

Reactivity Studies of Sludge and Biomass Combustion

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Abstract

Sludge and biomass are wastes with energy value. Both can provide a renewable energy in the form of gaseous fuels through thermal conversion processes. Proper understanding of the thermal properties and reaction kinetic of sludge and biomass is important for efficient design, operation and modeling of the conversion process. This study was carried out to obtain the kinetics data of the sludge and biomass in pure oxygen atmosphere at 30 mlmin⁻¹ with the combustion temperature ranging from 50 to 900°C. The effect of sample size and heating rate on thermal degradation was studied and kinetic parameters of sludge, bagasse and sawdust combustion are described using Arrhenius equation. Two distinct reaction zones were observed for sludge, bagasse and sawdust samples. Both the activation energy and pre-exponential factors were significantly higher in the first zone than that of in the second zone for sludge and bagasse where as an opposite trend was observed for sawdust.

Keywords: Activation Energy, Biomass, Combustion, Sludge.

1. INTRODUCTION

Present commercial energy is largely dependent on fossil fuels, which makes future sustainable development very difficult. There are drastic changes in the composition and behavior of our atmosphere due to the rapid release of polluting combustion products from fossil fuels. A significant amount of the NO_x and SO_x emissions from the energy sector is related to the use of fossil fuels for electricity generation. As the demand for electricity is growing rapidly, the emissions of these pollutants can be expected to increase unless alternatives are made available. Among the energy sources that can substitute fossil fuels, biomass wastes appear as one of the potential option [1].

Sludge from a petroleum refinery has several advantages. Calorific value of dry sludge corresponds to coal and energy content may be recovered through combustion [2]. The sludge from a petroleum refinery in Melaka has an annual production approximated 100,000 tonnes from drying and filters press alone. The limitation faced by land filling and recycling and the ban on sea disposal of sludge has lead to the expectation that the role of combustion of sludge will increase in future.

Various forms of biomass energy account for approximately 15% of the world energy supply [3]. Having an equatorial climate and fertile land, Malaysia is covered by large areas of tropical rainforest and agricultural vegetation. This provides a large resource base for biomass energy especially from plantation residues, mainly associated with the palm oil, forestry, wood, sugar cane plantation and rice milling industry [4]. It is estimated that there are about 20.8 million tones of potential biomass residues available in the country, which can generate about 700MW for energy consumption [11]. Even if only one third of the present annual output of biomass waste in the country is used to produce energy, an estimated RM2.0 billion a year can be saved in the country's import bill.

Thus, studies on the refinery sludge waste and abundant renewable forest and agriculture-based materials are necessary to see the potential of these materials to be used as solid fuel for energy production. The objective of this study is to determine the kinetic parameters of sludge, bagasse and sawdust.

2. THEORY

2.1 Determination of Kinetic Parameters

Based on Mansaray and Ghaly [18], kinetic parameters are determined by using typical curves of thermogravimetric data over an entire temperature range continuously. Whenever a peak is observed on a TGA trace as the sample is subjected to a controlled temperature ramp, it can be assumed that there has been a conversion, which can be represented as in Equation 1:



Theoretically, for a solid fuel, the char reactivity towards a reactive gas is usually defined in terms of the conversion rate per remaining mass [6].

$$R = -\frac{1}{m} \frac{dm}{dt} = \frac{1}{1-X} \frac{dX}{dt} \quad (2)$$

where

$$m = m_o(1 - X) \quad (3)$$

According to Pyris Software Kinetic Guide, for most system, the value of n is equal to 1. The degree of chemical conversion (X) is assumed to obey the following rate equation:

$$\frac{dX}{dt} = k(1 - X)^n \quad (4)$$

The Arrhenius relationship is given by the following equation:

$$k = Z \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Kinetics parameters are determined through experimental kinetic data. Coats and Redfern [7] have formulated equation from a single integral thermogravimetric analyzer (TGA) curve (weight loss vs. temperature) as in equation (6).

$$w(T) = \frac{dw}{dT} = \left(\frac{Z}{\beta}\right) e^{\frac{-E_a}{RT}} \quad (6)$$

Thus, the correlation between Equation (4), (5) and (6) was simplified into the following reaction rate expression as described in Equation (7).

$$\left[\frac{(m_0 - m)}{(m - m_f)}\right] \left[\frac{1}{(T - T_0)}\right] \beta = Z \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

Equation (7) was reduced to a linear form by taking the natural logarithm of both sides of the equation to obtain the following equation:

$$\ln \left\{ \left[\frac{(m_0 - m)}{(m - m_f)} \right] \left[\frac{1}{(T - T_0)} \right] \beta \right\} = \ln Z + \left(\frac{-E_a}{RT} \right) \quad (8)$$

