Risk Evaluation on the Basis of Pressure Rate Measured by Automatic Pressure Tracking Adiabatic Calorimeter

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INTRODUCTION

Characteristics of APTAC

- The automatic pressure tracking adiabatic calorimeter (APTAC) had been used in order to estimate the hazards of the thermal decomposition of the reactive substances.

- The APTAC is an adiabatic calorimeter with a large-scale sample mass and low thermal inertia.

- The adiabatic control system of APTAC is the same as the accelerating rate calorimeter (ARC), which is familiar for the adiabatic calorimeter.
Characteristics of APTAC

- The APTAC maintains an adiabatic condition once an exothermic reaction from sample is detected.
- The adiabatic condition means no heat loss from sample to outside through the sample vessel.
- The adiabatic condition is achieved by making the sample and the ambient temperatures exactly equal.
- The pressure outside of the sample cell is controlled to cancel the generated pressure inside the sample cell to cancel the pressure difference during a reaction.
Problem

- The data obtained by the APTAC is important information for the design for the safe industrial process.
- However, the measurement data with the APTAC are limited and not enough for discussing the properties of the APTAC data in detail.
Purpose

- The pressure data is important for designing the pressure relief in the chemical reactor.
- The analysis and the evaluation method of the pressure data measured with the APTAC were emphasized in this paper.
- The decomposition of DTBP was investigated on the basis of pressure data measured with the APTAC.
The thermal decomposition of di-tert-butylperoxide (DTBP) was investigated in order to examine the temperature data and the pressure data of the APTAC.

The thermodynamics parameters and the gas production were discussed on the basis of the experimental data of various concentrations and weights of DTBP/toluene solution.

In addition, the thermal decomposition of DTBP was studied on the basis of the experimental data.
EXPERIMENT
Apparatus

- thermocouple
- pressure transducer and tube
- heater
- Teflon sheath
- sample
- stirrer tip
- magnadrive stirrer
- single shot injection
- relief valve
- vacuum
- exhaust
- N₂ cylinder
- pressure control valve
- magnadrive stirrer
- drop-outpot
- sample
- stirrer tip
- Teflon sheath
- pressure transducer and tube
- heater
- thermocouple
- vacuum
- exhaust
- N₂ cylinder
- pressure control valve
- magnadrive stirrer
- single shot injection
- relief valve
- vacuum
- exhaust
- N₂ cylinder
- pressure control valve
- magnadrive stirrer
- single shot injection
- relief valve
Temperature control

- Three N type thermocouples are used to measure:
  - (1) the temperature inside the sample,
  - (2) the surface temperature of the sample cell wall,
  - (3) the ambient temperature.

- The APTAC maintains an adiabatic condition once an exothermic reaction from sample is detected.

- The measured sample temperature is used in the adiabatic control of the APTAC.
Because the pressure outside of the sample cell is controlled to be equal to the pressure occurred inside the sample cell by the reaction, the glass cells such as made of weak materials or the sample cells with the low thermal inertia of a large-scale mass can be used in the experiments.
Correction of thermal inertia

φ-factor

- The φ-factor indicates the thermal inertia.
- The φ-factor is close to one when the sample mass is large.
- The φ-factor is defined as:
  \[ \varphi = 1 + \frac{M_c C_c}{M_s C_s} \]  
  Eq. (1)
- \( M_c \) (g) is the sample cell mass, \( M_s \) (g) sample mass, \( C_c \) (J/g/K) the sample cell specific heat, and \( C_s \) (J/g/K) is the sample specific heat.
- The \( C_c \) and \( C_s \) values are the specific heats averaged by each temperature closed to the heat onset temperature and the maximum temperature.
- The data of the specific heat are obtained in the literature.
All experiments were performed in a closed cell environment with the ambient air above the sample.

DTBP/toluene solutions were used to examine the properties of the data obtained by the APTAC.

The range of DTBP concentrations is between 20wt.% and 60wt.% in the DTBP/toluene solution.

Sample weights of DTBP/toluene solution are from 3.1g to 40.0g.

The range of the $\varphi$-factors is between 1.8 and 9.1.
Volume of the glass sample cell is 130cm$^3$. The borosilicate glass sample cells were used in the measurement of DTBP/toluene solutions.

The glass vessel is used to prevent the catalytic effect of the metal vessel surface in the experiments.

