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Short communication

New concept of thermokinetic analysis with artificial neural networks

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ABSTRACT

Inspired by the recent victory of the computer program Alpha Go [1] over the world strongest human Go player and by the ability of this program based on artificial neural networks (ANN) for self-learning, we present the attempt to perform the thermokinetic analysis using ANN models. Various virtual combinations of kinetic parameters and reaction model types were used to generate thermoanalytical signals similar to experimental ones for neural network training. Results prove that trained artificial neural network models can be successfully used for the kinetic analysis. For methodological purposes, various types of input parameters have been considered, showing the weakness of analysis based on the single heating runs along with the high resolution ability of constant rate thermal analysis. The principal capability of neural networks to perform kinetic analysis within wide ranges of activation energy and pre-exponential factor for a number of reaction models has been demonstrated.

Introduction

The progress in thermokinetic analysis techniques is rigidly connected with development of sophisticated mathematical methods and computational power. For example, the replacement of calculations based on single nonisothermal curve with simultaneous analysis of multiple heating rate runs became possible, among others reasons, due to the computational capability increase. Modern thermokinetic methods enabling to describe the complex processes, such as advanced Vyazovkin isoconversional technique [2] along with the combined kinetic analysis of deconvoluted peaks [3], are examples of this trend too.

Artificial neural networks (ANN) are the models inspired by biological neural systems *e.g.* brain [4], and represent the oriented graphs with nodes—"neurons". Connections between neurons have different strength, defined by numeric weights, adapted during training of the particular network. Optimized artificial neural networks are capable to approximate any continuous non-linear function [5], being highly tolerant to noisy or missing data [6,7].

Neural networks become widely used in various areas, including playing games [1], image classification [8], predicting of impact sensitivity of energetic materials [9]. ANN models are widely used in analytical chemistry to fit the multicomponent kinetic dependencies and to support the process control [10–13]. Only few papers deal with the application of neural networks in the field of thermal analysis [6,14–17]. Thus, the experimental conversion data for the carbon fibers pyrolysis [17], and iron reduction [16] can be successfully described by ANN models. Interesting work has been reported by Sebastiao about the neurons activation functions using in the form of few reaction types, which allowed to fit the isothermal decomposition of rhodium(II) acetate [14,15]. Sbirrazzuoli [6] used the neural network models for thermoanalytical signal filtering and deconvolution and the kinetic parameters determination, although very narrow range of kinetic parameters studied, i.e. activation energy 74–80 kJ/mol and preexponential factor ln$A$ = 18–20, and reaction model fixed to 2nd order type.

Recent victory of computer program AlphaGo based on ANNs [1] over the world strongest human Go player shows that neural networks are capable to outperform human in solving of hardly formalized problems, and thermokinetic analysis for sure is one of those. One of the key features of the AlphaGo program is a self-learning, performed on games positions, and generated by the program itself. This idea has motivated the present study approach: to solve the inverse kinetic task – to find kinetic triplet from the conversion degree *versus* time dependencies – is quite a problem, whereas to solve the direct kinetic task – to find thermoanalytical signals knowing kinetic parameters – is easy to calculate. Thus, we can generate such a thermoanalytical data for a number of realistic kinetic models and then to train ANN to predict the kinetic parameters.

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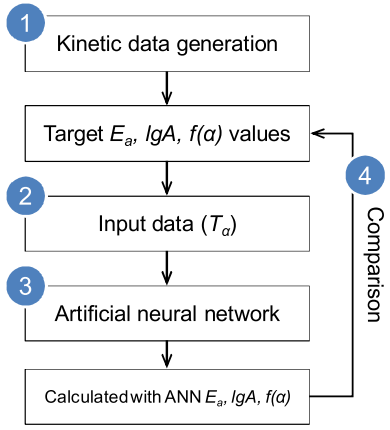

Fig. 1. Logical scheme of the present study (numbers of steps correspond to sections in text).

This short communication reports the attempt to use neural networks for determination of the kinetic parameters within its extended ranges, *i.e.*, activation energy Ea = 50–300 kJ/mol, pre-exponential factor lgA = 0.01–40 s^{-1}, and the number of reaction models up to 10 on the base of a few heating-rate and constant-rate thermoanalytical data. The aim of the presented study is to prove the principal capability to perform kinetic analysis with neural networks and to stimulate further development in this field.