Change of variables was then introduced to Equation (8), which results in a linear relation between the new variables that is described in Equation (9) and then the unknown variables, C and D were solved [8].

$$Y = CX + D \quad (9)$$

Finally, the kinetic parameters that are the activation energy and pre-exponential factor were determined from the following equations respectively.

$$E_a = -CR \quad (10)$$

$$Z = \exp(D) \quad (11)$$

2.2 Thermal Degradation and Kinetic Parameters at Various Condition

The thermal degradation and kinetic parameters of selected materials were studied at two different operating conditions as follow:

i. Effect of particle size

The effect of particle size on the thermal degradation and kinetic parameters of sludge, bagasse and sawdust combustion were determined at two different sizes that are 425 μ m and 1.18 mm.

ii. Effect of heating rate

The experimental heating rates were set at 35 $^{\circ}$ C and 50 $^{\circ}$ C per min for each respective experimental run.

3. METHODOLOGY

Sludge obtained from a refinery and biomass; sawdust and bagasse, obtained in Perak, Malaysia were selected as the samples. The samples were oven-dried at 104 $^{\circ}$ C to 110 $^{\circ}$ C. After that, the samples were grounded and sieved to obtain homogeneous samples at size of 425 μ m and 1.18 mm, respectively.

3.1 Proximate and Elementary Analysis

Both proximate and elementary analyses are determined using Thermal Gravimetric Analyzer (TGA by Perkin Elmer) and CHNS-900 (by LECO) respectively. A known amount of sample was placed in a Thermal Gravimetric Analyzer (TGA by Perkin Elmer). The sample was held at 50 $^{\circ}$ C

for 1 minute before being heated from 50 °C to 110 °C at 60 °Cmin⁻¹ with 99% purity nitrogen gas flow rate of 20 mlmin⁻¹. At 110 °C, the sample was on hold isothermally for 5 minutes and then heated up to 900 °C at 100 °Cmin⁻¹. The sample was then on hold at 900 °C for 15 minutes. The purge gas was then switched to 99.9% purity oxygen at a flowrate of 30 ml/min after 22 minutes of elapsed time. The thermograms produced were analyzed to determine the moisture, volatile matter, fixed carbon and ash. The elementary analysis was carried out using CHNS Analyzer and the calorific values were determined using the Oxygen Bomb Calorimeter (by IKA).

3.2 Thermal Analysis for Determination of Kinetic Parameters

The controlled parameters setting and experimental runs for the thermal analysis is given in Table 1. For each run, the samples were first held at 50 °C for 1 minute and then heated from 50 °C to 900 °C in oxygen atmosphere at a flowrate of 30 ml/min. The time taken to complete the thermal analysis is approximately 25 and 18 minutes for samples with heating rate of 35 °C and 50 °C respectively.

Raw material	Experiment No.	Particle size	Heating rate
Sludge	1	425 µm	35 °Cmin ⁻¹
	2		50 °Cmin ⁻¹
	3	1.18 mm	35 °Cmin ⁻¹
	4		50 °Cmin ⁻¹
Bagasse	5	425 µm	35 °Cmin ⁻¹
	6		50 °Cmin ⁻¹
	7	1.18 mm	35 °Cmin ⁻¹
	8		50 °Cmin ⁻¹
Sawdust	9	425 µm	35 °Cmin ⁻¹
	10		50 °Cmin ⁻¹
	11	1.18 mm	35 °Cmin ⁻¹
	12		50 °Cmin ⁻¹

Table 1: Controlled Parameters and Experimental Run for Thermal Analysis

4. RESULT AND DISCUSSION

4.1 Drying Process

The samples were dried in an oven at a constant temperature range of 104°C to 110 °C. The results showed that the moisture content (wet basis) of sludge, bagasse and sawdust was initially at 75.37%, 66.12 % and 16.12 % respectively in the beginning of the experiment (i.e. at 0 hour). Figure 1 illustrated the moisture content for the samples were observed to decrease gradually until the end of the experiment.

A rapid moisture loss during the initial state of drying was observed for the first 7 hours, 24 hours and 48 hours for sawdust, bagasse and sludge, respectively. This is attributed to the evaporation of moisture from the surface area of the sludge and biomass used [9]. According to Alves and Figueiredo [11], when heat is applied to wood particles, the particles begin to dry more intensely at the outer boundary, at which the temperature is high. Whereas the bound and free water tend to move outward by convection and diffusion although some may migrate towards the inner, colder parts of the solid, where recondensation occurs. However, as the drying process continued, the penetration of heat into the deeper part of the wood particle and the moisture movement to the surface become harder due to material resistance. Thus, resulting in slower rate of drying. This theory explains the results obtained for all drying curves of sawdust, bagasse and sludge.