The thermocouple for the temperature measurement inside the sample was covered with a Teflon tube.
Measurement conditions

- The threshold to detect an exothermic reaction is 0.05 K/min of the heat rate.
- The sample temperature is automatically incremented by 10K in the case that the exotherm more than 0.05K/min is not detected by the thermocouple inside sample.
- The shut down criteria of heat rate is 400K/min.
- Pressure rise inside the sample cells during the reactions are followed up to about 7,500kPa of the pressure and 75,000kPa/min of the pressure rate.
Decomposition kinetics

- When the reaction order is one, $k$ (rate constant) is expressed by the following the equation:
  \[ k = \frac{dT/dt}{T_{\text{max}} - T} \]  
  (reaction order = 1)  
  Eq. (2)

  - The sample temperature ($T$ in K) and the maximum temperature ($T_{\text{max}}$ in K) were measured experimentally.

- The activation energy and the frequency factor are expressed by the following equation:
  \[ \log(k) = \log(A) - \frac{1}{2.303} \cdot \frac{E}{R/T} \]  
  Eq. (3)

  - $E$ is the activation energy (J/mol), $k$ is rate constant (1/s), and $A$ is the frequency factor (1/s).
  - $R$ is the gas constant (8.314J/mol/K).

- $E$ and $A$ are obtained by $\log(k)$ versus $(1/T)$ plot.
  $E$ is the slope and $A$ is the intercept on the straight line.
Pressure and gas production

- The gas production rate \((dn/dt)\) in mol/min of the noncondensable decomposition gas production is expressed by the following equation:
  \[
  (dn/dt) = \left( \frac{V}{RT} \right) \left[ (dP/dt) - \left( \frac{P}{T} \right)(dT/dt) \right] \quad \text{Eq. (4)}
  \]
- The sample volume was calculated using their densities and the weight ratio in solution.
- The corrected volume was calculated by subtracting the sample volume from the sample vessel volume (130 cm³).
- The pressure \((P\) in Pa), the pressure rate \((dP/dt)\) in Pa/min), the sample temperature \((T\) in K) and the heat rate \((dT/dt)\) in K/min) values are the measured data with the APTAC.
Pressure and gas production

- The \( (dn/dt) \) value is the gas production rate from the DTBP/toluene solution.
- The measured pressure \( (P) \) involves the pressure of the filling gas and the vapor pressure of DTBP and toluene due to the vapor-liquid equilibrium in the addition to the pressure generated by the production gas in Eq.(4).
- The vapor pressure for the DTBP and toluene in the vapor-liquid equilibrium are calculated on the Antoine equation.
- The vapor pressure correction regarding to DTBP and toluene is applied to the measured pressure data.
Pressure and gas production

- The calculated vapor pressure of DTBP and toluene is subtracted from the measured pressure data to obtain the corrected pressure \( P_{ac} \). The \( P_{ac} \) value is the total pressure of the noncondensable decomposition gas and the filling gas.

- The \( (dn_{ac}/dt) \) value is the corrected gas production rate.

- A subscript of \( ac \) expresses the correction of the vapor pressure correction.

- The same equation as Eq.(4) is realized using \( (dn_{ac}/dt) \) and \( P_{ac} \):

\[
(dn_{ac}/dt) = (V/RT) [(dP_{ac}/dt) - (P_{ac}/T)(dT/dt)]
\]
Pressure and gas production

- The DTBP concentration can be represented by the following equation in the adiabatic condition:
  \[ x = x_o \frac{(T_{\text{max}} - T)}{(T_{\text{max}} - T_{\text{onset}})} \]  
  Eq. (5)
  where \( x \) (-) is the DTBP mass fraction in reaction, \( x_o \) (-) is the initial DTBP mass fraction, \( T_{\text{max}} \) (K) is the maximum temperature, and \( T_{\text{onset}} \) (K) is the heat onset temperature.

- The mass loss rate of DTBP at the certain temperature is given by the following equation:
  \[ -(\frac{dm}{dt}) = -m_o \cdot (x) \cdot (k) \]  
  Eq. (6)
  where \( (dm/dt) \) (g/min) is the mass loss rate of DTBP and the \( m_o \) (g) is the initial DTBP mass.

