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# A Semiempirical Kinetic Model for Dissolution of Colemanite in Aqueous CH<sub>3</sub>COOH Solutions

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In this study the dissolution of Colemanite in aqueous acetic acid solutions was investigated in a batch reactor employing the parameters of particle size, solid-to-liquid ratio, and temperature. It was found that the dissolution rate increases with increasing temperature and decreasing solid-to-liquid ratio and particle size. The most effective parameter was particle size with a power of  $-1.420$  after temperature and solid-to-liquid had less effect than the other parameters. The conversion rate increased up to  $3.365$  M acid concentration and then decreased with increasing acid concentration. No important effect of stirring speed was observed. The activation energy of the process was determined to be  $51.490$  kJ mol<sup>-1</sup>. It was determined by graphical and statistical methods that the reaction fits a model in the form of  $-\ln(1 - X) = kt$ . The following semiempirical mathematical model, which expresses the process well, was established:  $-\ln(1 - X) = 56\,664(D)^{-1.42}(S/L)^{-0.270} \exp(-6193.0/T)t$ , where  $X$  is the conversion fraction,  $D$  the particle size,  $S/L$ , the solid-to-liquid ratio, and  $T$  the reaction temperature.

## 1. Introduction

Boron compounds are very commonly used almost in all branches of industry in different ways. The production of boron compounds has substantially increased recently due to the increasing use of these compounds in nuclear technology, in rocket engines as fuel, and in the production of heat-resistant materials such as refractories and ceramics, high-quality steel, heat-resistant polymers, catalysts, etc. (Nemodruk and Karalova, 1965). Boron is available in nature in its compounds, mostly in sodium and calcium compounds. Colemanite, one of the most common boron compounds, has a monoclinic crystal structure with a chemical formula of  $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (Nemodruk and Karalova, 1965; Doon and Lower, 1975).

Commercially, the most-used compounds of boron are boric acid, boron oxides, and sodium perborate. In Turkey, in the production of these compounds, Ulexite and Colemanite are used as raw materials. There is an inverse proportion between scientific researches on boron and industrial interest in these researches. While there are numerous studies on boron compounds such as metal borates, fluoroborates, borhidrures, and carbon-boron compounds and these compounds have a share of approximately 99% of the scientific studies, the production of only four compounds of boron, borax, boric acid, calcium borate, and sodium pentaborate has a share of approximately 99% of industrial boron applications both quantitatively and economically (Thomson, 1977).

Some studies on the dissolution rate and kinetics were found in the literature about dissolution of boron minerals in the solutions of acetic acid (Imamutdinova and Abdrashitova, 1970), hydrochloric acid (Zdonovskii and Imamutdinova, 1963), sulfuric acid (Kononova and Nozhko, 1981), nitric acid (Imamutdinova and Bikhurova, 1967), oxalic acid (Kalacheva et al., 1980), etc. In addition, in some studies to enlighten the mechanism of the dissolution process by inorganic solutions, it was determined that the film layer of the formed products on the mineral surface affects reaction rate and the level of this effect differs for every acid, but it was obvious after a given concentration (Imamutdinova, 1967). The dissolution of Ulexite and Colemanite minerals in CO<sub>2</sub>-saturated water was investigated (Gülensoy and Ko-

cakerim, 1977, 1978), and the optimum dissolution conditions of Ulexite in CO<sub>2</sub>-saturated water were searched (Yapıcı et al., 1994). The dissolution kinetics of Ulexite (Kocakerim et al., 1993) and Colemanite (Alkan et al., 1985) in CO<sub>2</sub>-saturated water was investigated.

There are a lot of studies for the production of boron minerals, especially boric acid and borax, mostly patented studies, for instance, the production of boric acid from Ulexite using the mixture of sodium carbonate-bicarbonate solutions (Novak et al., 1982), and the production of boric acid and borax using hydrochloric acid (Su et al., 1980).

In the industrial process in which H<sub>2</sub>SO<sub>4</sub> was used as the leachant, the side product is CaSO<sub>4</sub> which causes environmental pollution. If acetic acid is used as the leachant, the final solution includes Ca<sup>2+</sup> and CH<sub>3</sub>COO<sup>-</sup> in addition to dissolved boron, and as this solution was heated, CaO is precipitated in the solution and acetone is formed so a valuable side product is obtained in this process. CaCO<sub>3</sub> can also be used as building material (Lucas and Pressman, 1961). The investigation of the kinetics prior to the design of a conventional reactor is essential for clarifying the effect of parameters and for determining some kinetic parameters.