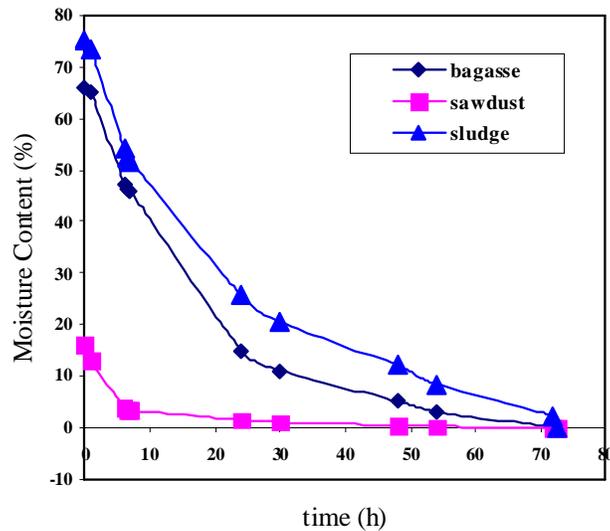


Figure 1: Drying Curve of Sludge, Bagasse and Sawdust

The duration of the rapid moisture loss for bagasse and sludge is longer than sawdust, which explained by the higher initial moisture content of bagasse and sludge, compare to sawdust. Longer time is required in order to release moisture content for material with higher initial moisture content when same heat or temperature applied.

4.2 Proximate and Elementary Analysis

Table 2 shows the results for both proximate and elementary analysis as well as calorific values of the selected materials. The moisture and volatile matters for sludge and bagasse are higher than sawdust. It was observed that some of the sludge and bagasse sample was not completely combusted, thus leaving some residue or ash of 25 and 4.6 weight percentage. The high value of ash in both sludge and bagasse compared to sawdust is contributed by the low value of carbon content. Charles [17] suggested that agricultural residues have lower carbon content as compared to wood residues. This is proven in the result obtained where the fixed carbon content of bagasse is less than sawdust. The values of proximate analysis for biomass samples were comparable with values obtained from literatures.

The fuel elements of biofuels are actually the volatile matters and the carbon content while moisture and ash contents contribute as the impurities [17]. The result obtained showed that the volatile matter of sludge and carbon content of sawdust is greater than bagasse. In contrast, the moisture as well as ash content of sawdust is less than sludge and bagasse. Furthermore, the energy content of sludge and biomass is measured by its calorific value. The calorific value for bagasse is 18.1MJ/kg which higher than that of sludge and sawdust, 16.9 and 17.0 MJ/kg

respectively. Lim [23] has reported the calorific value of sawdust and bagasse is around the same values, which is 18.86 MJkg^{-1} and 17.33 MJkg^{-1} , respectively. Just sawdust is slightly higher than of bagasse.

The sulfur content of bagasse and sawdust were much higher than of sludge. The nitrogen content of sludge has much higher than that of biomass. This fact constitutes an advantage from a fertilizer point of view if considering the agricultural use of refinery sludge, could be an important drawback for combustion to be considered but other metal content in it may harmful the land and underwater stream. The NO_x emission could be expected during their combustion. Nevertheless, NO_x emission has been found decreased by combustion experiences. Albertson et al [2] reported that this could be related to the high volatile content in sludge, which accelerates the air consumed during combustion, diminishes the rate O/N in the flame and represses the thermal generation of NO_x .

Sample	Moisture (%) db	Volatile Matters (%) db	Ash (%) db	Carbon, C (%) db	Hydrogen, H (%) db	Nitrogen, N (%) db	Sulfur, S (%) db	High Heat Value, HHV (kJ/kg) db
Sludge	3.9	55.8	25	21.4	3.4	2.2	0.98	16880
Bagasse	2.77	48.13	4.6	44.5	5.32	0.23	6.05	18110
Sawdust	1.54	17.5	0.98	56.4	2.5	0.05	2.35	17029

db = dry basis

Table 2: Result of Proximate and Elementary Analysis for Sludge, Bagasse and Sawdust

However, the overall result showed that sawdust is having a better potential as fuel element as compared to sludge and bagasse in terms of higher C/O, C/H and C/N ratio.