- The mass loss rate can be calculated with the kinetic parameters and the temperature data obtained by the APTAC. The DTBP decomposition reaction is assumed to be the first-order reaction.
Pressure and gas production

- One can express the production rate of the noncondensable decomposition gas \((dn/dt)\) using the gas production index \((N_{ncg})\) and the mass loss rate by the following equation:
  \[
  (dn/dt) = -N_{ncg} \cdot (dm/dt)/M_w
  \]
  Eq. (7)
  where \(N_{ncg}\) is the gas production index and \(M_w\) (g) is molecular weight of DTBP (146.22 g).

- \(N_{ncg}\) shows the mole ratio of the gas production occurred by the decomposition of DTBP to DTBP contained in the sample.

- The \(\Delta n\) (mol) value is an amount of the noncondensable decomposition gas production occurred during the measured time interval from \(t_1\) to \(t_2\) (\(\Delta t\) in min) of the APTAC as the following equation:
  \[
  \Delta n = (dn/dt) \Delta t
  \]
  Eq. (8)
Pressure and gas production

- An amount of the noncondensable decomposition gas production at a certain time \((t_1)\) was represented by \(\Delta n\).

- The total amount of the noncondensable decomposition gas production \((n_{\text{total}} \text{ in mol})\) during the reaction is calculated as the following equation:

\[
\Delta n_{\text{total}} = \sum_{t_o}^{t_{\text{max}}} \Delta n . \quad \text{Eq. (9)}
\]

- The \(t_o\) and \(t_{\text{max}}\) values express the times close to the heat onset temperature and \(T_{\text{max}}\).
Pressure and gas production

- The maximum gas production index ($N_{\text{ncg, max}}$) is used for evaluating the intensity of the gas production.

$$N_{\text{ncg, max}} = -(dn/dt)_{\text{max}} \cdot M_w / (dm/dt)_{\text{max}}.$$  Eq. (10)

where $((dn/dt)_{\text{max}} \text{ (mol/min)})$ is the maximum gas production rate of the noncondensable decomposition gas and $((dm/dt)_{\text{max}} \text{ (g/min)})$ is the maximum mass loss rate.

- The total gas production index ($N_{\text{ncg, total}}$) can be expressed by the total of the noncondensable gas production ($\Delta n_{\text{total}}$ in mol) as the following equation:

$$N_{\text{ncg, total}} = -\Delta n_{\text{total}} \cdot M_w / m_o.$$  Eq. (11)

- The $N_{\text{ncg, total}}$ is the intrinsic parameter in the gas production generated by the thermal decomposition of DTBP.

- The $N_{\text{ncg, max}}$ and the $N_{\text{ncg, total}}$ values are dimensionless.
RESULTS and DISCUSSION

Fig. 1 Example of heat rate and pressure rate
DTBP 40wt.%/toluene solution.
The sample weight is 13.0g ($\varphi=3.1$).
Heat rate and pressure rate of DTBP

- A number of experiments were conducted using DTBP/toluene solution to investigate the properties of the APTAC and the DTBP decomposition.
- The sensibility and the response of the APTAC are better than those of the equipments controlling by the temperature of the sample vessel wall such as the ARC.
- Figure 1 shows an example of the heat rate and the pressure rate of DTBP 40wt.%/toluene solution. The sample mass is 13.0g (φ =3.1).
- The heat rate maximum is 227 K/min.
Fig. 2  The relationship between the sample weight and the activation energy. The samples are DTBP/toluene solutions with the concentrations between 20wt.% and 60wt.%. 
Fig. 3 The relationship between the sample weight and the frequency factor. The samples are DTBP/toluene solutions with the concentrations between 20wt.% and 60wt.%.
Decomposition kinetics

- The activation energy and the frequency factor are nearly the same as the literature values. $E$ and $\log(A)$ in the literature are 155.64 kJ/mol and 15.62 (1/s), respectively.
  - This result shows the experimental method and the data analysis is appropriate in the measurement of the APTAC.
- $E$ and $\log(A)$ are nearly the constant for the DTBP concentrations.
  - This result shows the reaction process does not vary in the different DTBP concentrations.
Example of $1/T$ vs. $-\log(k)$

DTBP 40wt.%/toluene solution. The sample mass is 13.0g ($\phi = 3.1$).
Decomposition kinetics

- The kinetic plot in the decomposition of DTBP/toluene solution shows the reaction number can be regarded as the first-order of the overall reaction in all of the concentrations because the fitting curves are straight.