In the present study, the dissolution kinetics of Colemanite in acetic acid solutions was investigated, and a kinetic model representing the process was established.

## 2. Experimental Section

The Colemanite mineral used in the study was provided from a region of Emet, Kütahya, Turkey. After cleaning the mineral manually from the visible impurities, it was ground and sieved by ASTM standard sieves to obtain the nominal particle size fractions of 0.137, 0.115, 0.0965, and 0.081 mm in diameter.

Since the mineral was chosen specifically and cleaned mechanically by hand, the purity of the mineral is very high. The chemical analysis of the ore by volumetric methods gave the following results: 27.35%, CaO; 50.27%, B<sub>2</sub>O<sub>3</sub>; 21.82%, H<sub>2</sub>O; 0.56%, insoluble and other (Scott, 1963).

The parameters expected to effect the dissolution were chosen as temperature, acid concentration, particle size,

**Table 1. Parameters and Their Range Used on the Experiments**

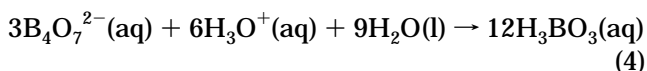
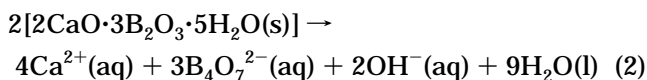
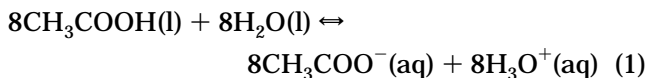
parameter	value
particle size (mm)	0.137, <sup>a</sup> 0.115, 0.097, 0.081
acid concentration (mol L <sup>-1</sup> )	1.675, 2.52, 3.365, <sup>a</sup> 4.22, 5.93, 7.65, 10.3
temperature (°C)	10.620.0, 25.0, <sup>a</sup> 30.0, 35.0, 40.0, 50.0
solid/liquid ratio (g L <sup>-1</sup> )	5, 10, <sup>a</sup> 20, 35
stirring speed (s <sup>-1</sup> )	21, 42, <sup>a</sup> 63

<sup>a</sup> The constant values used when the effect of other parameters was investigated.

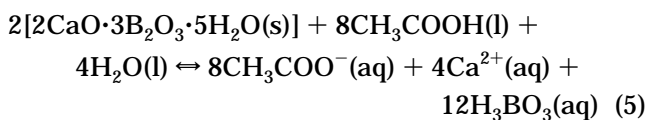
solid-to-liquid ratio, and stirring speed. The parameters, their range, and values are given in Table 1. The experiments were carried out in a 250-mL spherical glass reactor equipped with a mechanical stirrer, a thermostat to control the reaction temperature within  $\pm 0.5$  °C, and a cooler to avoid the solution loss by evaporation. After putting the 0.1 L acetic acid solution in a certain concentration into the reactor, the content of the reactor was heated to the desired temperature, and a given amount of the ore of a given particle size fraction mentioned above was added into the reactor while the stirring was going on. At the end of the reaction period, the solid and liquid parts were separated by filtration, and Ca<sup>2+</sup> was then analyzed in the solution to determine the conversion percentage by a compleximetric method (Scott, 1963). For each experimental condition the experiment was repeated twice, and the arithmetic average of the result of the two experiments was used in the kinetic analysis.

### 3. Results and Discussion

**3.1. Dissolution Reactions.** When colemanite is added into the acetic acid solution, the reactions taking place in the medium can be written as follows:

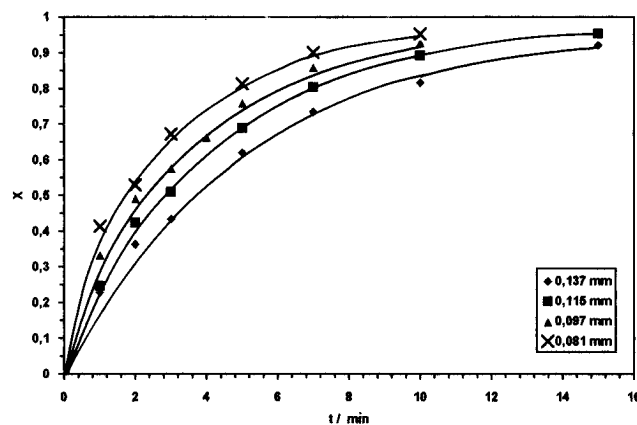


The overall reaction can be written as follows:

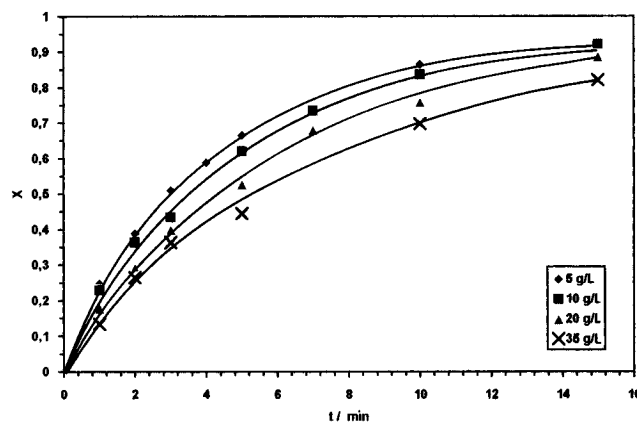


**3.2. Effect of Parameters.** The effect of parameters on the dissolution process was investigated for each parameter using the values given in Table 1. In the experiments, while the effect of one parameter was studied, the values of the other parameters, shown with asterisks in Table 1, were kept constant. The data obtained from the experiments were plotted in time versus conversion fraction, described as  $X_{\text{Ca}^{2+}} = (\text{the amount of dissolved calcium in the mineral})/(\text{the amount of calcium in the original mineral})$ .

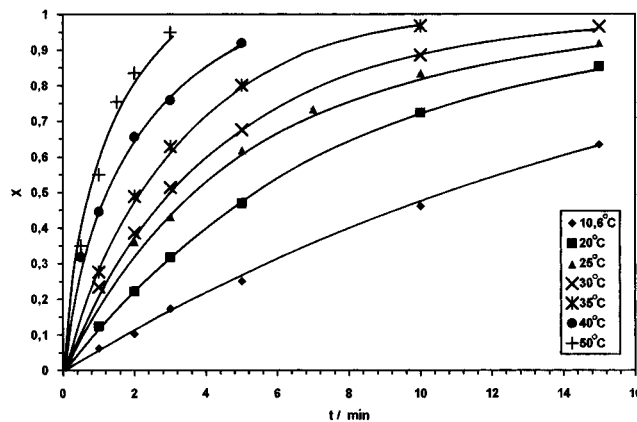
As seen in Figure 1, as the particle size decreases, the dissolution rate increases, which can be attributed to the increase of the contact surface, on which the main



**Figure 1.** Effect of particle size on dissolution of Colemanite.



**Figure 2.** Effect of solid-to-liquid ratio on Colemanite.



**Figure 3.** Effect of temperature on dissolution of Colemanite.

dissolution reaction occurs, with the decrease of the particle size per amount of the solid. The behavior of the dissolution for various solid-to-liquid ratios is shown in Figure 2. This figure shows that decreasing solid-to-liquid ratios are in favor of the dissolution process, which can be explained by the decrease of solid amount per amount of the reagent in the suspension. Figure 3 shows that increasing temperature has an increasing effect on the dissolution, as expected due to the exponential dependence of the rate constant in the Arrhenius equation. Since the experiments showed that stirring speed has no effect on the process, it was discarded from the analysis, as can be seen in Figure 4.

The experiments to see the effect of CH<sub>3</sub>COOH concentration on the dissolution process showed that the dissolution rate increases with increasing acid concentration up to an acid concentration of 3.365 M and a further increase in acid concentration caused decreasing

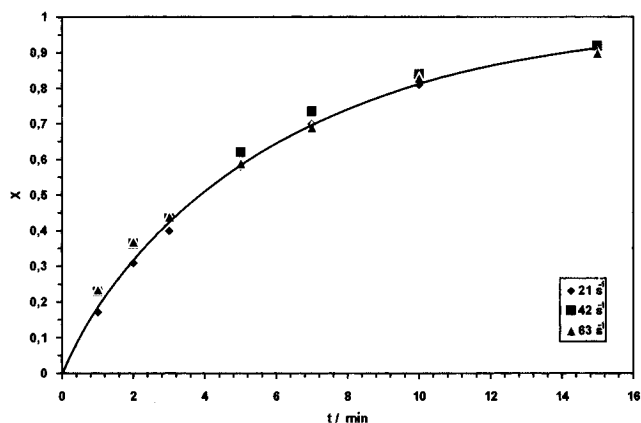


Figure 4. Effect of stirring speed on dissolution of Colemanite.