4.3 Thermal Analysis

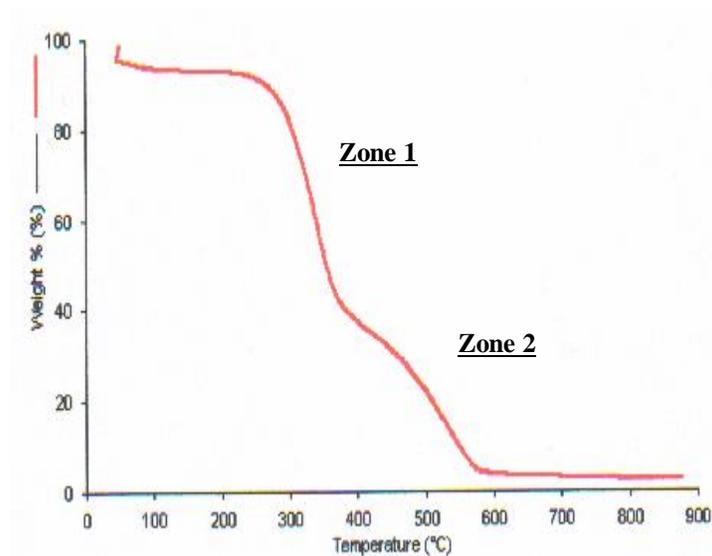


Figure 2: TGA thermograms by one of the experimental runs

Figure 2 shows the TGA thermograms produced for thermal analysis by one of the experimental runs. The continuous records of weight loss and temperature were obtained to determine the thermal degradation characteristics as well as kinetic parameters of samples tested. It produces

two zones of degradation, which are decomposition, (Zone 1) and combustion reaction, (Zone 2) respectively. It was necessary to determine and use different kinetic parameters to describe the thermal degradation over the entire temperature range with higher accuracy [21].

Therefore, the thermal degradation characteristics and the kinetic parameters (activation energy and pre-exponential factor) of each sample were determined for the first and second reaction zones separately, and results obtained were depending on or subjected to the operating conditions.

4.3.1 Thermal Degradation

The results of thermal degradation of sludge, bagasse and sawdust in the first and second reaction zones are summarized in Table 3 and 4 respectively. The 2 zones region were plotted to see the effects of differences in particles size and heating rate as shown in Figure 3, 4 and 5.

It was observed from the thermograms that increasing the temperature from 50°C to 110°C resulted in weight losses. According to Mansaray and Ghaly [21], this is due to loss of water present in the samples and external water bounded by surface tension. In the first zone, the degradation temperature of sludge started from 120°C to 143°C and bagasse started approximately from 206 °C to 217 °C, whereas for the sawdust started from 259 °C to 270 °C. It was also observed that rapid degradation of sludge and bagasse took place in the first zone due to the rapid evolution of the volatile products.

The total degradation for sludge and bagasse were in the range of 51.3% to 56.7% and 42.0% to 48.6%, respectively, while sawdust has the total degradation range from 14.1% to 17.3%. The end of the first reaction zone was accepted as the beginning of the second reaction zone. The final temperature of the second reaction zone was approximately 397 °C to 565°C for sludge, 585 °C to 674 °C for bagasse, and 733 °C to 793 °C for sawdust. Result shows that for the second reaction zone the total degradation for sludge was in the range of 19.3% to 21.7 %, bagasse was in the range of 43.9 % to 45.3%, while sawdust was in the range of 76.4% to 79.5%. The residual weights of the sludge, bagasse and sawdust at the end of the experiment (at 900 °C) were in the range of 21.0 % to 24.25 %, 4.31 % to 4.71 % and 0.94% to 0.98%. These values were close to the initial ash contents of the original samples (Table 2), which indicate that, thermal degradation was completed at above the final degradation temperatures for all samples.

Sample	Exp. run	Water evolved (% db*)	Initial deg. Temp. (°C)	Final Temp. (°C)	Total deg. (%)
Sludge	1	3.1	120	213	54.7
	2	3.4	137	231	56.7
	3	3.5	115	243	51.3
	4	4.3	143	268	53.4
Bagasse	1	1.7	206	378	46.8
	2	2.1	217	381	48.6
	3	2.3	207	385	42.0
	4	2.7	211	389	43.4
Sawdust	1	1.1	259	415	16.8
	2	1.3	270	433	17.3
	3	1.5	259	422	14.1
	4	1.8	267	426	15.9