- The (-log(k)) data values are not on the fitting line near the onset and the end of reaction.
Fig. 4 The example of the time history of the mass loss rate calculated by the measurement data of the APTAC. The sample is DTBP40wt.%/toluene solution with the sample mass of 13.0g.
The time at the maximum mass loss rate closed to the time at the maximum temperature. The time difference between the maximum mass loss rate and the maximum gas production rate is less than about 0.3(s) when the DTBP concentration is more than 30wt.% and the weight is more than 5g.

There is the tendency the time difference is large in the case of the samples with the small amount of DTBP in the DTBP 20wt.% /toluene solution.
Fig. 5 The relationship between the maximum mass loss rate \((dm/dt)_{max}\) and DTBP weight (g) in toluene in various concentrations of DTBP.

\[-(dm/dt) = -m_0 \cdot (x) \cdot (k)\]
Maximum mass loss rate

- The \((\text{dm/dt})_{\text{max}}\) value increases exponentially for the DTBP weight.
- The \((\text{dm/dt})_{\text{max}}\) value increases drastically when the DTBP weight in DTBP/toluene solution is beyond 3g excluding the case of the sample of 20wt.%.  
- *The \((\text{dm/dt})_{\text{max}}\) value increases with the increase of the DTBP concentration when the DTBP weight is more than 3g.
Gas production

\[
(\frac{dn}{dt}) = \left( \frac{V}{RT} \right) \left[ (\frac{dP}{dt}) - \left( \frac{P}{T} \right) (\frac{dT}{dt}) \right]
\]

\[\Delta n = (\frac{dn}{dt}) \Delta t\]

Fig. 6 The time history of the gas production with and without the vapor correction of DTBP and toluene in the vapor-liquid equilibrium. The sample is DTBP 40wt.%/toluene with 13.0g of sample weight.
Gas production

- The time history of the noncondensable decomposition gas production ($\Delta n$ and $\Delta n_{ac}$) with and without the vapor correction of DTBP and toluene in the vapor-liquid equilibrium.
  - The sample is DTBP 40wt.%/toluene with 13.0g of sample weight.
- The correction means the vapor correction in the vapor-liquid equilibrium in Fig. 6.
- The moving averages over ten points before and after the certain point are drawn to smooth the line in the time history.
  - The $T_{onset}$ and $T_{max}$ values become the each averaged value as the calculation results of the moving average when the moving averages are calculated.
Gas production

- A subscript of ac expresses the correction of the vapor pressure correction.
- There is the same tendency with $\Delta n$ and $\Delta n_{ac}$ of the vapor correction and without the vapor correction.
  - The decomposition gas occupies the large part in the sample vessel with compared to the vaporization of DTBP and toluene.
- The gas production increases drastically in the end of the reaction.
Maximum gas production rate

\[
\frac{dn_{ac}}{dt} = \left(\frac{V}{RT}\right) \left[\left(\frac{dP_{ac}}{dt}\right) - \left(\frac{P}{T}\right)\left(\frac{dT}{dt}\right)\right]
\]

Fig. 7 The relationship between \((dn_{ac}/dt)_{\text{max}}\) and DTBP weight (g) in toluene in various concentration of DTBP.

The \((dn_{ac}/dt)_{\text{max}}\) value was calculated by the vapor pressure correction of DTBP and toluene in the vapor-liquid equilibrium.
Maximum gas production rate

- The \((dn_{ac}/dt)_{max}\) value increases exponentially for the DTBP weight.
- The \((dn_{ac}/dt)_{max}\) value increases drastically when the DTBP weight in DTBP/toluene solution is beyond 3g excluding the case of the sample of 20wt.%. 
- *The \((dn_{ac}/dt)_{max}\) value increase with the increase of the DTBP concentration when the DTBP weight is more than 3g. The behavior of the \((dn_{ac}/dt)_{max}\) value is in the similar manner of the behavior of \((dm/dt)_{max}\).
Total gas production

\[ \Delta n_{ac,\text{total}} = \sum_{t_0}^{t_{\text{max}}} \Delta n_{ac} \cdot \Delta t \]

\[ \Delta n_{ac} = \frac{\Delta n_{ac}}{\Delta t} \]

Fig. 8 The relationship between \( \Delta n_{ac,\text{total}} \) and number of moles of DTBP(mol) in toluene in various concentration of DTBP. The \( \Delta n_{ac,\text{total}} \) values were calculated by the vapor pressure correction of DTBP and toluene in the vapor-liquid equilibrium.
Total gas production

- The $\Delta n_{ac,\text{total}}$ value increases proportionally to the number of DTBP mol number. This indicates that the DTBP decomposition gas increases in proportional relation to the mass of DTBP in DTBP/toluene solution.

