MECHANISM AND REACTION KINETICS OF PEAT DECOMPOSITION

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ABSTRACT

Peat is one of natural resources with high potential which have not been used well, either as land or peat itself as a material. This researc aims to determine steps of rate limiting reaction, with data of kinetic parameter based on unreacted core model, and empirical model for correlation of conversion, reaction time at various variables. Research on peat pyrolisis was done batch wise in fixed bed reactor. Variation of time, temperature and bead diameter was done in the first year to formulate reaction mechanism and kinetic parameters. Second year was planned to study variation of gas flow, process pressure, and effect of catalyst which then used to optimize decomposition process. Data taken was the changes in peat masses in reactor at all time which was done by direct weighing. Also it was found the time needed for complete decomposition (□), which obtained at constant value of solid residue, tar and gas. Based on heterogenic kinetic model of it was found that all data could be well correlated using unreacted core model. Therefore, in the process of peat decomposition it can be assured that the limiting reaction was chemical reaction, following 1st order reaction. Similar to the effect of time, the rising of pyrolisis temperature also cause volatilized material rise in amount, thus collision frequency (k_o) and activation energy (E) rising. From correlation of temperature (T) to k, it was found that collision frequency, k_o=1.407.10^{-4} minutes, activation energy, E = 4326.2 cal/gmol, and k = 0.14(10^{-3}) exp (-4326.2/RT)

***Keywords**: pyrolisis, fixed bed, peat, reaction kinetic*

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Introduction

Indonesia has many kind of tropical peat (*ombrogeneus*) which were the largest in the world, more than 60% of its kind could be found in Indonesia. This kind of turf has relatively low sulfur and ash content. Processing of tropical peat mainly by means of pyrolysis produces solid residue (charcoal), tar and gasses. The boundaries for developing peat decomposition by pyrolysis were limited kinetic data and decision for thorough reaction rate equation. It was mainly caused by complex interconnection bwtween parameters affecting the reaction. Nevertheless, the assumptions used to formulate model were high in variation (Trianna dan Rochimullah, 2002). The different approach used resulted in different decompotition reaction rate model formulated by individual research (Trianna dan Mulyadi, 2006). Up to date, kinetic model and empirical equation formulated by previous research mostly used model mechanism of progressive-conversion model. For example, Varhegyi dan Antal (1989); Alves dan Figueiredo (1989); Caballero, et al. (1995); and Bilbao, et al. (1995). Therefore, formulation of reaction rate equation could be approached by pseudo homogenous reaction model.

1. Kinetic Formulation of Decomposition rate

By assuming that the diffusion to release vapor resulted from pyrolysis reaction happened spontaneously and mass transfer barrier could be ignored, then the overall reaction rate equation was limited by chemical reaction. Therefore decomposition was happened by *progressive-conversion model.* Reaction rate stated in mass fraction per time could be written as:

$$dC/dt = - k_h (C - C_\infty)^n \qquad (1),$$

with
τ = time needed for solid, tar and gas residue a become constant (i.e. at $m = m_\infty$),
n = reaction order,
k_h = constant for pseudo homogenous rate reaction, minutes^{-1}

Application of equation (1), which was generally done by first order approach (Bilbao, et al., 1995), defines that infinite time (τ) was needed to make solid, tar and gas residues become constant. The value of τ calculated starting when isothermal process began and the value of m_∞ was not affected by heating rate but by isothermal temperature. Based on theory by Arrhenius oleh Cabalero, et al., (1995), equation (1), could be written as:

$dC/dt = -k_o\, e^{-E/RT}\, (C - C_\infty)^n$ (2),

Caballero, et al., (1995), and Liliedahl and Sjostrom (1994), assumed that equation (2) follows first order reaction equation, therefore:

$dC/dt = -k_o\, e^{-E/RT}\, (C - C_\infty)$ (3),

In isothermal process, integration of equation (3) with boundary condition between t = 0 to t = t , obtaioned:

$\ln (1 - C_\infty) - \ln(C - C_\infty) = k_o\, e^{-E/RT}\, (t)$ (4).

or;

$\ln (m_t - m_\infty) = \ln(m_{to} - m_\infty) - k\, t$ (5).

