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Determination of the kinetic constants of a chemical reaction in heterogeneous phase using parameterized metaheuristics

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Abstract

Kinetic parameters of a chemical reaction can be determined using numerical metods by integrating the equation of the reaction rate. For example, the reaction in the human stomach when neutralizing the acid with an antacid tablet can be simulated by integrating the equation for the dissolution rate of calcium carbonate present in the tablet together with the joint resolution of the balances for determining at any time the concentration of all species present in the solution. So, there is a classical optimization problem to determine the values of the kinetic parameters that best fit with the experimental data for a given reaction mechanism. The optimization problem can be afforded with metaheuristic methods. To obtain a satisfactory metaheuristic it is necessary to develop and experiment with various methods and to tune each for the problem. The use of a unified parameterized scheme for metaheuristics facilitates the development of metaheuristics and their application. In this paper the application of parameterized metaheuristics to the problem of determination of kinetic parameters is analysed. Local and global search methods (GRASP, Tabu Search, Genetic algorithm and Scatter Search) and combinations of them are applied for the simulation of the above-mentioned reaction. The use of a parameterized metaheuristic scheme allows us to easily experiment and tune different metaheuristics, so improving the results obtained with a basic optimization method.

Keywords: Chemical reaction, kinetic constants, parameterized metaheuristic schemes

1. Introduction

This paper focuses on estimation with metaheuristic methods of the kinetic parameters of a chemical reaction. The simulation of the processes that happens in the human stomach when neutralizing the acid with an antacid tablet is used as proof of concept. A chemical reaction in heterogeneous phase that takes place in a batch stirred tank reactor is studied [1, 2], and the dissolution process of an antacid tablet is simulated. It is a reaction combined with mass transfer of carbonate ions present in the solid phase upon contact with an acid solution. The solid phase consists of an antacid tablet, which contains a certain amount of calcium carbonate. The reaction medium represents the approximate pH of the human stomach (with values between 3 and 4). The kinetic parameters of the reaction (order and combined reaction rate constant) are determined using the Euler numerical method for integrating the equation for the dissolution rate of calcium carbonate in the tablet. Together with the joint resolution of the balances, the concentration of all species present in the solution are determined at any time. The effect of different parameters like stirring speed, the initial pH of the medium, the total amount of acid and base and the state of aggregation of the tablet are studied.

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We have a classical optimization problem consisting of the estimation of the kinetic parameters that best fit with the experimental data for a given reaction mechanism [3, 4]. The solution of the problem can be approximated with available optimization tools, for example the "Solver" in Excel. The results obtained are used as starting point, and they make it possible to assert on the order of magnitude of the kinetic constants, allowing us to establish the search domain for metaheuristic methods, which are used to improve the initial results.

Metaheuristics have been successfully applied to non-linear optimisation problems in many dimensions where more traditional methods are often found to fail. Also, deterministic, gradient-based optimisation methods do not search the complete parameter space and can tend to converge towards local extremes of the fitness function, which is clearly unsatisfactory for problems where the fitness varies non-monotonously with the parameters. On the other hand, metaheuristics are able to depart from local optima due to their inherent randomness.

The use of a unified parameterized scheme for metaheuristics facilitates the development of metaheuristics and their application by reusing the basic functions. The scheme has been applied successfully to different problems [5]: obtaining satisfactory Simultaneous Equation Models from a set of values of the variables, a tasks-to-processes assignation problem with independent tasks and memory constrains, and an optimization of power consumption in operation of wells [6]. The parameterized metaheuristic scheme is used and adapted here to the problem of estimation of the kinetic parameters in a chemical reaction. Four pure metaheuristics (GRASP, Tabu Search, Genetic algorithm and Scatter Search) are included in the parameterized scheme, which allows us to experiment with the basic metaheuristics and their combinations/hybridizations. Experiments have been conducted with a total of fifteen metaheuristics (basics and combinations); the initial solution is improved and the preferred method for this problem is analysed.

The rest of the paper is organized as follows. Section 2 summarizes the problem to be solved and describes the terminology used. Section 3 shows the general parameterized scheme of metaheuristics and its application to the problem in hand. The experimental results are shown in Section 4. Section 5 summarizes the conclusions and proposes future work lines.

2. A problem of determination of the kinetic constants of a chemical reaction in heterogeneous phase

When chemical reactions occur in heterogeneous phase the variables that affect the reaction rate are not only temperature, pressure or composition. These systems have more than one phase and the problem is more complex: it may be that the materials move from one phase to another during the reaction. In this case, the mass transfer rate becomes important and should be included in the terms of the reaction rate.

When reaction rates in complex systems are compared or combined, we have to take into account that if the change of property (concentration, temperature, ...) is effected by several parallel paths independent of each other, the overall rate is simply the sum of all individual rates.

2.1. Dissolution of calcium carbonate

According to [7], the kinetic of dissolution of calcium carbonate is a function of the concentration of the various carbonate species in the solution and, therefore, a function of the partial pressure of carbon dioxide and pH. A model for the dissolution of calcium carbonate was developed in [8]. According to this model, depending on the pH, there are four different ways in which the dissolution of calcium carbonate occurs. At pH values lower than 3.5 the speed of the reaction is proportional to the concentration of H_3O^+ according to reaction path 1:

$$CaCO_3 + H_3O^+ \leftrightarrow Ca^{2+} + HCO_3^- + H_2O \tag{1}$$

where the dissociation of acetic acid and carbonic and bicarbonate equilibriums is present due to an acidic environment and to their being open to the atmosphere.

At these pH values, a dependence of the reaction rate with the stirring speed is observed. This indicates that ion transportation is the controlling factor in the speed of the process.

At higher pH values the reaction rate becomes less pH dependent, but more dependent on the partial pressure of carbon dioxide (reaction path 2). In this case the process is controlled by the transport of ions and by the reaction itself [9]:

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2 \cdot HCO_3^- \tag{2}$$