Adaptive Random Search Method + Genetic Algorithms for Reaction Kinetics Modelling: CO$_2$ Absorption Systems

Carol Toro-Molina[1], Rodrigo Rivera-Tinoco[2], Chakib Bouallou[1*]

[1] MINES ParisTech – Centre Energetique et Procédés Paris (CEP). 60, Bd Saint Michel, 75006 Paris, France.
[2] INOSS Group S.A. de C.V. Jesús Contreras No. 18, Cto. Escultores. Cd. Satélite. Naucalpan, Edo. De Méx. C.P. 53100. Mexico.
chakib.bouallou@mines-paristech.fr

This paper presents a novel hybrid algorithm based on the Adaptive Random Search Method (ARSM) and enhanced with Genetic Algorithms (GA) theory. This algorithm is first validated by modelling Carbonyl sulfide (COS) absorption by N-methyldiethanolamine (MDEA) aqueous solutions. Results show an excellent fit between modelled values and experimental data. Then, the method is tested to model CO$_2$ absorption by NH$_3$ aqueous solutions. In general, results show that the proposed method is faster and slightly more accurate than classic methods such as Downhill simplex, and simple GA.

1. Introduction

Mathematical modelling of reaction mechanisms frequently involves solving of non-linear equations that demand the use of suitable optimization routines to find the global solution that leads to the minimal difference between experimental data and modelled values. Gradient-based optimization algorithms, usually used to solve these problems, suffer from getting trapped in local minima and the convergence of these methods can be achieved only if they are well initialized. Moreover, strong time constraints incurred by these gradient algorithms hamper their use when considerable number of minimization processes are to be performed. To overcome these limitations, stochastic optimization techniques are a reliable solution that has been used in the past to model chemical reactions. For instance, (Isopescu and Iavric, 2009) estimated kinetic parameters for the precipitation process of calcium carbonate and validated the mechanisms using GAs throughout minimization of two objective functions. (Pontikakis and Stamatelos, 2004) employed GAs for the identification of catalytic kinetics and achieved good fit of the modelled values to the experimental data. (Zamonstny and Belohlav, 1999) estimated the catalytic hydrogenation of cinnamaldehyde, however, instead of GAs, these authors used an Adaptive Random Search Method (ARSM) where a random step length uses a variable distribution of random numbers to ensure a reliable convergence to the global optimum and at reasonable convergence speed.

In this work, an hybrid algorithm has been developed based on the ARSM and enhanced with GAs theory. This new algorithm is used to create a computational framework for kinetic modelling of various reaction mechanisms. For instance, this study aims to

validate the hybrid optimization technique and to highlight the pathway to get new kinetic results for CO_2 absorption, as absorption methods with several solvents are widely proposed at the last years but lack on kinetic values (Mangalapally et al., 2009, Zhao et al., 2011). Besides to the latter, to understand CO_2 absorption a rigorous mathematical modelling is required as highly complex reaction mechanisms could present limiting steps that unable the adequate removal of CO_2 from a gaseous stream. Our long term target is to use this algorithm to address this last issue.

2. Optimization technique

2.1 Description

Let us consider an objective function $f(x)$ as the difference between experimental and modelled values of gas pressure, and x a vector composed of i kinetic variables that belong to the absorption reactions. Intervals for each variable (k) which contain the possible solution of the reaction mechanism are set, as well as a cardinal number n that corresponds to the number of x vectors (population) to be evaluated in the objective function ($f(x)$). First, random values of the kinetic constants are created and stored in the n vectors $(k_1, k_2, \dots k_i)_n$. Second, the objective function is evaluated for each vector and the average $\sum f(x)_n/n = \bar{f}(x)$ is computed. All vectors containing k_i values that lead to $f(x) < \bar{f}(x)$ are retained to redefine new intervals for the respective kinetic constants. The values for the variables that allow the objective function to reach a minimum $(f(x_i)_{min})$ are directly retained and used as a pivot-reference vector. An iterative routine enable to evaluate the objective function until a maximum number of iterations is reached, or, until the difference between mean ($\bar{f}(x)$) and min ($f(x)_{min}$) is lower than a fixed value ε.
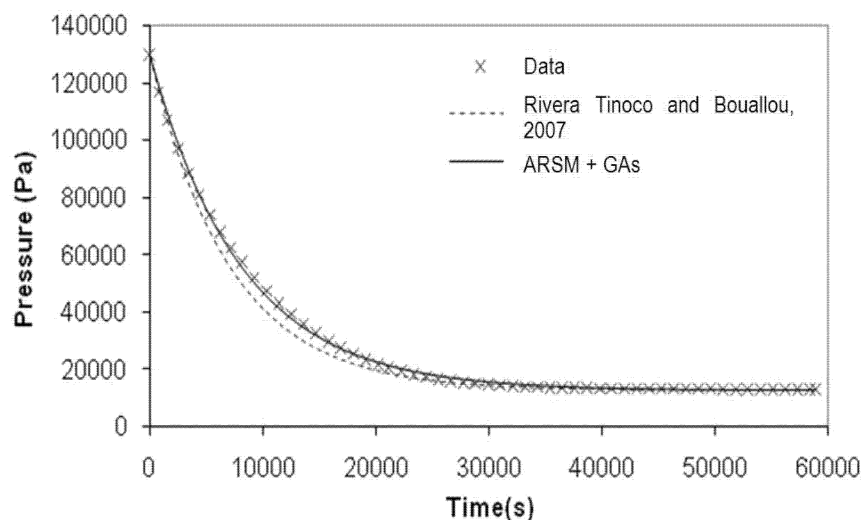

