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Kinetic Parameter using Genetic algorithm

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Abstract:
Parameter estimation is a key step in establishing the kinetic models. For consecutive chemical reactions, the determination of the rate constants is very difficult and a time consuming process. The aim of this research work is to estimate kinetic parameters using genetic algorithm. The use of such algorithm can be very helpful in the control of industrial processes as well as in the study of the reaction mechanisms. Determination of the accurate values of the rate constants would help in establishing the optimum conditions of reactor design including pressure, temperature, and other parameters of the chemical reaction. Many non linear regression techniques like non linear least square method were used for estimating kinetic parameters. In this paper genetic algorithm is used for estimation of kinetic parameters. A genetic algorithm is applied to get the best fit between the calculation results and the experimental data. A case study of esterification of ethylene glycol with acetic acid is taken. This includes 4 kinetic parameters model. The rate equations (system of simultaneous differential equations) of the reaction were solved to get the analytical concentration versus time profiles. The simulation results are compared with experimental results at each measured point. All deviations between experimental and calculated values are squared and summed up to form a new function. This function is minimized using genetic algorithm that gives the optimal rate constants. The proposed methodology could be used to determine the rate constants of any reaction at a certain temperature, with the possibility of expanding the program for other types of reactions. The proposed program was independent on the nature of the reaction, only the rate equations and the initial conditions had to be modified for any new reaction.

Keywords: *kinetic parameters, kinetic model, optimization, genetic algorithm, esterification reaction.*

1. Introduction:

Chemical kinetics is the study of the characteristics of chemical reactions. Models for chemical kinetics are established on the basis of the predicting reaction mechanisms which are consistent with experimental data. Based on those models, we can deduce the rate constants, active energy and many other reaction parameters which are the foundation for designing reasonable reactors. Kinetic models are usually systems of nonlinear ordinary differential equations with several adjustable parameters. So for estimating kinetic parameters various non linear regression equine is used like non linear least square method, Nelder-Mead method, simulated annealing, genetic algorithm etc.

A genetic algorithm (GA) is a procedure used to find approximate solutions to search problems through application of the principles of evolutionary biology. Genetic algorithms use biologically inspired techniques such as genetic inheritance, natural selection, mutation, and sexual reproduction (recombination, or crossover). Along with genetic programming (GP), they are one of the main classes of genetic and evolutionary computation (GEC) methodologies. Definition of genetic algorithm is "Genetic algorithms are computerized search and optimization algorithms based on the mechanics of natural genetics and natural selection". The advantage of the GA approach is the ease with which it can handle arbitrary kinds of constraints and objectives; all such things can be handled as weighted components of the fitness function, making it easy to adapt the GA scheduler to the particular requirements of a very wide range of possible overall objectives.

Genetic algorithm is used for the optimization. So in this paper I used genetic algorithm for estimating kinetic parameters of the esterification of ethylene glycol with acetic acid.

2. Esterification of ethylene glycol with acetic acid

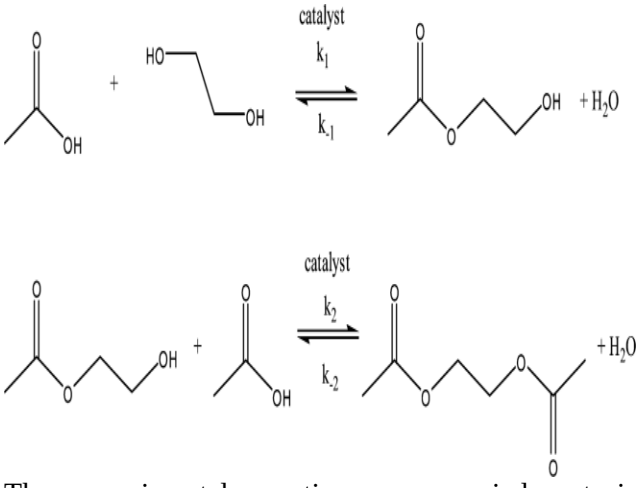
The esterification reaction is widely used in the chemical reaction process to form ester. Esterification reaction is generally carried out between alcohol and

carboxylic acid with or without presence of acid catalyst. There are many work has been done previous with different alcohol and acetic acid reaction system to form value added products, but ethylene glycol and acetic acid reaction system has been found limited work in few literature . However the valuable products as ethylene glycol mono and di-acetate obtained from ethylene glycol and acetic acid reaction system, which is used as different application in many chemical and other industries.

Esterification of ethylene glycol with acetic acid in the presence of SERALITE SRC-120 and molecular sieve 13X as catalysts. I will do simulation work to obtain the value of chemical equilibrium constant. The equilibrium constant K1, K-1, K2 and K-2 has been calculated based on mole fraction and conversion of product and reactant respectively.

3. Reaction mechanism:

Acetic acid reacts with ethylene glycol in the presence of ion-exchange resin as a catalyst to produce the ester as ethylene glycol mono and di-acetate. Esterification reaction is very slow at without catalyst and it is also a type of reversible reaction. Due to reverse reaction it produce excess amount of water during reaction and the water reduces formation of ester as a products. This reverse reaction is following as hydrolysis reaction.



The experimental reaction was carried out in generally following two steps, first the reaction between ethylene glycol and acetic acid over acid catalyst and formation of ethylene glycol mono-acetate, second following consecutive step is ethylene glycol mono-acetate to ethylene glycol di-acetate. The equilibrium constant K1, K-1, K2 and K-2 has been calculated in mole fraction basis and also determined the percentage selectivity and conversion of product and reactant respectively.

