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Evaluation of Thermal Decomposition Kinetics of Borax Pentahydrate Using Genetic Algorithm Method by Isothermal Analysis

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The thermal calcination of borax pentahydrate was investigated for both dehydration and decomposition steps at temperatures between 392 and 573 K in a controlled fluidized bed drier. The best kinetic parameters (reaction rate constants, reaction order and equilibrium values) of both steps were determined by the genetic algorithm (GA) method for each calcination temperature in respect of relative standard deviation. The values of the kinetic parameters showed that the dehydration step of borax pentahydrate was controlled by a homogeneous reaction of the order of about 2/3 whereas the decomposition step was controlled by a reaction order of about 1. These kinetic parameters determined by GA were also utilized to compare the experimental results with theoretical calculations.

Activation energy was calculated to be 92.88 kJ/mole and 15.94 kJ/mole for the dehydration and decomposition steps, respectively.

Key Words: Borax pentahydrate, dehydration kinetics, decomposition kinetics, genetic algorithm, fluidized bed drier, activation energy.

Introduction

Borax pentahydrate (BPH) is one of the most important commercial boron compounds produced in large tonnages. BPH and borax decahydrate (BDH) are used in many areas, such as perborate production and detergent formulation. However, the most suitable borax compound for the manufacture of high quality glass, ceramic materials, enamels and frit is anhydrous borax (BA), produced from BPH and BDH¹. On the other hand, crystalline BDH, together with its pentahydrate (BPH), contain 47.2% and 29.5% water, respectively. Thus the dehydration of BPH to BA decreases transport costs considerably with respect to the B₂O₃ component.

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The crystalline BPH structural formula can best be represented as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2.67\text{H}_2\text{O}$, which means that 2 moles of water are in the molecular structure and the remainder is the real crystal water². It is predicted that 2.67 moles of water of the crystallization of BPH can easily be eliminated by thermal treatment, but the removal of the remaining 2 moles of structural water is much more difficult.

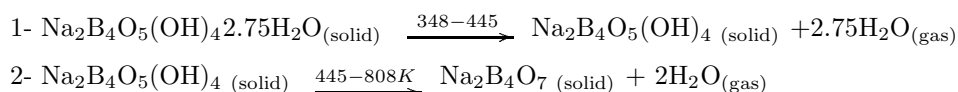
In order to establish calcination schedules and to determine the size of the equipment, it is necessary to know the time required to calcinate BPH from one water content to another specified water content. Measurement of the rate of batch calcination is relatively simple and provides considerable information on batch and continuous operation³.

Although many studies have been carried out⁴⁻⁵ on the decomposition of BPH to BA in fluidized beds, we have not noticed any studies on the calcination kinetics of BPH by isothermal analysis. The main advantage of isothermal compared to nonisothermal methods is that the reaction mechanism can be determined, and hence, the meanings of the activation energy, order of reaction and frequency factor are certain. The use of nonisothermal kinetic methods has been seriously questioned⁶ and much criticized⁷⁻⁹. Therefore, the results obtained for the calcination of borax dihydrate and anhydrous borax from BPH is suitable for application for industrial purposes. Neither have we seen any application of the genetic algorithm (GA) method for the determination of the kinetic parameters of solid-state in isothermal conditions. The GA method has had many applications in chemical engineering. Very recently, Grau et al.¹⁰ presented an approach for the optimal feeding profile in a fed-batch reactor using GA, and Sahin et al.¹¹ used the GA method to obtain the kinetic parameter of thermal analysis.

The main aim of this study is to determine the kinetic parameters of the dehydration and decomposition steps of BPH by the GA method.

Calcination of borax pentahydrate

In the literature, the thermal decomposition of many solid materials has been reported to occur in steps¹²⁻¹⁴. In a previous study¹⁵, the DTA and simultaneous TG-DTG analysis of the BPH used in the experiments showed that the calcination of BPH was realized in two steps, and the total weight loss was calculated as 29.82%, which corresponds to the removal of 4.75 moles of water in a temperature range of 316 to 808 K. These calcination steps can be formulated as



The following changes were observed during calcination of BPH to BA:

- When the dehydration step was carried out at a temperature higher than 393 K, X-ray patterns showed that the crystal structure of BPH becomes amorphous, which causes cracks and channels. Thus, water escapes from these channels without constituting a barrier.
- The bulk density decreased from $0.312 \text{ g}\cdot\text{cm}^{-3}$ to $0.085 \text{ g}\cdot\text{cm}^{-3}$ between the temperatures of 423 K and 573 K during the decomposition of borax dihydrate to anhydrous borax⁵. These results show that the decomposition of borax causes puffing and therefore, the mass transfer step is negligible in respect to that of the surface step; i.e., the kinetics of the surface reaction control the rate.

