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Author: James S. Campbell John R. Grace C. Jim Lim David W. Mochulski

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A New Diagnostic when Determining the Activation Energy by the Advanced Isoconversional Method

James S. Campbell, John R. Grace, C. Jim Lim and David W. Mochulski

Department of Chemical and Biological Engineering, University of British Columbia,

2360 East Mall, Vancouver, Canada, V6T 1Z3.

Corresponding author: James S. Campbell, +16044429441, jcampbell@chbe.ubc.ca

Highlights

- An Optimization Indicator is introduced which identifies and diagnoses possible error in TGA data.
- The results suggest that limestone activation energies <200 kJ.mol^{-1} for calcination in nitrogen are questionable.
- Strong activation energy vs. conversion trends for limestone calcination are likely due to errors.

Abstract

The Advanced Isoconversional (AIC) method involves minimization of a function which uses conversion data at a minimum of three heating rates to determine an activation energy (E_a) at different values of conversion (α). Reactions that can be described by a single model give an E_a which is independent of α, while reactions which are described by more than one model give an E_a which varies with α. Shifts in the conversion curves due to error can lead to E_a vs. α trends which falsely indicate, or mask, true multi-model kinetics. It was found that the minimum value obtained during optimization of what we call the 'Optimization Indicator' (Ω) can indicate whether trends in E_a vs. α are likely to be error-derived in the case of single-model reactions or artifacts in the case of multi-model reactions. E_a and Ω for the calcination of *$CaCO_3$* are used to demonstrate the experimental application of this new diagnostic.

Keywords

Nonisothermal kinetics

Advanced Isoconversional method

Optimization Indicator

1. Introduction

The kinetic equation for a single-mechanism, solid-state reaction at a particular heating rate (β) describes the rate of reaction ($d\alpha/dT$) as a function of two variables: temperature (T) and conversion (α):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$