2. Empirical formulation of decomposition rate

This formulation was generally done by exponential or polynomial model approach. Empirical formulation of decomposition rate was initially done by Badzioch and Hawksley (1970) by simulation using Gauss distributioin model and defined that:

C = matter volatile mass normalization, which $C = m_t/m_{to}$,
C_∞ = matter normalisation at $t = \tau$, which $C_\infty = m_\infty/m_{to}$
m_{to}= peat mass at initial isothermal temperature, gram,
m_t = residue mass at time = t, gram,
m_∞ = residue mass at $t = \tau$ at isothermal temperature, gram,
then:

$-[dC/dt] = k_1 C + k_2 C^3$ (6).

Next step was developed by Liliedahl and Sjostrom (1994), by formulating:

$m_t = m_{to}\, e^{(-k't)}$, then decomposition rate can be written:

$-[dm_t/dt] = k'\, m_{to}\, e^{(-k' t)}$ (7).

At t=t, *volatile matter* fraction that decomposed reached (x_s), so Liliedahl and Sjostrom (1994) defined *volatile matter* convertion as *devolatilization degree* which the value was:

$x_s = [m_{to} - m_t]/ [m_{to} - m_\infty]$ (8).

Trianna and Rochimullah (2002) done *unreacted core* model research (heterogen reaction) but was limited at first order reaction rate equation. The mathematic formulation model of decomposition reaction developed by Trianna and Mulyadi (2006) resulted in functional relation between convertion and reaction time stated by:

$x_s = -0{,}0152 + 0{,}1179\, t^{0{,}5}$. (9).

By substituting equation (8) to (5) then obtained:

$-\ln [(1 - x_s)] = k\, t$ (10).

If the reaction has been control, and reaction mechanism follow the constant size particles, and taking place in unreacted-core model, then

$-(1/a)[(dC)/dt] = k\, C_\infty = -[1/(a.m_{to})][dm_t/dt]$ (11).

By assuming solid particle was a sphere with equal size equation (11) become;

$-d\boldsymbol{r}/dt = k(m_{to} /\rho)\, C_\infty,$

$t = [(\boldsymbol{r}_o\, \rho)/(m_\infty\, k)](1 - \boldsymbol{r}/\boldsymbol{r}_o)$ (12)

or

$\boldsymbol{r}/\boldsymbol{r}_o = (1-x_s)^{1/3}$ (13).

By substituting (12) to (13):

$[1-(1-x_s)^{1/3}] = [(m_\infty\, k)/(\boldsymbol{r}_o\, \rho)]\, t = [1/\tau]\, t$ (14)

Material and Method

Peat raw material used was obtained from Pontianak. After being sun dried and separated it was then sieved according to diameter used in experiments. Peat was dried under the sun until water content reached 15%. The Peat was analyzed for water content, ash content, volatile matter, and fixed carbon, consecutively using method of ASTM D 3302-97 a, ASTM D 3174-97, and ASTM D3175-89a. Other method used to determine water content was by heating the peat inside oven at 110^{o}C. It was then cooled down in exicator and weighed until reached constant weight. Changes in weight is the water content inside turf. Analysis result shows that water content was 11,3 % , as content 13,9%, 48,2 % volatile matter, and fixed carbon was 28,2%. Size of peat beads was determined by standard sieving *teyler*. Turf was crushed and sieved. The smallest sieving size was 149 micron or 100 mesh, while the largest was 1410 micron or 12 mesh. Variations of bead size studied were 100, 80, 60, and 12 mesh.

Unit for pyrolisis was showed in figure 1. The reactor where pyrolisis took place was made from rust resistance steel. Tar cooler made from stainless steel and gas vessel was made from polyethylene/glass.

Research procedure, peat of certain size and weight was put into reactor (4). Heater (5) then turned on. Time (t) was counted after the desired temperature reached and reading of weighing/balance (6) was done to measure solid residue mass (m_{to}). Measurement of solid mass residue (m_t) was done repeatedly after some period of time. Same treatment also valid for the measurement of tar (bio-oil).