In the isothermal condition, if the calcination is continued for the time required, the water content of the solid will fall to equilibrium value $n_e(\text{mol})$, corresponding to the relative humidity and temperature

of the inlet air. At this point, calcination reaches equilibrium and stops. At any time of calcination, the amount of removable water, $n-n_e$, is called the free water content¹⁶.

This type of reaction can be expressed as

$$-\frac{dx}{dt} = k(x - x_e)^r \quad (1)$$

where x is the mole fraction content of the sample at time t , x_e is the equilibrium mole fraction of sample and, r is the reaction order.

Eq. 1 can be reduced to the Erofeev form of Mampel's unimolecular law for $r = 1$; it conforms to the three-dimensional and two-dimensional shrinking core model for $r = 1/3$ and $1/2$ respectively. The equation follows Avrami's nucleation law (constant density of nuclei one-dimensional nucleus) for $r = 0^{12}$ since Eq. 1 resembles the nonisothermal analysis equation.

After integration for $r \neq 1$ the following general equation is obtained:

$$\frac{1}{(r-1)} \left(\frac{1}{(x-x_e)^{r-1}} \right) = k.t + C \quad (2)$$

The constant, C , can be determined by using boundary condition; $t = 0$, $x = x_o$. Under this condition the last form of Eq. 2 is

$$\frac{1}{(r-1)} \left(\frac{1}{(x-x_e)^{r-1}} - \frac{1}{(x_o-x_e)^{r-1}} \right) = k.t \quad (3)$$

where k is the reaction rate constant.

In this study the relative standard deviation was calculated by the following route:

Eq. 3 can be subdivided into two parts in the event of knowing reaction order "r" and equilibrium mole fraction x_e

$$\text{part 1 } Y_1 = \frac{1}{r-1} \left(\frac{1}{(x-x_e)^{r-1}} - \frac{1}{(x_o-x_e)^{r-1}} \right) \quad (4)$$

This side of Eq. 3 can be calculated easily under the assumption of a constant "r" value and equilibrium mole fraction value, x_e .

$$\text{part 2 } Y_2 = k.t \quad (5)$$

Thus the values of relative standard deviation (σ) can be calculated as follows:

$$\sigma = \sqrt{\frac{\sum (Y_1 - Y_2)^2}{N - 1}} \quad (6)$$

The constants (k , r , x_e) of Eq. 3 can be determined without any assumption and linearization by the GA method. However, the decreasing number of unknown constants results in a high efficiency for searches by the GA method¹⁷. For instance, constant values of k in Eq. 3 were calculated for each constant value of r and x_e obtained randomly in the GA program as follows:

$$k = \frac{\sum_{r=0}^{r=r_i} \frac{1}{r-1} \left(\frac{1}{(x-x_e)^{r-1}} - \frac{1}{(x_o-x_e)^{r-1}} \right)}{\sum_{t=0}^{t=t_i} t} \quad (7)$$

The efficiency of GA method was increased by using this formula.

Materials and Methods

The experimental system is shown in Figure 1. In order to see the fluidization properties during calcination, a heat-resistant glass column 600 mm long and 40 mm in inner diameter was used. The distribution plate was made of 2 mm thick stainless steel containing 39 holes, each 0.1 mm in diameter. The outer surface of the column was insulated with 40 mm thick ceramic wool. The temperature of the fluidization air was measured by Ni-Cr thermocouples fixed at the bottom of the distribution plate.