db = dry basis

Table 3: Thermal Degradation in First Reaction Zone

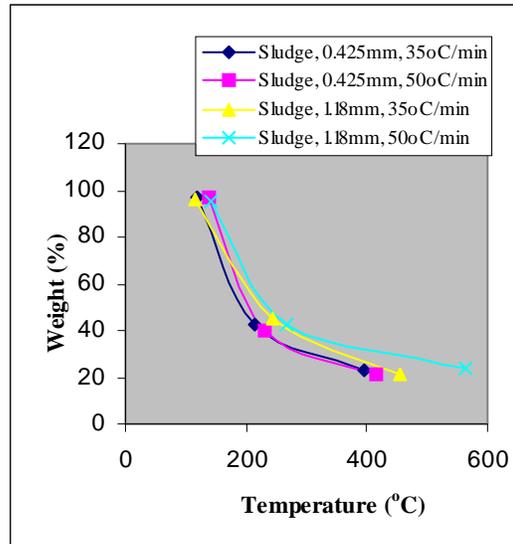


Figure 3: Thermal Degradation of Sludge

Sample	Exp. run	Initial deg. Temp. (°C)	Final Temp. (°C)	Total deg. (%)	Residual weight (%db)
Sludge	1	213	397	20.7	23.13
	2	231	415	21.7	21.00
	3	243	455	19.3	21.27
	4	268	565	20.4	24.25
Bagasse	1	378	585	44.4	4.31
	2	381	606	45.3	4.63
	3	385	667	43.9	4.71
	4	389	674	45.1	4.63
Sawdust	1	415	733	77.4	0.94
	2	433	793	79.5	0.98
	3	422	726	76.4	0.97
	4	426	752	78.2	0.97

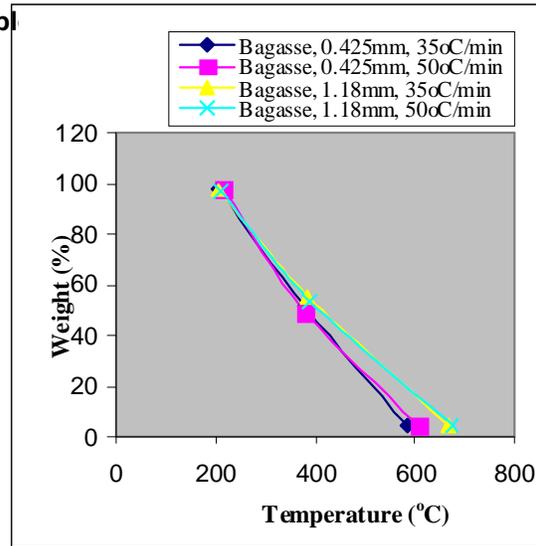


Figure 4: Thermal Degradation of Bagasse

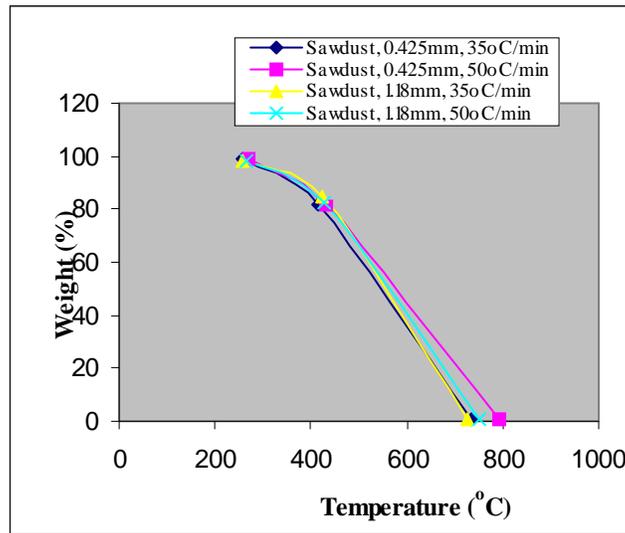


Figure 5: Thermal Degradation of Sawdust

The total degradation for sludge was lower in the second reaction zone as compared to the first reaction zone due to the fact that rapid volatilization in the first zone and left with low carbon content to degrade. The total degradation for bagasse is slightly lower in the second zone than in the first zone, may be due to the fact that lignin was decomposed to char [24]. However, sawdust total degradation in the second zone was higher than in the first zone. Hornof *et al.* [27] studied the effect of lignin content on the thermal degradation of wood pulp and found that the reactions above 330 °C are mostly dominated by the decomposition of lignin, which is the case mostly in the second reaction zone.

From the result obtained, it shows that the total degradation of sawdust is higher than of bagasse. This is because; sawdust is having higher carbon content and lower ash content as compared to bagasse as shown in Table 2.

4.3.2 Kinetic Parameters

The kinetic parameters (activation energy and pre-exponential factor) of each sample were determined for the first and second reaction zones separately by applying the least squares method to the thermogravimetric data. The kinetic parameters obtained for both first and second reaction zones are presented in Table 5.