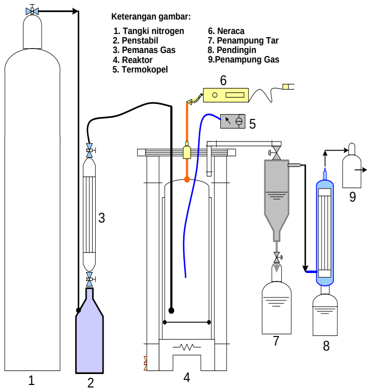

Figure 1. Pyrolisis Unit

Result and Discussion

Preliminary experiment was done to obtain the characteristic of heating and cooling of pyrolisis reactor. Heating was done from room temperature up to the highest temperature studied, i.e. 420 ^{o}C (figure 2). To reach the mentioned temperature, 45 minutes was needed.

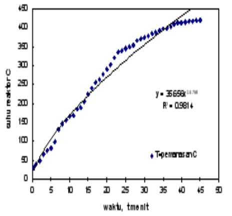

Figure 2. Plot between Heating Temperature and time

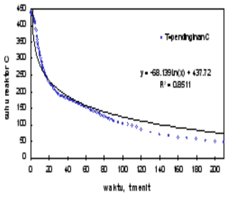

Figure 3. Plot between Cooling Temperature and time

Next, refrigeration of reactor was conducted. Temperature degradation in each moment was shown in figure 3. Hence, collection of result from reactor was done after refrigeration take place for three hours.

Turf used was originated from Pontianak, West Kalimantan. After dried under the sun, it was then separated and sieved according to diameter to be used in research. The raw material was analyzed for water content, ash content, volatile matter, and fixed carbon, consecutively using method of ASTM D 3302-97 a, ASTM D 3174-97, and ASTM D3175-89a. Size of turf beads was determined by standard sieving *teyler*. Turf was crushed and sieved. The smallest sieving size was 149 micron or 100 mesh, while the largest was 1410 micron or 12 mesh. Variation of bead size studied were 100, 80, 60, and 12 mesh.

Relation of Conversion with Time and Temperature, pyrolysis of turf or conversion of *volatile matter* was calculated by m_{to}, m_t, dan m_{∞}. To calculate conversion, turf mass inside reactor (measured as solid residue) was measured at various time and temperature. Conversion of volatile matter or *devolatilization degree* was calculated by $x_s = [m_{to} - m_t]/ [m_{to} - m_{\infty}]$. The value of $(m_{to} - m_t)$ was the volatilized mass at turf at every moment and the total mass of turf that could be volatilized was $(m_{to} - m_{\infty})$. Conversion if volatile matter in turf (x_s) was shown in figure 4. In figure 4, it can be seen that conversion of volatile matter un turf (x_s) was highly affected by processing time. It was caused by the higher probability of volatile matter to decomposed, therefore x_s increases. However, the rise was no longer seen after 45 minutes of pyrolisis time. Infinite time (τ_{data}) was the time needed to reach constant condition of solid residue, tar and gas. The value of τ_{data} measured after the process reached isothermal to the time at the turf mass inside reactor reahed constant. The value of turf mass measured as m_{∞}. Next, the data was used to calculate τ_r using equation:

$$[1-(1-x_s)^{1/3}] = t/\tau_r$$

.

or $X_1 = t/\tau_r$ with $x_1 = [1 -(1-x_s)^{1/3}]$,
According to the effect of t to x_s, the relation between t and x_1 was obtained and shown in figure 6.