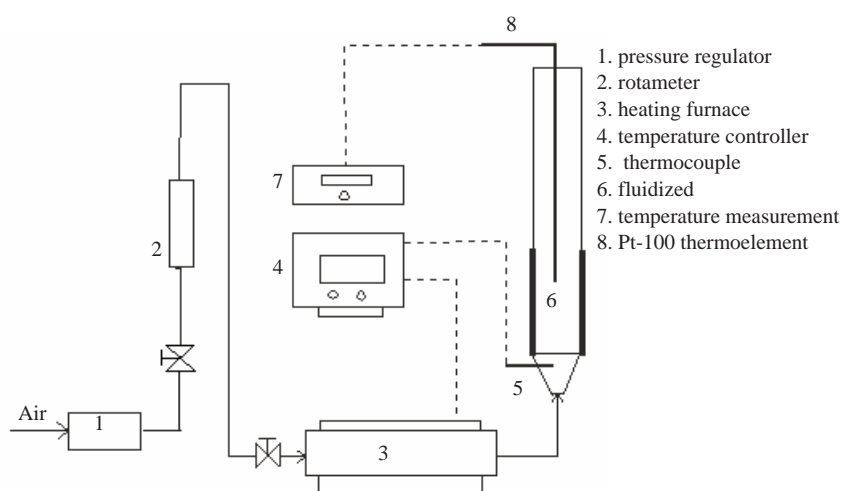


Figure 1. Schematic diagram of experimental system.

The thermal dehydration and decomposition steps of BPH were investigated in a fluidized bed at 392 K and 400 K; 408 K, 412 K and 423 K, 473 K, 523 K and 573 K.

The fluidization air was heated by a temperature-controlled furnace and then fed into the a fluidized bed at a rate determined by fluidization. During constant temperature experiments, particles were fed to the top of fluidized bed calcinator and these were at the thermal equilibrium at the experimental temperature. At a predetermined time interval, samples were taken out by a vacuum tube. The titrimetric method using standard HCl(0.1 N) solution as the titrant and methyl orange as the indicator was used to determine the $\text{Na}_2\text{B}_4\text{O}_7$ content of the sample¹⁸. The water content was calculated analytically by the $\text{Na}_2\text{B}_4\text{O}_7$ content of the sample. Bulk density was measured by a standard method¹⁹.

The particle size of BPH used in experiments was chosen in the range of $-600 + 500 \mu\text{m}$ and bulk density was 0.191 gr/cm^3 . Technical grade BPH obtained from ETİHOLDİNG (Kırka-Turkey) was used in the experiments. The original $\text{Na}_2\text{B}_4\text{O}_7$. content of the samples was determined to be 69.98% by the titrimetric method.

The GA method was applied to determine the kinetic parameters of the thermal calcination of BPH. The operation steps of GA are illustrated in Figure 2.

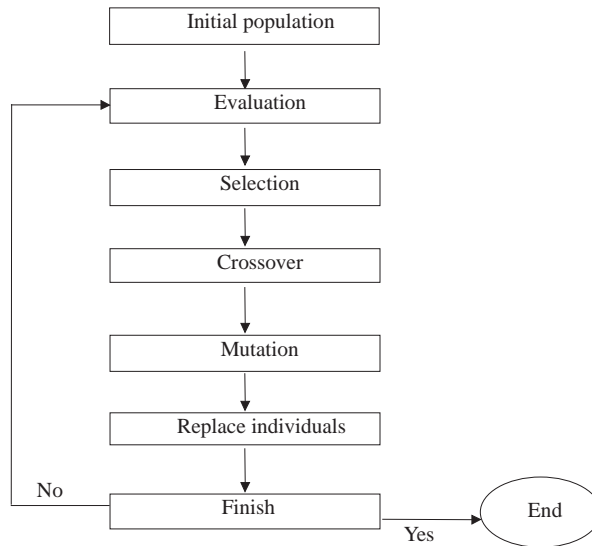


Figure 2. Genetic algorithm (GA) procedure.

The initial population of individuals is usually generated randomly within certain boundaries. The boundaries used in this study are summarized as follows:

Initial solution space: generated randomly

$$0 < r < 3$$

$$x_e \leq x_{final}$$

Size of population : 100

Number of iteration steps: 50 (max)

Type of crossover: uniform crossover

Total mutation probability for each constant: 70 %

The evaluation function (selection mode) increase and decreases GA performance during the solution process. Therefore all the individuals in the population were evaluated and their fitnesses were used as the basis for selection, determined by standard deviation. As a result, selection is implemented by eliminating the low fitness individuals from the population and inheritance is implemented by making multiple copies of high-fitness individuals.