It is observed that the activation energy is proportional to the pre-exponential factor as governed by the Arrhenius equation as in Equation 5. For the first zone, the activation energy of sludge falls in the range of 42.98 to 45.05 kJ/mol, bagasse falls in the range of 76.77 to 98.96 kJ/mol whereas for sawdust, the activation energy of sawdust falls in the range of 38.60 to 48.59 kJ/mol. The pre-exponential factor for the first reaction zone lies between 3.71×10^4 to $7.11 \times 10^5 \text{ min}^{-1}$ for sludge, 2.09×10^5 to $2.26 \times 10^7 \text{ min}^{-1}$ for bagasse and 1.77×10^2 to $3.97 \times 10^2 \text{ min}^{-1}$ for sawdust.

Sample	Exp. Run	Ea (kJ/mol)		Z (1/min)	
		1 ^{st.} zone	2 ^{nd.} zone	1 ^{st.} zone	2 ^{nd.} zone
Sludge	1	44.29	35.68	5.43×10^5	6.80×10^4
	2	45.05	37.71	7.11×10^5	7.11×10^4
	3	42.98	32.45	3.71×10^4	7.03×10^3
	4	43.97	34.97	3.94×10^4	7.23×10^3
Bagasse	1	97.32	72.72	1.45×10^7	3.80×10^4
	2	98.96	61.26	2.26×10^7	8.63×10^4
	3	76.77	69.29	2.09×10^5	5.52×10^3
	4	78.12	64.50	3.27×10^5	8.82×10^3
Sawdust	1	38.60	142.37	3.33×10^2	6.04×10^{10}
	2	48.59	152.14	3.97×10^2	7.10×10^{10}
	3	42.67	78.23	1.77×10^2	1.01×10^5
	4	43.34	116.70	1.87×10^2	1.22×10^5

Table 5: Kinetic Parameters of First and Second Reaction Zones

For the second reaction zone, the activation energy of sludge is between 32.45 to 37.71 kJ/mol, bagasse is between 61.26 to 72.72 kJ/mol while for sawdust, the value lies between 78.23 to 152.14 kJ/mol. Result obtained also shows that for the second reaction zone, the pre-exponential factor of sludge, bagasse and sawdust is between 7.03×10^3 to $7.11 \times 10^4 \text{ min}^{-1}$, 5.52×10^3 to 8.63×10^4 and 1.01×10^5 to $7.10 \times 10^{10} \text{ min}^{-1}$, respectively.

Figure 6 shows that the kinetic parameters for sludge and bagasse in the second reaction zone are lower than the first reaction zone. However, the kinetic parameters for sawdust in the second reaction zone are higher than in the first zone. Binning and Jenkins [10] and Ergudenler and Ghaly [19] also reported lower kinetic parameters in the second reaction zone compared to the first reaction zone for bagasses.

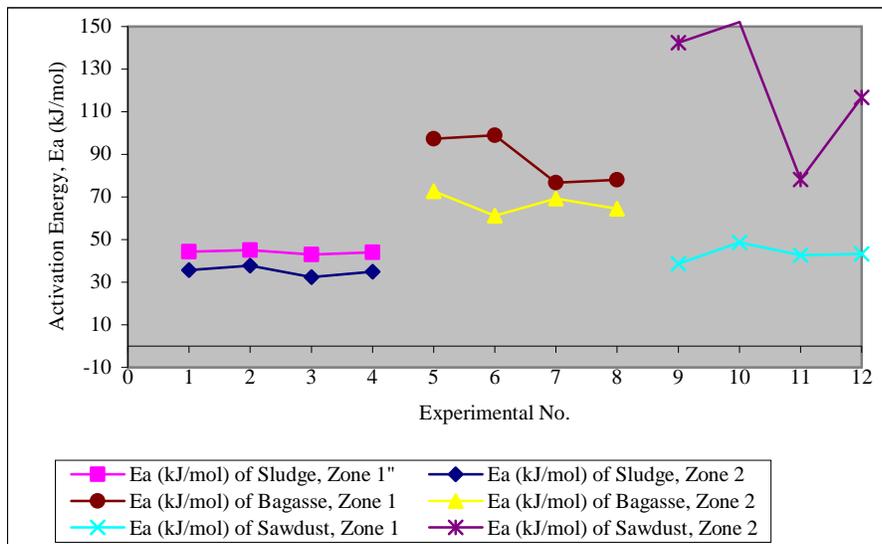


Figure 6: Activation Energy Analysis by Arrhenius Model

4.3.3 Effects of Operation Conditions on Thermal Degradation Characteristics and Kinetic Parameters

4.3.3(a) Effect of Particle Size

As the particle size was increased from 425 μm to 1.18 mm, the total degradation, activation energy and pre-exponential factor decreased in both first and second reaction zones. According to Shodor [31], one of the conditions for molecules to react, which is stated by the collision theory, is to have the right geometry. In conjunction with that, increasing the surface area of solids may increase the rate of a reaction. The reasons are, by increasing the surface area or in other words by decreasing the particle size, it will allow for more collisions of particles and give more molecules the right geometry to react. In contrast, by increasing the particle size will result in less collision and therefore slower reaction will take place thus causing the thermal degradation characteristics and kinetic parameters to decrease regardless of the reaction zones.

