et al. 1998; Shen et al. 2010). However, the degradation of cellulose occurs mainly in the range between 588 and 673 K (Yang et al. 2007). In addition, lignin is thermally the most stable and decomposes within a broad temperature range (Raveendran et al. 1996). It is therefore too simplistic to describe the thermal decomposition of lignocellulosic biomass material by a single DAEM model. Recently, the multi DAEM model has been adapted by researchers to represent three main components including hemicellulose, cellulose and lignin (Várhegyi et al. 2011; Cai et al. 2013; Tran et al. 2016). The reaction rate is then described by Eq. (5) wherein *c*i is the contribution factor of *i* component.

In addition to that, Napier grass contains considerable amount of protein and lipid, 27% and 14.8%, respectively (Dongmeza et al. 2009; García-Galván et al. 2012). In other words, Napier grass consists of five main components including protein and lipid apart from holocellulose and lignin. Therefore, it is reasonable to assume a multi DAEM model consisting of five pseudo-components for the pyrolysis of Napier grass. A similar approach done by Bui at al. was successful to reflect the pyrolysis kinetic of microalgae residues (Bui et al. 2016). Following this assumption, the pyrolysis can be kinetically represented by Eq. (6).

In Eq. (5) and Eq. (6), the conversion degree of every pseudo-component follows Eq. (4a, b) and the overall conversion rate equals to the summation of partial conversion rates.

**2.2 Numerical method**

The non-linear least square method was applied to the kinetic modelling and simulation of the assumed models. The objective function to minimize is described in Eq. (7).

where and stand for the experimental and modelled conversion rate, *N* is the number of experimental points. The fit quality is appraised by Eq. (8) (Branca and Di Blasi 2003)

**3. Results and discussion**

Results from the kinetic analysis are presented in Figures 1, 2 and 3 for both cases of *n* = 1 and *n* ≠ 1, whereas the extracted kinetic parameters are tabulated in Table 2. Note that the Napier grass curves and data are obtained from simulation assuming five pseudo-components, while only three pseudo-components were assumed for the cassava stalk and rice straw data. As can be visually inspected, the simulated curves fit well the experimental data. This is confirmed by the high fit qualities of around 99% in Table 2. The simulations with *n* ≠1 allow small improvement in fit quality. For instance, it is just 0.22% increment in the case of Napier grass. Other investigations also confirmed that the reaction orders higher than one allowed better description of experimental data (Manyà et al. 2003; Bach, Tran et al. 2015). Nonetheless, other researchers argued that the pyrolysis process of lignocellulosic biomass materials can be represented by first order reaction, *n* = 1 (Broström, Nordin et al. 2012). Indeed, for the case *n*≠1, the reaction order was not far away from unity for the present study.

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*Figure 1: DAEM simulation for Napier grass with (A) n=1; (B) n≠1*

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*Figure 2: DAEM simulation for Cassava stalk with (A) n=1; (B) n≠1*

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*Figure 3: DAEM simulation for Rice Straw with (A) n=1; (B) n≠1*

The calculated kinetic parameters shown in Table 2 are consistent with other studies (Grønli et al. 2002; Manyà et al. 2003). It is observed that the value of standard deviation for hemicellulose was highest among the others whereas that of lignin was smallest. It means that the activation energy of hemicellulose varies within a wider range than those for other pseudo-components. The mean activation energy of hemicellulose from Cassava stalk was about 167 kJ mol-1, consistent with the literature of 154-165 kJ mol-1 (Teng and Wei 1998). Nevertheless, it was claimed that the decomposition of hemicellulose is described by activation energy in the range of 80-90 kJ mol-1 (Orfão et al. 1999) or 105-111 kJ mol-1 (Várhegyi et al. 1997). Among the three samples, hemicellulose of the cassava stalk sample exhibited the highest activation energy, being within the range of 166.61-167.85 kJ mol-1, followed by 149.21-151.27 kJ mol-1 for the rice straw and 98.04-100.64 kJ mol-1 for the Napier grass. However, cellulose of the rice straw sample had the highest activation energy, being within the range of 233.37-233.53 kJ mol-1, followed by 176.21-187.02 kJ mol-1 for the cassava stalk and 171.05-184.81 kJ mol-1 for the Napier grass. When it comes to the activation energy of lignin component, the Napier grass sample showed the highest value within 61.10-64.41 kJ mol-1, followed by 41.57-46.08 kJ mol-1 for the rice straw and 31.60-33.24 kJ mol-1 for the cassava stalk. In addition, the activation energy of lipid and protein component of the Napier grass is within 147.14-148.10 kJ mol-1 and 123.08-124.22 kJ mol-1, respectively. The predicted content of these two components is 11% and 19%, respectively.