Figure 1: COS absorption by MDEA aqueous solutions at 323 K, 1258 mol/m³ MDEA.

2.2 Validation Method

Benchmark pressure decline values of COS absorption by N-methyldiethanolamine (MDEA) aqueous solutions are used to validate our ARSM + GAs method. As shown in Figure 1, a more accurate fit between experimental data and modelled values is achieved. The ARSM + GAs method seems to lead to better results than Simplex methods. The modelling of COS absorption data is based on the COS mass transfer and chemical reaction at the gas/liquid interface, considering Henry's law and the zwitterion mechanism as presented by (Rivera-Tinoco and Bouallou, 2007). Data are experimental values presented by these authors. Optimization time prove to be half of the one required when simplex techniques are used.
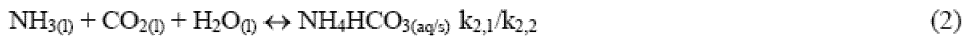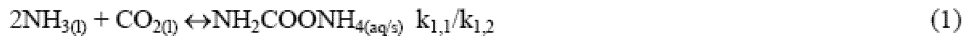
3. Modelling of CO_2 absorption by ammonia aqueous solutions

3.1 Experimental

Experiments are carried out in a thermoregulated Lewis-type cell reactor and enlarge the data set available firstly obtained by (Gonzalez Garza et al., 2009). The reactor presents a constant gas-liquid interface area and it is provided with a Rushton turbine in its lower part. A tube allows either to evacuate or to introduce acid gas (COS or CO_2) into the cell. The kinetics of gas absorption is measured by recording the absolute pressure drop through a pressure transducer, working in the range (0 to 250) kPa. At a given temperature and vapour pressure (P_l), pure gas (CO_2 or COS) was introduced for a very short time into the upper part of the cell. Once the gas was in the cell, stirring is started, and the pressure drop resulting from absorption is recorded.

3.2 Modelling and results

Several reaction mechanisms have been proposed to explain the absorption of CO_2 by ammonia aqueous solutions. In order to test the hybrid algorithm here presented, the modelling of two main mechanisms is performed. A simple one-step mechanism was proposed by (Edwards et al., 1978) and then other authors came up with more complex multi-step mechanism, such as (Park et al., 2008) who considered six chemical reactions, involving the reaction rates $R_{1,1}$, $R_{1,2}$, $R_{2,1}$, $R_{2,2}$, $R_{3,1}$, and $R_{3,2}$ (equations 4-9) represented as a chemical balance by equations 1, 2 and 3.