4.3.3(b) Effect of Heating Rate

The effect of heating rate on thermal degradation and kinetic parameters of the sample shows that as the heating rate was increased from 35°C to 50°C, the total degradation and kinetic parameters were also increased in the first and second reaction zone.

Basically, the total degradations value corresponds to the volatile evolution phenomenon. According to the research done by Sampath [32], during devolatilization, a substantial thermophysical and thermochemical heat requirement is associated with volatile evolution. Maloney [33] work suggests that the coal or biomass structure is initially constrained and, at high heating rates, a finite time is required for the structure to relax and respond to the thermal input. This induction period may be responsible for pushing volatile evolution to a higher temperature. Hence, as the heating rate increased, the total degradation was also increased regardless of the reaction zones.

The kinetic parameters also increased as the heating rate was increased. This is in accordance with to the collision theory, increase in temperature will give more molecules the right energy (so called the activation energy) thus, increases the rate of reaction. This is proven by the results obtained in this study.

5. CONCLUSION

Two distinct reaction zones were observed for sludge, bagasse and sawdust. Based on Arrhenius equation, the kinetic parameters; activation energy and pre-exponential factors, were found to be significantly higher in the first reaction zone than that of in the second zone for sludge and bagasse where as an opposite trend was observed for sawdust.

6. REFERENCES

1. E. Natarajan, A. Nordin, A.N. Rao. "Overview of Combustion and Gasification of Rice Husk in Fluidized Bed Reactors". Biomass and Bioenergy, 14(5): 533-546, 1998
2. O.E. Albertson, A. Baturay. "Deodorization and Cleaning of Medium Temperature Wet Off-gases Derived from Burning of Wet Waste Sludge". Environmental International, 17(2-3): 11-111, 1991
3. M. Hoogwijk, A. Faaij, R. van den Broak, G. Berndes, D. Gielen, W. Turkenburg. "Exploration of the ranges of the global potential of biomass for energy". Biomass and Bioenergy, 25(2): 119-133, 2003
4. A.A. Tajuddin. "Hydroelectricity and TNB's Other Renewable Energy Initiatives". In Kamaruzzaman, Mohd Yusoff Hj. Othman, Baharuddin Yatim of World Renewable Energy Congress '99 Malaysia. 1999
5. A. Ergundenler, A.E. Ghaly. "Determination of reaction kinetics of wheat straw using thermogravimetric analysis". Applied Biochemistry and Biotechnology, 34/35(1):75-91, 1992
6. A.F. Ismail, A.H. Shamsuddin, F.M.A. Mahdi. "Reactivity Studies of Rice Husk Combustion Using TGA". In Kamaruzzaman, Mohd Yusoff Hj. Othman, Baharuddin Yatim of World Renewable Energy Congress '99 Malaysia. 1999
7. A.W. Coats, J.P. Redfern. "Kinetic Parameters from Thermogravimetric Data". Nature 201: 68-69, 1964
8. John H. Mathews. "NUMERICAL METHODS: for Mathematics, Science and Engineering". Prentice-Hall International Limited, London, UK. 1992
9. K.M. Sabil. "Study on the Production of Charcoal by Carbonization Using Mangrove Wood in Malaysia". In Proceedings of Second Engineering Congression Engineering Innovation and Sustainability: Global Challenges and Issues. Sarawak, Malaysia. 2002
10. A.S. Bining, B.M. Jenkins. "Thermochemical reaction kinetics for rice straw from an approximation integral technique". In ASAE Paper No. 92-6029. St. Joseph, MI, USA. 1992
11. S.S. Alves, Figueredo. "A model for pyrolysis for wet wood". Chemical Engineering Science, 44(12): 2861-2869, 1989
12. A. V. Bridgewater. "Progress in Thermochemical Biomass Conversion", Blackwell Science Ltd., pp. 47-48, 61-63, 632-633 (2001)
13. A.V. Bridgewater. "Developments in Thermochemical Biomass Conversion", Blackie Academic & Professional, pp. 294-296 (1997)
14. "Govt Agrees to Palm Oil Biomass for Power Project". In Business Times, 28/2/2001