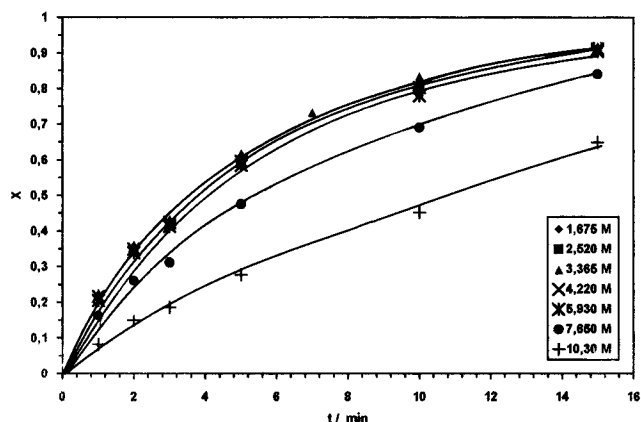


Figure 5. Effect of acid concentration on dissolution of Colemanite.

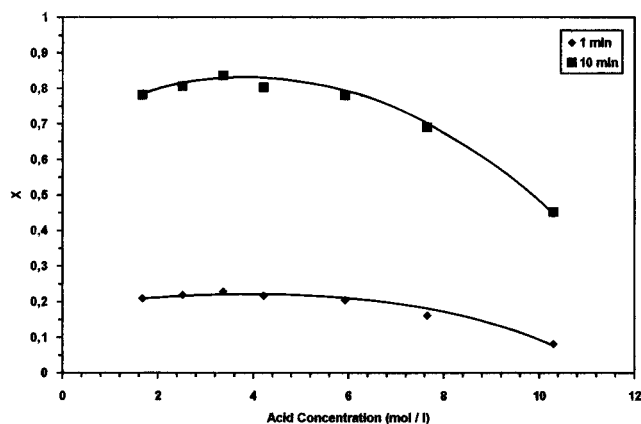


Figure 6. Conversion of Colemanite with acid concentration for two reaction periods.

dissolution, as seen in Figure 5. Figure 6 shows more clearly the behavior of the dissolution process with acid concentration. Similar behavior was observed with some boron minerals dissolved in different acidic solutions (Imamutdinova, 1967; Imamutdinova and Abdrasthova, 1970; Imamutdinova and Vladykina, 1969). This behavior can be explained by the fact that  $\text{Ca}^{2+}$  and  $\text{B}_4\text{O}_7^{2-}$  from the solid particle and  $\text{H}_3\text{O}^+$  from the bulk solution diffusing into the fluid film layer gives a very fast reaction in the film layer, and as boric acid reaches the saturation value near the solid particle, it forms a difficult-soluble solid film layer around the particle, causes the system to have diffusional character, and results in slowing down the dissolution process (Imamutdinova and Bikchurova, 1967). It was reported that the formation of boric acid on the minerals dis-

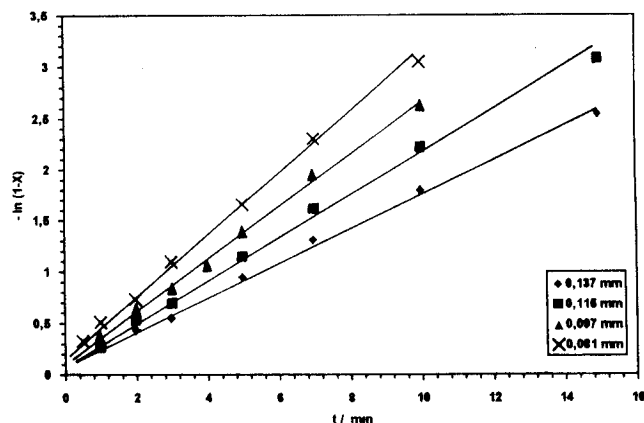


Figure 7. Agreement of experimental data with a first-order pseudohomogeneous kinetic model for different particle sizes.

solved in acidic solutions, including acetic acid, was proven using thermographic, microscopic, and X-ray diffraction analysis, so that they concluded that the dissolution rate can be controlled by the dissolution of boric acid formed on the solid particle, while Kononova and Nozhko (1981) reported that they determined no boric acid film on the solid surface and decided that the system was an interfacial interaction, kinetic-controlled process.