Genetic operations such as mutation and crossover do not work directly with binary string codes. Thus, the entire population of individuals is created in a computer as a binary string and then this population is evaluated by the use of crossover and mutation.

Crossover takes two selected current generation structures, splits and strings at the same randomly determined point and then creates the new generation structures by swapping the tail portion of the string. One example of uniform crossover between two parent individuals can be given as follows:

$$\begin{array}{r}
 1 \ 1 \ \underline{0} \ 1 \ 0 \ \underline{1} \ 1 \ \rightarrow 107 \text{ (parent string 1)} \\
 1 \ 1 \ \underline{1} \ 0 \ 1 \ \underline{0} \ 1 \ \rightarrow 117 \text{ (parent string 2)} \\
 \downarrow \text{ uniform crossover} \\
 1 \ 1 \ \underline{1} \ 1 \ 0 \ \underline{0} \ 1 \ \rightarrow 121 \text{ (child string 1)} \\
 1 \ 1 \ \underline{0} \ 0 \ 1 \ \underline{1} \ 1 \ \rightarrow 103 \text{ (child string 2)}
 \end{array}$$

Mutation, on the other hand, randomly changes a little in a structure, thereby introducing a new individual. The setup of mutation parameters in this work can be shown by an example as follows:

$$\begin{array}{ccccccc}
 1 & \underline{1} & 0 & 0 & 1 & 1 & 0 \rightarrow 102 \\
 & & & & & & \\
 & & & & & & \downarrow \text{mutation} \\
 & & & & & & \\
 1 & \underline{0} & 0 & 0 & 1 & 1 & 1 \rightarrow 71
 \end{array}$$

Detailed information about other operation steps and other variations of GA have been discussed extensively by Wolf²⁰, Davis²¹ and Grefenstte²².

The data obtained from the experiment (x, t) was used to calculate the kinetic parameters of both the dehydration and decomposition steps of BPH by GA. The implementation of the computer program and the elimination of the data (x, t) can be summarized as follows:

- a- One hundred values of “r” and “x_e” were generated randomly using the boundary condition. Then each “r” and “x_e” value was used in Eq. 7 to calculate “k” values utilizing all x and t data.
- b- One hundred values of “r”, “x_e” and “k” found in clause “a” were used in both Eqs. 4 and 5 to calculate 100 values of relative standard deviation by using Eq. 6. The minimization of the standard deviation values thus obtained was evaluated and then the other operations (selection, crossover and mutation) of GA were performed. At the end of these operations, one iteration step had been completed.
- c- In the dehydration step, complete crystal water removal at the temperatures of dehydration was realized when the BPH particles had been dehydrated as much as the time required²³. Thus, the equilibrium values, n_e(mole), for all temperatures at which dehydration was carried out can be taken as n_e = 2. The other parameters were found as mentioned in the “a” and “b” clauses.
- d- In order to observe the behavior of the GA program, it was run by using x and t data until the number of iteration steps reached 25. During this operation the behavior of “r”, “x_e” and “k” was observed through minimum standard deviation.
- c- For the dehydration and decomposition steps, the GA program reached the stationary values of kinetic parameters (r, x_e and k) for each run at the end of 15 and 20 iteration steps, respectively. Thus, the number of iteration steps was limited to 15 and 20 for dehydration and decomposition, respectively.

Results and Discussion

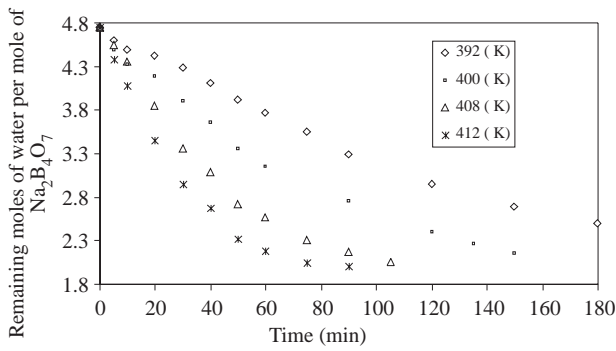
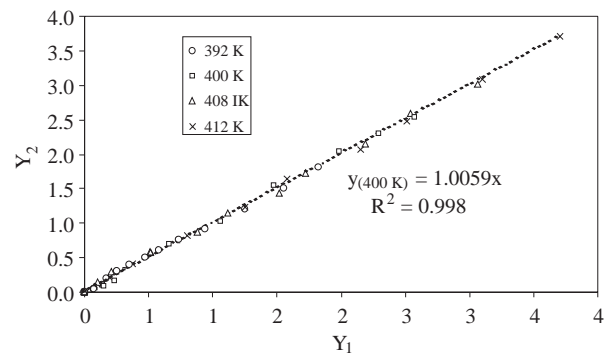
a- Dehydration step:

This step contains the removal of crystal water from BPH particles. Figure 3 shows the moles of water per mole of Na₂B₄O₇ at different bed temperatures as a function of time. As can be seen from this figure, the higher the bed temperature, the higher the dehydration rate and the shorter the dehydration time will be to reach any specified water content. The GA program was run four times for each dehydration temperature. Table 1 shows the best data obtained at the end of 15 iteration steps.

Table 1. The changes of kinetic parameters of dehydration step of BPH with run number.

| Temperature (K) | Run No | r | n_e | $k \cdot 10^3$ | Standard deviation. 10^2 | $R^2 \cdot 10^2$ |
|-----------------|----------|-------------|----------|----------------|----------------------------|------------------|
| 392 | 1 | 0.68 | 2 | 7.245 | 2.573 | 99.68 |
| 392 | 2 | 0.64 | 2 | 7.112 | 2.335 | 99.68 |
| 392 | 3 | 0.66 | 2 | 7.178 | 2.438 | 99.67 |
| 392 | 4 | 0.67 | 2 | 7.212 | 2.502 | 99.66 |
| 400 | 1 | 0.67 | 2 | 12.207 | 2.912 | 99.80 |
| 400 | 2 | 0.68 | 2 | 12.300 | 2.949 | 99.80 |
| 400 | 3 | 0.66 | 2 | 12.116 | 2.913 | 99.80 |
| 400 | 4 | 0.69 | 2 | 12.394 | 3.025 | 99.79 |
| 408 | 1 | 0.66 | 2 | 20.347 | 3.513 | 99.78 |
| 408 | 2 | 0.67 | 2 | 20.539 | 3.621 | 99.78 |
| 408 | 3 | 0.69 | 2 | 20.929 | 4.047 | 99.75 |
| 408 | 4 | 0.68 | 2 | 20.732 | 3.800 | 99.77 |
| 412 | 1 | 0.69 | 2 | 30.297 | 3.735 | 99.86 |
| 412 | 2 | 0.65 | 2 | 28.810 | 3.471 | 99.84 |
| 412 | 3 | 0.67 | 2 | 29.536 | 3.112 | 99.89 |
| 412 | 4 | 0.66 | 2 | 29.168 | 3.185 | 99.87 |

The kinetic parameters marked in Table 1 were taken to compare $Y_{experimental}$ values represented by Eq. 4 and $Y_{calculated}$ values represented by Eq. 5. The approximation of $Y_{calculated}$ to $Y_{experimental}$ is shown in Figure 4. For the different dehydration temperatures, closeness to the diagonal corresponded to the equality of both sides of Eq. 3 implying that there is a good evidence for the accuracy of the determination of the kinetic parameters (r , x_e and k).


Figure 3. The effect of temperature on the dehydration of BPH to borax dihydrate.

Figure 4. Plots of values of $Y_{calculated}$ vs. $Y_{experimental}$.

In order to calculate the activation energy of the dehydration step from the Arrhenius equation, the marked kinetic parameters (in Table 1) with equal “ r ” and different temperatures were used. The Arrhenius equation can be expressed as,

$$k = A \exp^{-\frac{E}{RT}} \quad (8)$$

where k is the rate constant, E is the activation energy, A is the frequency factor that is related to the chance that a collision between the molecules occurs with the proper configuration needed for a successful reaction, R is the gas constant and T is the absolute temperature.