- This result is consistent with the experimental fact that the decomposition process is the same in various concentrations of DTBP.
Gas production index

- $N_{n_{cgb},ac,total}$ is the gas production index which is one of the intrinsic properties. $N_{n_{cgb},ac,total}$ shows the mole ratio of the gas production occurred by the decomposition of DTBP to DTBP contained in the sample.
  - For example, The $\Delta n_{ac,total}$ value of the DTBP/toluene sample is 0.037 mol in DTBP40wt.% with 13.0g. The number of moles of DTBP in the DTBP/toluene sample is 0.036mol. $N_{n_{cgb},ac,total}$ is calculated to be 1.0.

- The averaged $N_{n_{cgb},ac,total}$ is 1.0 when all data are calculated. This value indicates DTBP of one mol generates the decomposition gas of 1.0 mol in the whole reaction.

- The averaged $N_{n_{cgb},total}$ is 1.8. The averaged $N_{n_{cgb},total}$ involves the vapor pressure of DTBP and toluene.
Gas production index at maximum mass loss rate

$$N_{ncg,\text{ac, max}} = -(dn/dt)_{\text{max}} \cdot M_w / (dm/dt)_{\text{max}}$$

Fig. 9 The relationship between $N_{ncg,\text{ac, max}}$ and DTBP weight (g) in toluene in various concentration of DTBP. The $N_{ncg,\text{ac, max}}$ values were calculated by the vapor pressure correction of DTBP and toluene in the vapor-liquid equilibrium.
Gas production index at maximum mass loss rate

- The time of \((dm/dt)_{max}\) should correspond to the same time with the time of \((dn_{ac}/dt)_{max}\) in the ideal condition in the experiments.
- The \(N_{ncg,ac,max}\) was calculated using \((dm/dt)_{max}\) and \((dn_{ac}/dt)_{max}\) though there was the time difference between the \((dm/dt)_{max}\) and \((dn_{ac}/dt)_{max}\) in the actual experimental results.
- The \(N_{ncg,max}\) value is used for evaluating the intensity of the gas production.
Gas production index at maximum mass loss rate

- Because $N_{ncc, ac, max}$ is larger than $N_{ncc, ac, total}$, it is assumed that the complicated decomposition occurs near the end of reaction.

- This assumption is supported by the experimental result that the $(-\log(k))$ data are not on the fitting line of the kinetic plot $((-\log(k) \text{ vs. } 1/T))$ in the end of reaction.
Gas production index at maximum mass loss rate

- The DTBP sample of less than 2.3g in DTBP/toluene solution involved the error because the temperature data varied widely. The dividing the gas production rate by mass loss rate expanded the error in $N_{ncg,ac,\text{max}}$. The data of the DTBP sample of less than 2.3g are deleted in Fig.9.
- The $N_{ncg,\text{max}}$ values range from 5.7 to 16.2.
- The $N_{ncg,ac,\text{max}}$ values range from 3.0 to 12.8. The $N_{ncg,\text{max}}$ and $(dn_{ac}/dt)_{\text{max}}$ are the corrected values considering the vapor pressure.
- The intensity of the gas production can be evaluated by $N_{ncg,\text{max}}$. The $N_{ncg,\text{max}}$ value expresses nearer situation to the real gas production than the $N_{ncg,ac,\text{max}}$ value because the vapor pressure effect is considered in the $N_{ncg,\text{max}}$ value.
CONCLUSIONS(1)

- The activation energy and the frequency factor of DTBP are nearly constant and the same as the literature values in the concentrations between 20wt.% and 60wt.%. This result suggests the process of the decomposition reaction is the same though the DTBP concentration changes, and the experimental method and the data analysis are appropriate in the measurement of the APTAC.
The time history of the gas production was evaluated with various weights and concentrations.

- The DTBP decomposition gas increases in proportional relation to the mass of DTBP in DTBP/toluene solution.
- This result is consistent with the experimental fact that the decomposition process is the same in various concentrations of DTBP.

The total gas production index $N_{ncg, ac, total}$, which has the vapor pressure correction, is 1.0 in the decomposition of DTBP.

- This experimental result indicates DTBP of one mol generates the decomposition gas of 1.0 mol in the whole reaction.