*Table 2. Extracted kinetic data*

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | *n* = 1 | | | | | | *n* ≠ 1 | | | | | |
| Sample |  | *A*  min-1 | *E*o kJmol-1 | *σ*  kJmol-1 | *c* | Fit  % | *A*  min-1 | *E*o  kJmol-1 | *σ*  kJmol-1 | *c* | *n* | Fit  % |
| Napier | H | 7.52E+06 | 100.64 | 18.04 | 0.20 | 98.70 | 4.91E+06 | 98.04 | 17.58 | 0.20 | 1.02 | 98.93 |
| grass | C | 2.78E+11 | 171.05 | 30.66 | 0.24 |  | 2.79E+12 | 184.81 | 33.13 | 0.24 | 1.20 |  |
|  | L | 2.75E+02 | 61.10 | 10.95 | 0.26 |  | 4.47E+02 | 64.41 | 11.55 | 0.26 | 1.16 |  |
|  | Ld | 1.15E+08 | 147.14 | 22.34 | 0.11 |  | 1.57E+08 | 148.01 | 22.96 | 0.11 | 1.32 |  |
|  | P | 4.75E+07 | 123.08 | 22.06 | 0.19 |  | 5.94E+07 | 124.22 | 22.26 | 0.19 | 1.07 |  |
| Cassava | H | 9.00E+10 | 166.61 | 29.86 | 0.32 | 98.41 | 1.11E+11 | 167.85 | 30.09 | 0.33 | 1.05 | 99.00 |
| stalk | C | 2.39E+11 | 187.02 | 32.57 | 0.44 |  | 5.66E+10 | 176.21 | 31.24 | 0.43 | 1.06 |  |
|  | L | 5.88E+00 | 31.60 | 5.68 | 0.24 |  | 7.98E+00 | 33.24 | 5.97 | 0.24 | 1.18 |  |
| Rice | H | 5.14E+09 | 149.21 | 26.32 | 0.29 | 98.85 | 7.33E+09 | 151.27 | 26.65 | 0.29 | 1.04 | 99.15 |
| Straw | C | 1.53E+13 | 223.37 | 36.95 | 0.48 |  | 1.60E+13 | 223.53 | 36.98 | 0.48 | 1.04 |  |
|  | L | 4.16E+01 | 41.57 | 9.13 | 0.23 |  | 9.63E+01 | 46.08 | 10.24 | 0.23 | 1.20 |  |

In another study, it was reported that the activation energy of Napier grass pyrolysis within 87.8 to 289.2 kJ mol−1 for the conversion up to 70% (Phuakpunk et al. 2020). However, for the higher conversion, 80% and 90%, the reported values were 494.3 kJ mol−1 and 887.2 kJ mol−1, respectively. These values are unrealistic for lignocellulosic materials (Anca-Couce et al. 2020). From the present study, the activation energies for Napier grass are ranging from 61.10 to 184.81 kJ mol−1 for the higher conversion, 80% and 90%, which are more realistic.

**4. Conclusions**

Thermal pyrolysis of the three types of Thai biomass including Napier grass, cassava stalk and rice straw was studied by means of a thermogravimetric analyzer for bioenergy application in Thailand. The collected TG data was employed for kinetic analyses assuming the multiple DAEM (five pseudo-components for the Napier grass, but only three for the cassava stalk and rice straw), with reaction order *n* = 1 and *n* ≠ 1. The results showed that the multi DAEM model described well the experimental data with higher fitting quality. The assumption of multiple kinetic schemes appeared more reasonable than that of similar studies reported in the literature assuming a single kinetic scheme. Consequently, the kinetic parameters extracted from the present study are more realistic and within reasonable ranges.