**3.3. Kinetic Analysis.** The kinetic data of the present study were analyzed using graphical and statistical methods. As the experimental results were analyzed using fluid–solid heterogeneous reaction models (Levenspiel, 1972; Wen, 1968) by graphical and statistical methods, it was found the data fit none of the heterogeneous kinetic models. When the data were analyzed using homogeneous models, it was found that the process can be expressed by a first-order pseudohomogeneous kinetic model,

$$dX/dt = k(1 - X) \quad (6)$$

or

$$-\ln(1 - X) = kt \quad (7)$$

As can be seen graphically in Figure 7, or an example, for different particle sizes. The findings of Imamutdinova and Vladykina (1969) and Imamutdinova and Bikchurova (1967) could be a result of the salting out of the particles from the solution. The process is of a very complex nature and can include gradual dissolution of probable boric acid film and diffusion of the reacting reagent through this film in addition to the other usual steps, diffusion through fluid film layer, reaction on the surface of a solid, etc. The fact that the process can be represented by a first-order pseudohomogeneous reaction model can be explained by the mechanism shown schematically in Figure 8, which is a modified mechanism of one of the fluid–fluid heterogeneous systems (Levenspiel, 1972). The concentration of reagent species does not drop appreciably within the film; it can be taken to be constant throughout. Reaction taking place in the reaction zone is fast enough, and the overall system can be represented by a pseudohomogeneous first-order reaction model. The slowing down of the process rate with increasing acid concentration can be explained by the possible solid film layer of boric acid around the particle or by the dissolution equilibrium of boric acid in an aqueous medium as follows for the first step.

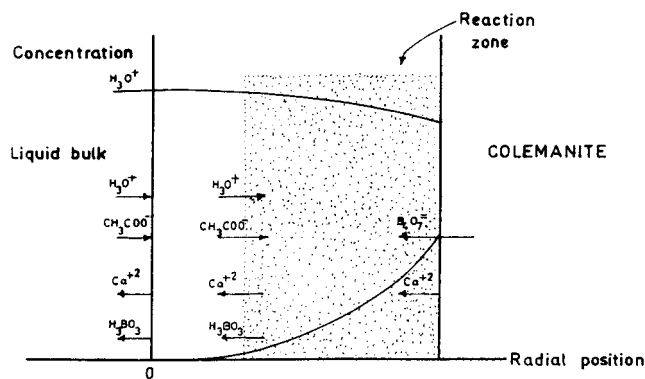
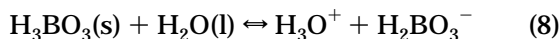


Figure 8. Mechanism of the dissolution process.



It is clear that increasing acid concentration shifts the reaction to the left, decreasing the dissolution of boric acid. This was determined experimentally, as given in Figure 9, so there is a possibility of forming a boric acid layer around the particle with increasing acetic acid concentration, causing a slowdown of the process.

To include the effect of the parameters on the kinetic model, the following empirical model was developed by multiple regression

$$-\ln(1 - X) = k_0(D)^a(S/L)^b \exp(-E_A/RT)t \quad (9)$$

where  $D$  = particle size (mm),  $S/L$  = solid-to-liquid ratio ( $\text{g} \cdot \text{L}^{-1}$ ),  $X$  = conversion fraction,  $E_A$  = activation energy ( $\text{J} \cdot \text{mol}^{-1}$ ),  $t$  = time (min), and  $k_0$ ,  $a$ ,  $b$  = constants.