$$2NH_{3(l)} + CO_{2(l)} \leftrightarrow NH_2COONH_{4(aq/s)} \quad k_{1,1}/k_{1,2} \tag{1}$$

$$NH_{3(l)} + CO_{2(l)} + H_2O_{(l)} \leftrightarrow NH_4HCO_{3(aq/s)} \quad k_{2,1}/k_{2,2} \tag{2}$$

$$NH_2COONH_{4(aq)} + CO_{2(l)} + 2H_2O_{(l)} \leftrightarrow 2NH_4HCO_3 \quad k_{3,1}/k_{3,2} \tag{3}$$

$$R_{1,1} = k_{1,1}C_{NH3l}{}^2 \times C_{CO2l} \quad (4) \qquad R_{1,2} = k_{1,2}C_{NH2COONH4} \quad (5)$$

$$R_{2,1} = k_{2,1} C_{NH3l} \times C_{CO2l} \quad (6) \qquad R_{2,2} = k_{2,2}C_{NH4HCO3} \quad (7)$$

$$R_{3,1} = k_{3,1} C_{NH2COONH4} \times C_{CO2l} \quad (8) \qquad R_{3,2} = k_{3,2} C_{NH4HCO3}{}^2 \quad (9)$$

Both mechanisms consider that only the CO_2 at the interface participates in chemical reactions and defines the CO_2 absorption rate from the gas phase. The latter can be expressed as shown in the following equation:

$$\frac{dC_{CO_{2_g}}}{dt} = k_L aE \left[\frac{P_{CO_2}}{H_{CO_2}} - C_{CO_2} \right] \frac{V_l}{V_g{}^2} \tag{10}$$

In this equation, k_L is the mass transfer coefficient, a, the interfacial surface area, E, the enhancement factor and V_g, the gas volume. At the interface, vapor-liquid equilibrium is assumed and the CO_2 content depends on the partial pressure in the gaseous phase (P_{CO2}) and the unreacted and dissolved CO_2 in the bulk liquid phase (C_{CO2l}). Henry's law constant (H_{CO2}) is considered to estimate the physical adsorption of CO_2 into the liquid phase. At any time, P_{CO2} can be obtained from the measured total (P_T) and inert (P_I) pressures. The CO_2 absorption is modelled assuming ideal behaviour of the gas phase and the CO_2 concentration in the bulk liquid phase as a function of time, which is equal to zero at t = ∞. The latter means the total CO_2 consumption by the chemical reaction.

Considering the mass-transfer balance and the reaction mechanism proposed by (Edwards et al., 1978) are presented compiled in (Gonzalez Garza et al., 2009). For the mechanism proposed by (Park et al., 2008), the differential equations for the chemical species involved in the reactions are given by:

$$\frac{dC_{CO_2l}}{dt} = k_L aE \left[\frac{P_{CO_2}}{H_{CO_2}} - C_{CO_2l} \right] \frac{1}{V_g} - R_{1,1} + R_{1,2} - R_{2,1} + R_{2,2} - R_{3,1} + R_{3,2} \tag{11}$$

$$\frac{dC_{NH_3,l}}{dt} = -R_{1,1} + R_{1,2} - R_{2,1} + R_{2,2} \tag{12}$$

$$\frac{dC_{NH_2COONH_4,l}}{dt} = R_{1,1} - R_{2,2} + R_{3,1} - R_{3,2} \tag{13}$$