Overall, the activation energies are within 31.6–223.53 kJ mol−1. The activation energy of lignin is within 31.60–64.41 kJ mol−1, followed by 98.40–167.85 kJ mol−1 and 171.05–223.53 kJ mol−1 for hemicellulose and cellulose, respectively. The reaction orders are within 1.02–1.32 for the assumption of *n* ≠ 1. In addition, the activation energy of lipid and protein component of the Napier grass is within 147.14-148.10 kJ mol−1 and 123.08-124.22 kJ mol−1, respectively. The predicted content of these two components is 11% and 19%, respectively, which are also in good agreement with the literature. These data can be used as input data for modelling of energy systems as well as reactor and process design (Kempegowda et al. 2012).

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**References**

Anca-Couce, A., et al., Biomass pyrolysis TGA assessment with an international round robin (2020). Fuel, 276.

Anthony D. B. and J. B. Howard (1976). "Coal Devolatilization and Hydrogasification." AIChE Journal 22(4): 625-656.

Anthony D. B., J. B. Howard, H. C. Hottel and H. P. Meissner (1975). "Fifteenth Symposium (International) on CombustionRapid devolatilization of pulverized coal." Symposium (International) on Combustion 15(1): 1303-1317.

Bach Q.-V., K.-Q. Tran, Ø. Skreiberg and T. T. Trinh (2015). "Effects of wet torrefaction on pyrolysis of woody biomass fuels." Energy 88: 443-456.

Biagini E., A. Fantei and L. Tognotti (2008). "Effect of the heating rate on the devolatilization of biomass residues." Thermochimica Acta 472(1-2): 55-63.

Branca C. and C. Di Blasi (2003). "Global Kinetics of Wood Char Devolatilization and Combustion." Energy & Fuels 17(6): 1609-1615.

Broström M., A. Nordin, L. Pommer C. Branca and C. Di Blasi (2012). "Influence of torrefaction on the devolatilization and oxidation kinetics of wood." Journal of Analytical and Applied Pyrolysis 96: 100-109.

Bui H.-H., K.-Q. Tran and W.-H. Chen (2016). "Pyrolysis of microalgae residues – A kinetic study." Bioresource Technology 199: 362-366.

Cai J., C. Jin, S. Yang and Y. Chen (2011). "Logistic distributed activation energy model – Part 1: Derivation and numerical parametric study." Bioresource Technology 102(2): 1556-1561.

Cai J. and R. Liu (2008). "Application of Weibull 2-mixture model to describe biomass pyrolysis kinetics." Energy and Fuels 22(1): 675-678.

Cai J., W. Wu, R. Liu and G. W. Huber (2013). "A distributed activation energy model for the pyrolysis of lignocellulosic biomass." Green Chemistry 15(5): 1331-1340.

Criado J. M., J. Málek and A. Ortega (1989). "Applicability of the master plots in kinetic analysis of non-isothermal data." Thermochimica Acta 147(2): 377-385.

De Caprariis B., P. De Filippis C. Herce and N. Verdone (2012). "Double-Gaussian Distributed Activation Energy Model for Coal Devolatilization." Energy & Fuels 26(10): 6153-6159.

Di Blasi C. (1993). "Modeling and simulation of combustion processes of charring and non-charring solid fuels." Progress in Energy and Combustion Science 19(1): 71-104.

Dongmeza E., S. Steinbronn, G. Francis, U. Focken and K. Becker (2009). "Investigations on the nutrient and antinutrient content of typical plants used as fish feed in small scale aquaculture in the mountainous regions of Northern Vietnam." Animal Feed Science and Technology 149(1–2): 162-178.