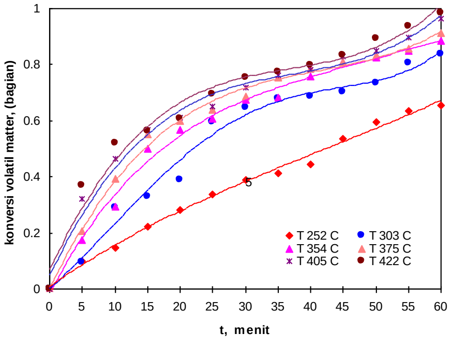

Figure 5. Relation of x_s and t

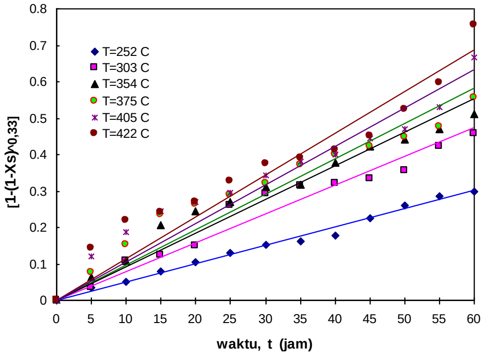

Figure 6. Relation of $[1 -(1-x_s)^{1/3}]$ with time

Numurical calculation could be applied to calculate τ_{count}. After τ_{count} determined, the the value of decomposition rate constant (k) could be calculated by equation:

$\tau_r = [(\boldsymbol{r}_o \rho)/(m_\infty k)]$ atau $k = [(\boldsymbol{r}_o \rho)/(m_\infty \tau_r)]$

Result of k value at various temperatures could be correlated well to the unreacted-core model. Doing so, process of turf decomposition could be certainly determined that chemical reaction was the control, and following first order reaction. As the effect of time, the rise in pyrolisis temperature caused increase in volatilized matter, thus increase in decomposed fraction (x_s). The rise was caused by increase of volatile matter movement so that collision frequency (k_o) and activation energy (E) rises, therefore decomposition rate constant (k) increase. From the influence of temperature (T) to k, then values of k_o and E could be determined by Arrhenius equation. Since points in figure 7 could generally approached by straight line, it was obtained: average error 1,04%, and value of collision frequency, k_0=1.407.10^{-4} minutes, gas constant, R = 1,987 cal/g.mol.^{0}K, and activation energy, E = 4326.2 cal/gmol. k = 0.14(10^{-3}) exp(-4326.2/RT). The effect of time to x_s, at various temperatures could illustrate the controlling reaction step.

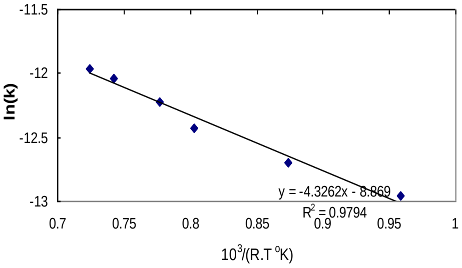

Figure 7. Relation of x_s and 10^3/(R.T ^{o}K)

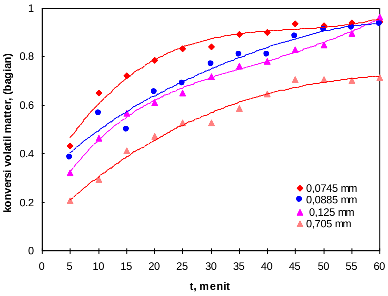

Figure 8. Relation of x_s and t and r

Experiment of bead size variation was done at 405^{o}C and studied r_o was about 0,00745 to 0,0705 cm. Figure 8 showed that the rise in bead diameter resulted in reduced conversion. The rise in bead size caused decrease in area for heat transfer per bead per mass unit of turf, hence decrease in pyrolisis rate. For bead at the same size, time gace significant affect to conversion. According to figure 8, the effect of increasing time to increasing conversion for each bead size has similar influence. In each studied bead size, rise up to 45 minutes could rise conversion significantly.

Conclusion

1. Rate of reaction controlled by chemical reaction, in the order of one, following unreacted-core model
2. Value of collision frequency, k_0=1.407.10^{-4} minute, and activation energy, E = 4326.2 cal/gmol, so that k = 0.14(10^{-3}) exp(-4326.2 / RT
3. Verifying value calculated from empiric formulation: [$\mathbf{x_s}$] = 0,6572 $(1/t)^{0,7808}$, with various model shows relatively same result. Especially at 252^{o}C with the time between 25 - 40 minutes.

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