Taking the natural logarithm of both sides of Eq. 8 gives

$$\ln(k) = \ln(A) - \frac{E}{RT} \tag{9}$$

From this equation, the $\ln(k)$ versus $1/T$ plot is shown in Figure 5. The data in Figure 5 can be best represented by the following linear equation:

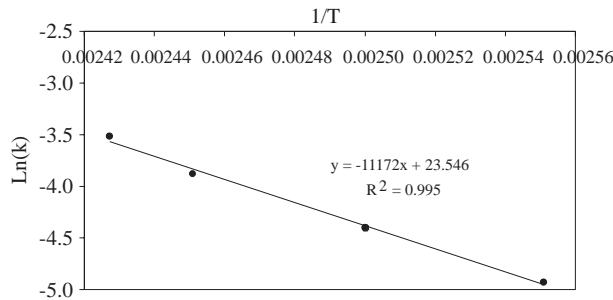


Figure 5. Arrhenius plot of the dehydration kinetics ($n = 0.67$).

$$\ln(k) = -\frac{11172}{T} + 23.88 \tag{10}$$

As can be seen in this last equation, the activation energy and frequency factor for dehydration steps are 92.88 kJ/mole and $2.349 \times 10^{10} \text{ min}^{-1}$, respectively, in the temperature range 392-413 K.

b- Decomposition step:

The dehydration of BPH after removing 2.67 moles of crystal water can be expressed as the thermal decomposition step. Figure 6 depicts the moles of water per mole of $\text{Na}_2\text{B}_4\text{O}_7$ at different bed temperatures as a function of time.

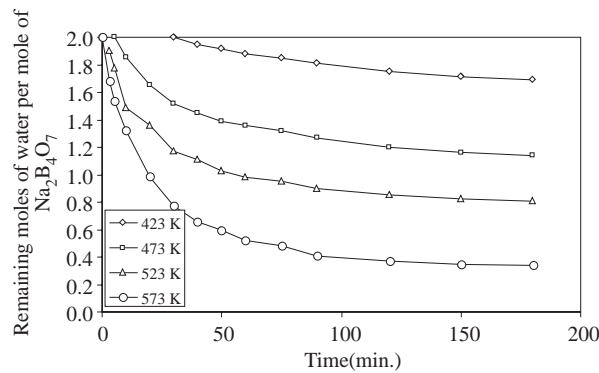


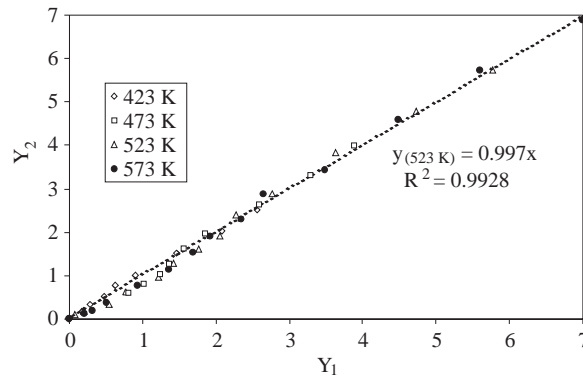
Figure 6. Paths of conversion of Borax dihydrate to BA at different temperatures.

In order to find the equilibrium mole fraction value “ x_e ” and reaction order “ r ” for each temperature at which dehydration was realized, the GA program was run four times. The best kinetic parameters (n_e , r , k) obtained at the end of 20 iterations were given in Table 2. As can be seen in this table the decomposition data obtained at different temperatures have different equilibrium values n_e . Thus, some kinetic parameters, which were obtained at different temperatures and had the same reaction order “ r ”, were marked in Table 2 to perform compression and to calculate activation energy.

Table 2. The changes of kinetic parameters of decomposition step of BPH with run number.

