

# Kinetics study of the finely dispersed limestone thermal decomposition reaction

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**Abstract – Termogravimetric studies on four various fractions diameters particles of calcium carbonate used in the industrial cyclone-calciner furnace for manufacturing of lime were carried out based on linear increase of the temperature. The values of activation energy E, preexponential factor A in Arrhenius equation, as well as the mechanism of the particles thermal decomposition reaction were defined.**

**The work results provide important data to further study the efficiency of the limestone thermal decomposition chemical reactions and optimizing furnace design and operation modes.**

Key words – activation energy, limestone, thermal decomposition, solid-state reaction, reaction rate.

## I. Introduction

One of the greatest problems in chemical engineering is the development and design of mashines and apparatus for processing of materials in finely dispersed condition. This applies particularly to the finely dispersed lime production process. These processes take place in cyclone type furnaces. The effectiveness of these apparatus depends on the hydrodynamics, heat transfer and termal decomposition kinetics processes.

The thermal decomposition kinetics of the finely dispersed limestone can be characterized based Eq.(1).

$$\frac{\partial \alpha}{\partial t} = k(T) \cdot f(\alpha) \quad (1)$$

where  $\alpha$  - the degree of conversion;  $k$  - the rate constant for process;  $f(\alpha)$  - the conversion function for a solid-state reaction.

$$\alpha = \frac{W}{W_k} \quad (2)$$

where  $W$  - current sample weight loss at the temperature;  $W_k$  – final sample weight loss at the temperature;

This is a typical solid-state strongly endothermic reaction (i.e.,  $\Delta H_R^\circ = 44,3$  kcal/molis), which is typical for the most decomposition reactions. This means that heat must be supplied to the reactant to sustain the decomposition.

The kinetics of this type reactions strongly depends on the reaction of mechanism that can be considered to be as  $f(\alpha)$ . The temperature dependence of the rate constant  $k$  for the process can be described by the Arrhenius equation:

$$k = A \cdot e^{-\frac{E}{RT}} \quad (3)$$

where  $A$  is the preexponential factor,  $E$  is the activation energy,  $T$  is the absolute temperature, and  $R$  is the gas constant.

Usually, the activation energy  $E$  and preexponential factor  $A$  for Arrhenius equation must be determined from experimental data to describe the termal decomposition process.

But the definition of the conversion function  $f(\alpha)$  is more important for understanding the thermal decomposition reaction mechanism of the finely dispersed lime.

The conversion function  $f(\alpha)$  for a solid-state reaction can be considered to be as follows:

$$f(\alpha) = a^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad (4)$$

where  $m$ ,  $n$  and  $p$  are empirically factors obtained from experiment [2].

Thus, kinetic investigations of decomposition reactions based on the function  $f(\alpha)$  and Arrhenius equation parameters can provide information about the reaction mechanisms and the influence of process variables such as temperature, particle size, mass of reactant, and the ambient atmosphere of the apparatus.

Our study aimed to analyze the limestone decomposition kinetics for the future analysis of the cyclone furnace efficiency based CFD-modeling.

## II. Material, measurement and method

The thermal decomposition on four various fractions diameters particles (0-50 $\mu$ m; 50-80  $\mu$ m; 80-140  $\mu$ m and 140-250  $\mu$ m) of calcium carbonate were carried out on an instrument Q – 1500 D derivatograph of system F. Paulik, J. Paulik and L. Erdey by registration of both an analytical signal of mass loss and thermal effects via the computer. The samples were analyzed in a dynamic mode at the heating rate of 10<sup>0</sup>C/min up to 1000<sup>0</sup>C under atmosphere of air. The weight of the samples was equal to 200 mg. Al<sub>2</sub>O<sub>3</sub> was used as a standard. The TG, DTG, and DTA curves were recorded simultaneously.

If the temperature increases at a constant rate,

$$\frac{\partial T}{\partial t} = const = q \quad (5)$$

therefore Eq.(1) can be represented as:

$$\frac{\partial \alpha}{\partial T} = \frac{A}{q} \cdot e^{-\frac{E}{RT}} f(\alpha) \quad (6)$$

In logarithmic form the Eq.(6) can be represented as:

$$\ln \frac{d\alpha / dT}{f(\alpha)} = \ln \frac{A}{q} - \frac{E}{R} \cdot \frac{1}{T} \quad (7)$$

According to Eq.(7), it can be plotted for different values of  $a$  as function of  $1/T$  and linear regression can be used to determine the mechanism and values of  $E$  and  $k$  calculated. This approach was used in this study.

## III. Results and Discussion

The experimental results for 80-140  $\mu$ m sample in the form of plots of TG, DTG and DTA curves are shown in Fig.1. Other samples were processed in the same way.

Based on Eq.(7), data from TG curves in the decomposition range  $\alpha$  from 0,2 to 0,9 were used to determine the kinetic parameters of the process.