García-Galván A., R. Belmar-Casso, L. Sarmiento-Franco and C. Sandoval-Castro (2012). "Evaluation of the metabolizable energy value for growing lambs of the Mucuna pruriens seed and the whole pod." Tropical Animal Health and Production 44(4): 843-847.

Grønli M. G., G. Várhegyi and C. Di Blasi (2002). "Thermogravimetric Analysis and Devolatilization Kinetics of Wood." Industrial & Engineering Chemistry Research 41(17): 4201-4208.

Jeguirim M., Y. Elmay, L. Limousy, M. Lajili and R. Said (2014). "Devolatilization behavior and pyrolysis kinetics of potential Tunisian biomass fuels." Environmental Progress & Sustainable Energy 33(4): 1452-1458.

Jia J.W., et al., Pyrolysis characteristics and kinetics of cassava residues (2014). In Advanced Materials Research. p. 325-329.

Jensen A., K. Dam-Johansen, M. A. Wójtowicz and M. A. Serio (1998). "TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis." Energy and Fuels 12(5): 929-938.

Kempegowda R.S., P.V. Pannir Selvam, Ø. Skreiberg and K.-Q. Tran (2012). "Process synthesis and economics of combined biomethanol and CHP energy production derived from biomass wastes." Journal of Chemical Technology and Biotechnology 87(7): 897- 902.

Manyà J. J., E. Velo and L. Puigjaner (2003). "Kinetics of Biomass Pyrolysis:  a Reformulated Three-Parallel-Reactions Model." Industrial & Engineering Chemistry Research 42(3): 434-441.

Moghtaderi B. (2006). "The state-of-the-art in pyrolysis modelling of lignocellulosic solid fuels." Fire and Materials 30(1): 1-34.

Orfão J. J. M., F. J. A. Antunes and J. L. Figueiredo (1999). "Pyrolysis kinetics of lignocellulosic materials—three independent reactions model." Fuel 78(3): 349-358.

Raveendran K., A. Ganesh and K. C. Khilar (1996). "Pyrolysis characteristics of biomass and biomass components." Fuel 75(8): 987-998.

Shen D. K., S. Gu and A. V. Bridgwater (2010). "Study on the pyrolytic behaviour of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR." Journal of Analytical and Applied Pyrolysis 87(2): 199-206.

Suramaythangkoor T. and S. H. Gheewala (2008). "Potential of practical implementation of rice straw-based power generation in Thailand." Energy Policy 36(8): 3193-3197.

Teng H. and Y.-C. Wei (1998). "Thermogravimetric Studies on the Kinetics of Rice Hull Pyrolysis and the Influence of Water Treatment." Industrial & Engineering Chemistry Research 37(10): 3806-3811.

Tran K.-Q., H.-H. Bui, and W.-H. Chen (2016). "Distributed activation energy modelling for thermal decomposition of microalgae residues." Chemical Engineering Transactions Vol. 50: 175-180.

Tran K.-Q., Q.-V. Bach, T. T. Trinh and G. Seisenbaeva (2014). "Non-isothermal pyrolysis of torrefied stump – A comparative kinetic evaluation." Applied Energy 136(0): 759-766.

Várhegyi G., M. J. Antal Jr, E. Jakab and P. Szabó (1997). "Kinetic modeling of biomass pyrolysis." Journal of Analytical and Applied Pyrolysis 42(1): 73-87.

Várhegyi G., B. Bobály, E. Jakab and H. Chen (2011). "Thermogravimetric Study of Biomass Pyrolysis Kinetics. A Distributed Activation Energy Model with Prediction Tests." Energy & Fuels 25(1): 24-32.

Vlaev L. T., I. G. Markovska and L. A. Lyubchev (2003). "Non-isothermal kinetics of pyrolysis of rice husk." Thermochimica Acta 406(1–2): 1-7.

Yang H., R. Yan, H. Chen, D. H. Lee and C. Zheng (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis." Fuel 86(12–13): 1781-1788.

Zhang J., et al., Thermal behaviors and kinetics for fast pyrolysis of chemical pretreated waste cassava residues (2020). Energy. 208.