| Temperature (K) | Run No | r | n_e | $k \cdot 10^3$ | Standard deviation. 10^2 | $R^2 \cdot 10^2$ |
|-----------------|----------|-------------|-------------|----------------|----------------------------|------------------|
| 423 | 1 | 1.10 | 1.73 | 24.778 | 4.777 | 99.50 |
| 423 | 2 | 1.02 | 1.73 | 20.149 | 4.488 | 99.56 |
| 423 | 3 | 1.02 | 1.71 | 17.605 | 5.030 | 99.17 |
| 423 | 4 | 1.02 | 1.72 | 18.777 | 4.660 | 99.35 |
| 473 | 1 | 1.10 | 1.23 | 35.810 | 6.978 | 99.74 |
| 473 | 2 | 1.11 | 1.23 | 36.059 | 7.085 | 99.77 |
| 473 | 3 | 1.08 | 1.23 | 33.898 | 7.478 | 99.65 |
| 473 | 4 | 1.04 | 1.24 | 33.239 | 6.816 | 99.79 |
| 523 | 1 | 1.10 | 0.93 | 51.209 | 5.275 | 99.90 |
| 523 | 2 | 1.12 | 0.93 | 53.500 | 5.325 | 99.93 |
| 523 | 3 | 1.11 | 0.93 | 52.339 | 5.763 | 99.92 |
| 523 | 4 | 1.24 | 0.92 | 63.136 | 8.276 | 99.88 |
| 573 | 1 | 1.06 | 0.44 | 59.286 | 8.006 | 99.88 |
| 573 | 2 | 1.07 | 0.44 | 60.618 | 7.821 | 99.89 |
| 573 | 3 | 1.05 | 0.44 | 61.982 | 8.956 | 99.23 |
| 573 | 4 | 1.10 | 0.44 | 65.749 | 8.253 | 99.79 |

The kinetic parameters marked from Table 2 were used to compare $Y_{experimental}$ (Eq. 4) values and $Y_{calculated}$ (Eq. 5) values (in Figure 7). As can be seen in Figure 7 the approximation of Eq. 4 to Eq. 5 is very good for the decomposition of BPH.


Figure 7. Plots of values of $Y_{calculated}$ vs. values of experimental ($n = 1.13$).

In addition the marked values with the same reaction order were used to calculate activation energy from the Arrhenius equation. For the decomposition of BPH, a $\ln(k)$ versus $1/T$ plot is given in Figure 8. This plot can be best represented by a line equation as follows:

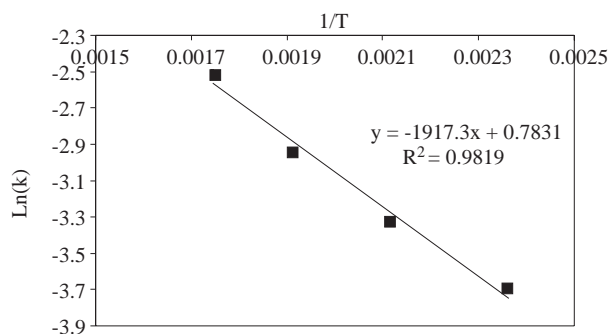


Figure 8. Arrhenius plot of the decomposition kinetics ($n = 1.10$).

$$\ln(k) = -\frac{1917.3}{T} + 0.7137 \quad (11)$$

The activation energy and frequency factor can be obtained from the slope and intercept of Eq. 11. The value of activation energy and frequency factor for decomposition of BPH were found to be 15.940 kJ/mole and 2.042 min^{-1} in the temperature range of 423-573 K, respectively.

Conclusion

An estimation of the thermal dehydration and decomposition rate constants of BPH was proposed and its use was explained to describe the random and systematic variations in the kinetic parameters by GA. Experimental evidence shows that the conversion of BPH to dihydrate and anhydrous borax in a fluidized bed drier is controlled by a reaction rate order between 0.64-0.69 and 1.01-1.13 with respect to water content of the solid material, respectively. The temperature dependency of the rate constants for both dehydration and decomposition conversion can be correlated by the Arrhenius equation to obtain an activation energy of 92.880 kJ/mole, 15.940 kJ/mole and a frequency factor of $2.349 \times 10^{10} \text{ min}^{-1}$, 2.042 min^{-1} , respectively. The high value of the frequency factor for dehydration shows that the collision probability of molecules forming a reaction is very high, but the reaction can only proceed for molecules having a higher energy than 92.88 kJ/mole. In the case of decomposition, with increasing temperature, the frequency factor decreased and a number of molecules with higher energy than 15.90 kJ/mole can react easily because of lower activation energy barriers.

Notation

| | |
|-------|-------------------------------------|
| x_o | initial mole fraction of water |
| x | remaining mole fraction of water |
| x_e | equilibrium mole fraction of water |
| r | reaction order |
| k | reaction rate constant |
| t | time, min |
| A | frequency factor, min^{-1} |
| E | activation energy, J/mole |
| R | gas constant, J/K mole |
| T | absolute temperature, K |

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