15. "Biomass future for by-products". In Business Times, 3/9/2001
16. C.M. Earnest, R.I. Fyans. "Recent Advances in Microcomputer Control Thermogravimetry of Coal and Coal Products", ASTM STP 997, pp. 3 (1988)
17. Y. W. B. Charles, B.H. Essel. "Biomass Conversion And Technology", John Wiley & Sons, (1996)
18. E.C. Greencia, T. Aida, H. Niiyama, "The heating rates of carbonization". In Proceeding of Conference Advanced Catalytic Science and Technology. Tokyo Institute of Technology, Tokyo, Japan, 1997
19. A.E. Ghaly, A. Ergundenler. "Thermal degradation of cereal straws in air and nitrogen". Applied Biochemistry and Biotechnology, 27(1):111–126, 1991
20. I.J. Goldfarb, R. Guchan, A.C. Meeks. "Kinetic analysis of thermogravimetry. Part II. Programmed temperatures". In Report No. ARML-TR-68-181. Ohio: Air Force Laboratory, Wright-Patterson AFB, 1968
21. K.G. Mansaray, A.E. Ghaly. "Determination of Kinetic Parameters of Rice Husk in Oxygen Using TGA". Biomass and Bioenergy, 17(1): 19-31, 1999
22. K.O. Lim. "The Energy Potential and Current Utilization of Agriculture and Logging Wastes in Malaysia". The Planter, 57:182-187, 1986
23. K.O. Lim. "Energy Productivity of Some Plantation Crops in Malaysia and the Status of Bioenergy Utilization". In Kamaruzzaman, Mohd Yusoff Hj. Othman, Baharuddin Yatim of World Renewable Energy Congress '99 Malaysia. 1999
24. T.A. Milne, M.N. Soltys. "Direct Mass Spectrometric Studies of the Pyrolysis of Carbonaceous Fuels: II. Qualitative Observations of Primary and Secondary Processes in Biomass". Analytical and Applied Pyrolysis, 5(2): 111-131, 1983
25. T.A. Milne, M.N. Soltys. "Direct Mass Spectrometric Studies of the Pyrolysis of Carbonaceous Fuels: I. A Flame Pyrolysis Molecular-beam Sampling Technique". Analytical and Applied Pyrolysis, 5(2): 93-110, 1983
26. R.J. Evans, T.A. Milne, M.N. Soltys. "Direct Mass Spectrometric Studies of the Pyrolysis of Carbonaceous Fuels: III. Primary Pyrolysis of Lignin". Analytical and Applied Pyrolysis, 9(3): 207-236, 1986
27. V. Hornof, B.V. Kokta, J.L. Valade, J.L. Fassen. "Effect of Lignin Content of Thermal Degradation of Wood Pulp". Thermochemica Acta, 19(1): 63-68, 1977
28. K. Raveendran, A. Ganesh, K.C. Khilar. "Pyrolysis Characteristics of Biomass and Biomass Components". Fuel, 75: 987-998, 1996
29. M. Rozainee, M. Rashid, S. Looi. "Production of Renewable Energy From Biomass and waste Materials Using Fluidised Bed Technologies". In Kamaruzzaman, Mohd Yusoff Hj. Othman, Baharuddin Yatim of World Renewable Energy Congress '99 Malaysia. 1999
30. M.S. Duvvuri, S.P. Muhlenkamp, K.Z. Iqbal, J.R. Weker. "The Pyrolysis of Natural Fuels". Fire and Flammability, 62: 467 – 468, 1975
31. <http://www.Shodor.org/unchem/advanced/kin/index.html>

32. R. Sampath, D.J. Maloney, W.M. Proscia, E.R. Monazam. "*Effect of Heating Rate on the Thermodynamic Properties of Pulverized Coal*". In Semi-Annual Progress Report. Department of Engineering, Clark Atlanta University, Atlanta, 1998
33. Maloney, D.J., Sampath, R., and Zondlo, J.W., "*Heat Capacity and Thermal Conductivity Considerations for Coal Particles During Early Stages of Rapid Heating, Combustion and Flame*". *Combustion and Flame*, 116: 94-104, 1999
34. S. Yusoff, "*Renewable Energy Form Palm Oil – Innovation on effective Utilization of Waste*". *Cleaner Production*, 14: 87-93, 2006
35. Z. Husain, Z.A. Zainal, M.Z. Abdullah. "*Analysis of Biomass-residue-based Cogeneration System in Palm Oil Mills*". *Biomass and Energy*, 24: 117-124, 2003
36. J. Werther, T.Ogada. "*Sewage Sludge Combustion*". *Energy and Combustion Science*, 25(1): 55-116, 1999