$$\frac{dC_{NH_4CO_3,l}}{dt} = R_{2,1} - R_{2,2} + R_{3,1} - R_{3,2} \tag{14}$$

Modelled values of CO_2 pressure derived from the simple reaction mechanism presented by (Edwards et al., 1978) are presented in Figure 2. Those values modelled under assumptions of complex reaction mechanism presented by (Park et al., 2008) are shown in Figure 3. As it can be noticed, for the simple mechanism the ARSM + GAs method achieve a very acceptable fit between modeled values and experimental data. For more complex mechanisms, an acceptable fit is performed; however, discrepancies in several points lead to the question: Is it the right mechanism? Indeed, (Park et al., 2008) suggested that six reactions are involved during the chemical absorption of CO_2; however, the convexity of the pressure profile seems not to bend during the first seconds of the experiment, when pressure is high. In order to obtain satisfactory values for the kinetic constant, further undergoing work using this ARSM + GAs tool is expected to shed light on which mechanisms truly represent the absorption of CO_2.
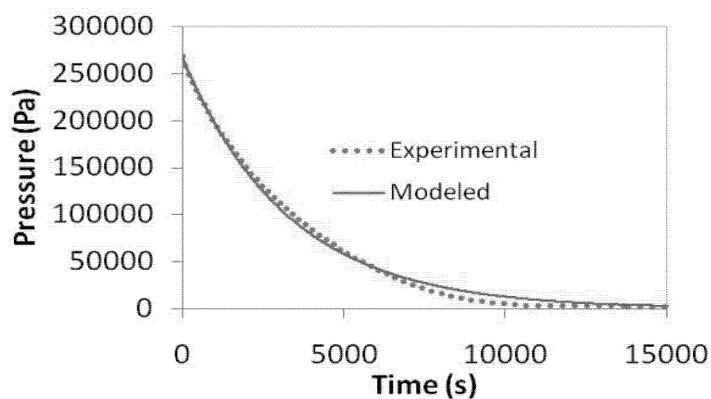
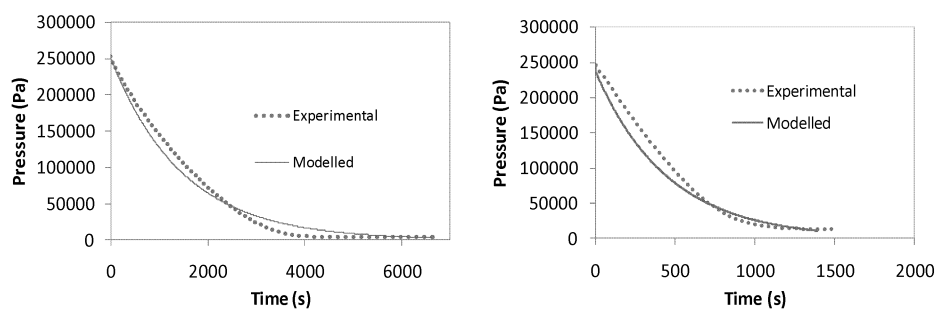*Figure 2: CO$_2$ absorption by NH$_3$ (780 mol/m^3) aqueous solutions at 278K.*

Figure 3: CO$_2$ absorption by NH$_3$ (970 and 1220 mol/m^3) aqueous solutions at 288K (left) and 303K (right) respectively.

4. Conclusion

In this work it is shown that the ARSM + Genetic Algorithms technique can be useful to obtain with lower calculating time an accurate fit between experimental pressure data and modelled values for gases absorption. Results prove that this new optimization procedure is very promising to efficiently deal with complex non-linear reaction mechanisms. Further work will follow on the modelling of CO$_2$ absorption by ammonia aqueous solutions as this optimization technique ease the comparisons between reaction mechanisms by mathematical modelling. Therefore, this computational tool will be used to determine the kinetics constant for more complex mechanisms of CO$_2$ absorption.

Acknowledgements

References

Edwards T.J., Maurer G., Newman J. and Prausnitz M., 1978, Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes, AIChE Journal, 24, 966-976.

Gonzales-Garza D., Rivera-Tinoco R. and Bouallou C., 2009, Comparison of ammonia, monoethanolamine, diethanolamine and methyldiethanolamine solvents to reduce CO_2 greenhouse gas emissions, Chemical Engineering Transactions, 18, 279-284.

Isopescu R. and Lavric V., 2009, Kinetic parameters estimation for precipitation using continuos approximation functions and genetic algorithms, Chemical Engineering Transactions, 18, 719-724.

Mangalapally H.P., Notz R., Hoch S., Asprion N., Siederc G., Garcia H. and Hasse H., 2009, Pilot plant experimental studies of post combustion CO_2 capture by reactive absorption with MEA and new solvents, Energy Procedia, 1, 963-970.

Park H., Jung Y.M., You J.K., Hong W.H. and Kim J.N., 2008, Analysis of the CO_2 and NH_3 reaction in an aqueous solution by 2D IR COS: Formation of bicarbonate and carbamate, The Journal of Physical Chemistry, 112, 6558-6562.

Pontikakis, G.N. and Stamatelos A.M., 2004, Identification of catalytic converter kinetic model using a genetic algorithm approach, Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering, 218, 1455-1472.

Rivera-Tinoco R. and Bouallou C., 2007, Kinetic study of COS absorption by methyldiethanolamine aqueous solutions from 415 to 4250 mol m^{-3} and 313 to 353 K, Industrial and Engineering Chemistry Research, 46, 6430-6434.

Zhao Y., Zhang X ., Zhen Y., Dong H., Zhao G., Zeng S., Tian X. and Zhang S., 2011, Novel alcamines ionic liquids based solvents: Preparation, characterization and applications in carbon dioxide capture, International Journal of Greenhouse Gas, 5, 367-373.

Zamostny P. and Belohlav Z., 1999, A software for regression analysis of kinetic data, Computers & Chemistry, 23, 479-485.