MECHANISM AND REACTION KINETICS OF PEAT DECOMPOSITION

Edi Mulyadi1), Nurul Wiji Triana
Departement of chemical engineering, Faculty of Industry Technology
UPN “Veteran” East Java Indonesia (60295)

email : edimulyad1@yahoo.com;

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 research 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 pyrolysis 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 (τ), 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 pyrolysis 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, \( k_o = 1.407 \times 10^{-4} \) minutes, activation energy, \( E = 4326.2 \) cal/gmol, and \( k = 0.14(10^{-3}) \exp (-4326.2/RT) \)

Keywords: pyrolysis, fixed bed, peat, reaction kinetic

Acknowledgements

Authors are grateful for financial support from DP2M DIKTI (Hibah fundamental)

Introduction

Indonesia has many kind of tropical peat (ombrogenous) 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 between parameters affecting the reaction. Nevertheless, the assumptions used to formulate model were high in variation (Trianna dan Rochimuth, 2002). The different approach used resulted in different decomposition 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:

\[
\frac{dC}{dt} = -k_h (C - C_x)^n
\]  

with

\( \tau = \) time needed for solid, tar and gas residue a become constant (i.e. at \( m = m_x \)),

\( n = \) 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 (\( \tau \)) was needed to make solid, tar and gas residues become constant. The value of \( \tau \) calculated starting when isothermal process began and the value of \( m_x \) 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:
$$\frac{dC}{dt} = -k_0 e^{-E/RT} (C - C_\infty)^n$$  \hspace{1cm} (2).

Cabalero, et al., (1995), and Liliedahl and Sjostrom
(1994), assumed that equation (2) follows first order
reaction equation, therefore:
$$\frac{dC}{dt} = -k_0 e^{-E/RT} (C - C_\infty)$$  \hspace{1cm} (3),

In isothermal process, integration of equation
(3) with boundary condition between \( t = 0 \) to \( t = t \),
obtained:
$$\ln (1 - C_\infty) - \ln(C - C_\infty) = k_0 e^{-E/RT} (t)$$  \hspace{1cm} (4),
or;
$$\ln (m_r - m_\infty) = \ln(m_{r0} - m_\infty) - k t$$  \hspace{1cm} (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 distribution model and defined that:
$$C = \text{matter volatile mass normalization, which } C = \frac{m}{m_{r0}},$$
$$C_\infty = \text{matter normalisation at } t = \tau , \text{ which } C_\infty = \frac{m_\infty}{m_{r0}},$$
$$m_\infty = \text{peat mass at initial isothermal temperature, gram,}$$
$$m_r = \text{residue mass at initial isothermal temperature, gram,}$$
$$m_\infty = \text{residue mass at } t = \tau \text{ at isothermal temperature,}$$

then:
$$-[dC/dt] = k_1 C + k_2 C^3$$  \hspace{1cm} (6).

Next step was developed by Liliedahl and Sjostrom
(1994), by formulating:
$$m_k = m_{r0} e^{(-k_1 t)}, \text{ then decomposition rate can be}$$
written:
$$-[dm/dt] = k' m_{r0} e^{(-k_1 t)}$$  \hspace{1cm} (7).

At \( t=\tau \), volatile matter fraction that decomposed reached
\((x_\infty)\), so Liliedahl and Sjostrom (1994) defined volatile
matter conversion as devolatilization degree which the value was:
$$x_\infty = [m_{r0} - m_r]/[m_{r0} - m_\infty]$$  \hspace{1cm} (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 conversion and reaction time stated by:
$$x_\infty = 0.0152 + 0.1179 t$$  \hspace{1cm} (9).

By substituting equation (8) to (5) then obtained:
$$-\ln [(1 - x_\infty)] = k t$$  \hspace{1cm} (10).

If the reaction has been control, and reaction
mechanism follow the constant size particles, and taking
place in unreacted-core model, then
$$-(1/a)\frac{dC}{dt} = k C_\infty = -[(1/a.m_{r0})][dm/dt]$$  \hspace{1cm} (11).

By assuming solid particle was a sphere with equal size
equation (11) become;
$$-\frac{dr}{dt} = k(m_{r0}/\rho) C_\infty,$$
$$t = \frac{(r_\infty - r_0)/(m_{r0} k)}{(1 - r/r_\infty)}$$  \hspace{1cm} (12)
or
$$r/r_\infty = (1-x_\infty)^{1/3}$$  \hspace{1cm} (13).

By substituting (12) to (13):
$$[1 - (1-x_\infty)^{1/3}] = [(m_{r0} k)/(r_\infty \rho)] \frac{t}{[1/\tau]}$$  \hspace{1cm} (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°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 telyer. 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 pyrolysis was showed in figure 1. The
reactor where pyrolisis took place was made from rust
resistance steel. Tar collector 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 (\( m_r \)). Measurement of solid
mass residue (\( m_r \)) was done repeatedly after some period
of time. Same treatment also valid for the measurement of tar (bio-oil).

**Figure 1. Pyrolysis Unit**

**Result and Discussion**

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

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 \( m_{\infty} \), \( m_t \), dan \( m_s \). 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 \( x_s = \frac{[m_{\infty} - m_t]}{[m_{\infty} - m_s]} \). The value of \( (m_{\infty} - m_t) \) was the volatilized mass at turf at every moment and the total mass of turf that could be volatilized was \( (m_{\infty} - m_s) \). 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 pyrolysis time. Infinite time \( (\tau_{\text{data}}) \) was the time needed to reach constant condition of solid residue, tar and gas. The value of \( \tau_{\text{data}} \) measured after the process reached isothermal to the time at the turf mass inside reactor reahed constant. The value of turf mass measured as \( m_{\infty} \). Next, the data was used to calculate \( \tau_r \) using equation:

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

or \( X_1 = \frac{t}{\tau_r} \) 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 \( t \)](image-url)
Figure 6. Relation of $[1-(1-x_s)^{0.33}]$ with time

Numerical calculation could be applied to calculate $\tau_{\text{count}}$. After $\tau_{\text{count}}$ determined, the value of decomposition rate constant ($k$) could be calculated by equation:

$$\tau = [(r_o \rho)/(m_o k)]$$

or

$$k = [(r_o \rho)/(m_o \tau)]$$

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 pyrolysis 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, $k_o=1.407.10^{-4}$ minute, gas constant, $R = 1.987$ cal/g.mol.$^o$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 $10^3/(R.T^oK)$

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 pyrolysis rate. For bead at the same size, time gave 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, $k_o=1.407.10^{-4}$ 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: $[x_s] = 0,6572 \ (1/t)^{0.7808}$, with various model shows relatively same result. Especially at 252$^o$C with the time between 25 - 40 minutes.

Reference:


Trianna, N.W., dan Rochimoelah,M, 2002, Model Kinetika Reaksi Heterogen pada Proses Pyrolysis Prosiding SemNas Rekayasa Kimia dan Proses, ISSN 1411-4216, B-16, UNDIP