Experimental

The whole process of the kinetic analysis with the artificial neural networks comprises few steps (Fig. 1). At first, the virtual kinetic data, *i.e.,* number of stages, possible reaction models, and realistic values of activation energy and preexponential factor are generated for ANN training. At the next step the every kinetic triplet forms its own input data as α*(T)* dependency. Then the artificial neural network structure has to be determined and optimized by minimization of an error between the calculated output parameters (reaction model, activation energy, and preexponential factor) and correct ones, which were generated at step 1 for the training and test sets of data. Trained neural network is saved and then can be used to predict the output function on demand.

For actual investigation we consider the only one-stage reactions to show the principal ability of trained neural network to distinguish different reaction models from the experimental data. Modeling of the multi-stage processes will be studied further.

1. Data generation for training

For training of ANN the thermoanalytical, similar to experimental, data have been generated by considering various combinations of reaction model type, activation energy and preexponential factor. Target activation energy E_a and preexponential factor lg*A* values have been randomly generated in the ranges of 50–300 kJ/mol and 0.01–40 s^{-1}, respectively. During processing of generated kinetic triplet and calculation of the input data, the cases where the reaction starts below 30 °C and is not finished at 1500 °C have been excluded to avoid unrealistic pairs with high preexponent and low activation energy and vice versa, The resulting E_a-lg*A* pairs are shown in Fig. 2 inside the red rectangle. Two additional sets of generated data with E_a <50 kJ/mol and E_a > 300 kJ/mol were not used for models training and testing, but have been applied to check the validity of the kinetic predictions only. To reduce the analysis complexity, we have considered at first the following reaction models [18]: Avrami-Erofeev A3, Prout-Tompkins B1, contracting area R2, first-order F1; second-order F2, and 3-dimensional diffusion D3 and then extended row to 10 reaction types.

2. Selection of input data

To perform the kinetic analysis using ANN we have selected the thermoanalytical "experimental" signals as input points. These signals are generated as a matrix of conversion degree, temperature, time (*via* heating rate). To reduce the amount of points we have to apply discretization procedure with retaining of the kinetic features of the studied process. This pre-processing procedure is very important and could be further optimized, but now we consider two possibilities:

a) For non-isothermal experiment with the heating rate β we have selected temperature values at conversion degrees 0.02, 0.04. . .0.98 as input points. In turn, one, two and three heating rates have been modeled (rows #1–8, Table 1).
b) For the constant-reaction rate thermal analysis (CRTA) run [19], which is reported to have high resolution ability for reaction model discrimination [20], we have generated two CRTA runs with the rate of $c = 1 \times 10^{-3}$ and 10×10^{-3} min^{-1}. The

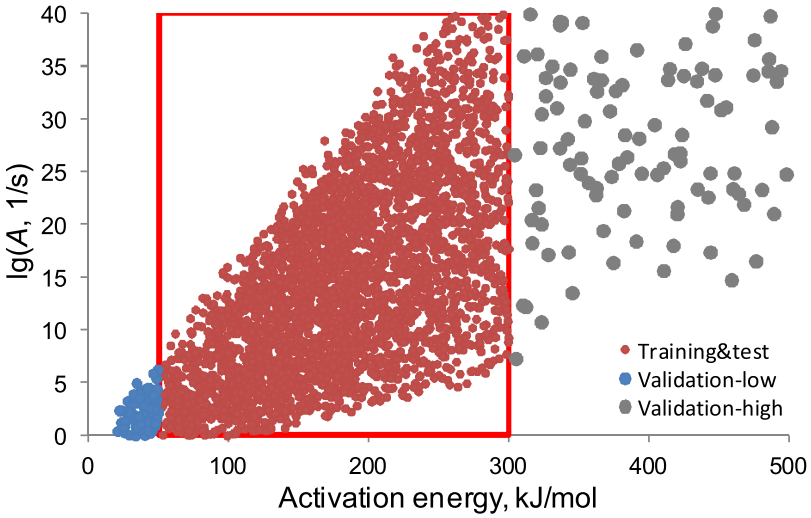

Fig. 2. "Target" values of activation energy and preexponential factor, which were used for training, testing (in red rectangle), and validation (grey and blue points) of artificial neurons network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).