Since acid concentration did not show a regularly changing effect, that is, a decreasing effect after an increasing effect up to a given value, it is not included in the model. Inserting the estimated values into eq 9 gives the following kinetic model.

$$-\ln(1 - X) = 56\,664(D)^{-1.420}(S/L)^{-0.270} \exp(-6193.0/T)t \quad (10)$$

Figure 10 shows the agreement between the experimental data and the predicted conversion values. The activation energy for the process was found to be  $51.490 \text{ kJ mol}^{-1}$ . For the experimental conditions of the present study, the most effective parameter is temperature and then particle size and solid-to-liquid ratio follow. It should be emphasized that this model is valid for the parameter range used in the study and for the constant values of  $42 \text{ s}^{-1}$  stirring speed, for  $3.365 \text{ M}$  acid concentration, and for the geometry of the reactor used in the study.

#### 4. Conclusions

In this study in which the dissolution of Colemanite in aqueous acetic acid solutions was investigated in a batch reactor, it was determined by graphical and statistical methods that the reaction fits the first-order pseudohomogeneous reaction model in the form of  $-\ln(1 - X) = kt$ . It was observed that the dissolution rate increased with increasing temperature and decreasing solid-to-liquid ratio and particle size. The most effective parameter was particle size with a power of  $-1.420$  after temperature. The solid-to-liquid ratio had less effect than the other parameters. The conversion rate increased up to  $3.365 \text{ M}$  acid concentration and then decreased with increasing acid concentration. No im-

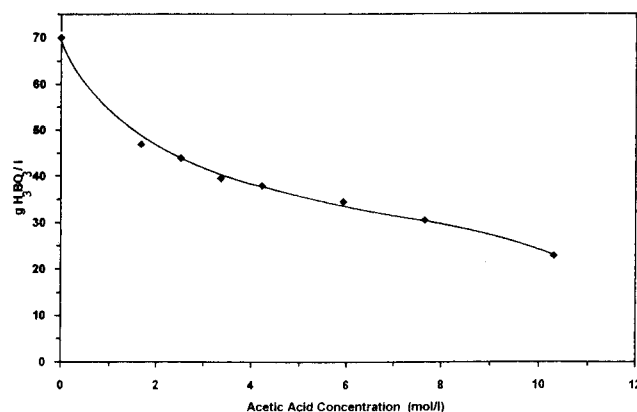


Figure 9. Saturation concentration of boric acid in acetic acid solutions at  $25^\circ\text{C}$ .

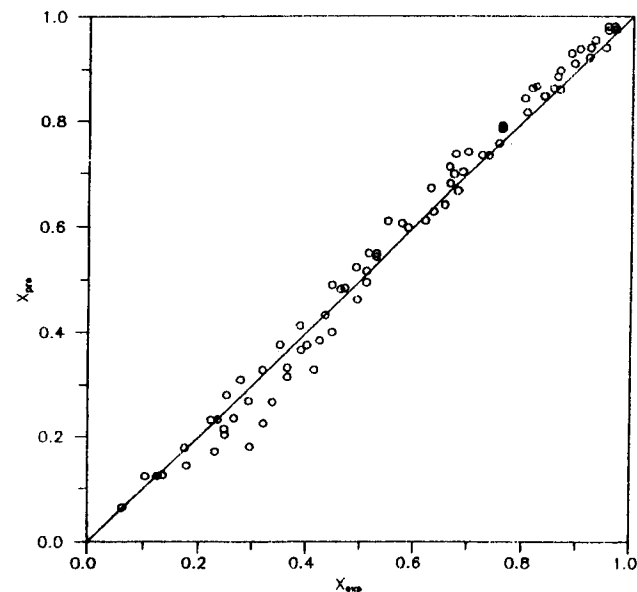


Figure 10. Comparison of experimental and theoretical values from a pseudohomogeneous first-order model.

portant effect of stirring speed was observed. The activation energy of the process was determined to be  $51.490 \text{ kJ mol}^{-1}$ . A semiempirical mathematical model, which expresses the process well, was developed.

#### Nomenclature

- $a$ : constant in eq 9
- aq: aqueous
- $b$ : constant in eq 9
- $M$ : acid concentration,  $\text{mol L}^{-1}$
- $D$ : particle size, mm
- $E_A$ : activation energy,  $\text{kJ mol}^{-1}$
- $S/L$ : solid-to-liquid ratio,  $\text{g L}^{-1}$
- $s$ : solid
- $k_0$ : constant in eq 9
- $T$ : temperature, K
- $t$ : time, min
- $X$ : conversion fraction

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