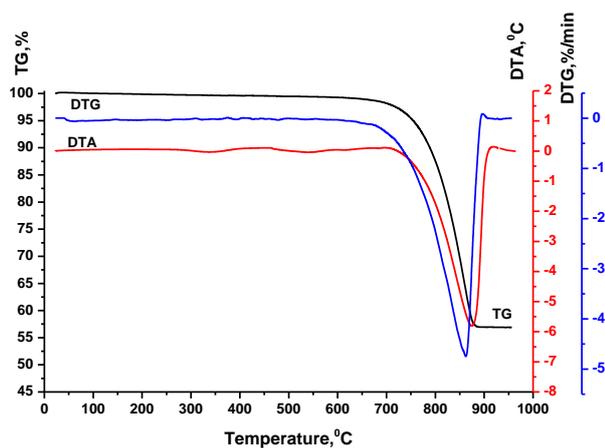
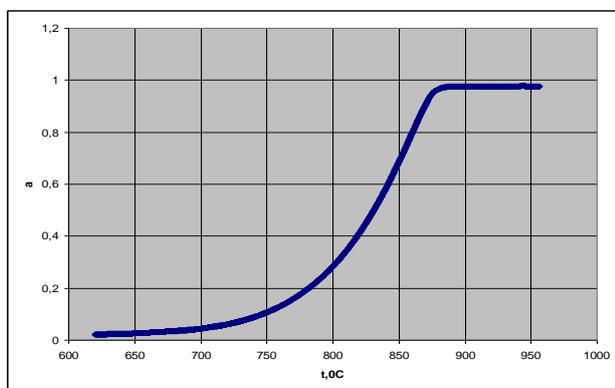
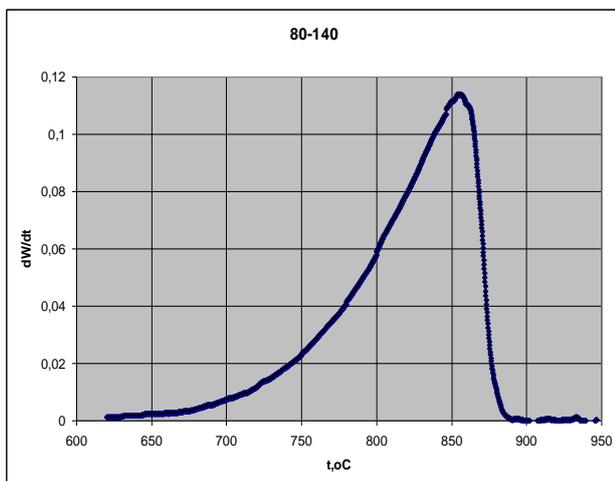


Fig. 1. The TG, DTG and DTA curves for sample 80-140  $\mu\text{m}$

Fig. 2 shows the integral and differential kinetic curves for sample 80-140  $\mu\text{m}$  obtained from the TG experimental data.



a) the integral kinetic curves



b) the differential kinetic curves

Fig. 2. Thermal decomposition kinetic curves

The figures showed that the weight loss is initiated at 600  $^{\circ}\text{C}$  and defined fully decomposed approximately at

875 and 885  $^{\circ}\text{C}$  for all samples, respectively and the maximum rate is for 860-870 $^{\circ}\text{C}$ .

According to the experimental results corresponding to four different fractions diameters of the sample the activation energy and the preexponential factor values were obtained. Also several the theoretical equations have been defined to analyze the reaction kinetics mechanism.

It was found that there are three distinct regions: first is below 700 $^{\circ}\text{C}$ , second is from 700-710 $^{\circ}\text{C}$  to 810-830 $^{\circ}\text{C}$  and the third is above it. The activation energie approximate values for the three regions are: 140-150, 200 and 360-380 kJ/mol to each sample, respectively.

These areas correspond one of three processes: 1 - it is the nucleation mechanisms; 2- it is the reaction at the interface between the reactant and the solid product; 3- it is the gas diffusion from the reaction surface through the porous product layer.

Nevertheless, the theoretical procedure used in this study cannot give the direct answer in the search for a true reaction mechanism. This is because there are many equations that can describe reaction mechanism in the different decomposition range  $\alpha$ . So, the numerical solution of Eq. (7) and calculation the conversion function  $f(\alpha)$  will provide only a rough idea of a spectrum of possible reaction mechanisms. So more research is needed, for example, as recommended in [3].

## Conclusion

In this study the thermal decomposition kinetics of finely dispersed limestone by Pustomyty lime plant was studied. The mechanism of reaction and kinetic constants were defined.

Analysis of non-isothermal thermogravimetric data results indicates the general mechanism of decomposition which includes three stages.

The kinetic parameters obtained from experimental data are in very good agreement with literature values.

In this context, the experimental data will be used for the CFD-simulation of the cyclone furnace work and design optimization.

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