4. Modeling:

Empirical Model:

Rate equation based on the individual component of the five component reaction system, included ethylene glycol, acetic acid as reactant and ethylene glycol mono acetate, ethylene glycol di-acetate and water as product has been written in following manner:

$$EG + AA \rightleftharpoons EGMA + H_2O$$
$$EGMA + AA \rightleftharpoons EGDA + H_2O$$

In this model, the esterification and hydrolysis reaction was modeled considering 2nd order reaction. An ideal homogeneous model was considered where all reactions took place in liquid phase with the catalyst used in granular form. Additionally, the mass-transfer resistances are considered to be negligible. The material balance of five components involved in the reaction system was done as shown by following five equations:

$$\frac{dC_{EG}}{dt} = -k_1 C_{EG} C_{AA} + k_{-1} C_{EGMA} C_{WATER}$$

$$\frac{dC_{AA}}{dt} = -k_1 C_{EG} C_{AA} + k_{-1} C_{EGMA} C_{WATER} - k_2 C_{EGMA} C_{AA} + k_2 C_{EGDA} C_{WATER}$$

$$\frac{dC_{EGMA}}{dt} = -k_2 C_{EGMA} C_{AA} + k_{-2} C_{EGDA} C_{WATER} + k_1 C_{EG} C_{AA} - k_{-1} C_{EGMA} C_{WATER}$$

$$\frac{dC_{EGDA}}{dt} = k_2 C_{EGMA} C_{AA} - k_{-2} C_{EGDA} C_{WATER}$$

$$\frac{dC_{WATER}}{dt} = k_1 C_{EG} C_{AA} - k_{-1} C_{EGMA} C_{WATER} + k_2 C_{EGMA} C_{AA} - k_{-2} C_{EGDA} C_{WATER}$$

5. Parameter estimation:

The adam-bash method was used to solve the differential equations involved in the models. The developed empirical model involves four rate constants. The experimental data at various temperatures and catalyst loading available in literatures were used to estimate the kinetic parameters involved in the models using genetic algorithm. The optimization function, *E*, used for estimation of parameters is given below.

$$E = \sum\left[\frac{C^{EG}_{exp,i} - C^{EG}_{model,i}}{C^{EG}_{max}}\right] + \sum\left[\frac{C^{AA}_{exp,i} - C^{AA}_{model,i}}{C^{AA}_{max}}\right] + \sum\left[\frac{C^{EGMA}_{exp,i} - C^{EGMA}_{model,i}}{C^{EGMA}_{max}}\right] + \sum\left[\frac{C^{EGDA}_{exp,i} - C^{EGDA}_{model,i}}{C^{EG}_{max}}\right] + \sum\left[\frac{C^{WATER}_{exp,i} - C^{WATER}_{model,i}}{C^{WATER}_{max}}\right]$$

6. Results and discussion:

The estimated kinetic parameters for different temperature and catalyst loading are shown in table. Comparison between previous methods like non-linear least square method which is done by earlier and my work (genetic algorithm) is shown in tables and graphs.

Literature 1: In this paper kinetic parameter estimated by non-linear least square method [3].

Literature 2: In this paper kinetic parameter estimated by L-M method [4].

Table 1 Estimated parameters at 0.5% catalyst loading and comparison between previous works and my work

	Literature 1(Non-linear least square)				Literature 2 (L-M Algorithm)				My Work (GA)			
Temperature(K)	333	343	353	363	333	343	353	363	333	343	353	363
Error	5.98885	2.2200	3.39	2.99	1.6777	1.34455	2.7005	3.113	0.6311	1.01119	2.3644	2.8777
K1(L/mol.min)	1.81E-4	3.79E-4	5.23E-4	8.06E-4	2.665E-4	4.49E-4	5.62E-4	9.1E-4	3.117E-4	4.3 59 E-4	5.9E-4	8.94E-4
K2(L/mol.min)	5.37E-3	1.61E-3	1.94E-3	2.33E-3	1.999E-3	2.15E-3	2.2E-3	2.91E-3	2.4358E-3	2.116 E-3	2.6 18E-3	3.2222E-3
K3(L/mol.min)	1.06E	1.18	1.42	2.34E	1.28E	1.48E-3	1.71E	2.17E	2.0317E-	1.9843E-3	2.417	2.594
	-3	E-3	E-3	-3	-3		-3	-3	3		E-3	E-3
K4(L/mol.min)	3.73E-3	3.86E-3	4.8E-3	7.01E-3	4.29E-3	4.97E-3	5.12E-3	6.32E-3	7.5899E-3	6.8414E-3	7.193E-3	7.3996E-3

Table 2 Estimated parameters at 1% catalyst loading and comparison between previous works and my work

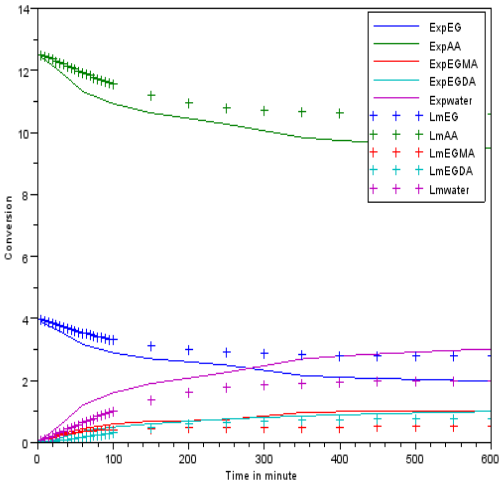
	Literature 1(Non-linear least square)				Literature 2 (L-M Algorithm)				My Work (GA)			
Temperature(K)	333	343	353	363	333	343	353	363	333	343	353	363
Error	2.9068	1.456	2.9411	2.76722	2.6222	1.3999	2.2477	4.019	0.977	1.02278	1.8443	1.37
K1(L/mol.min)	4.15E-4	8.31E-4	8.89E-4	1.8E-3	4.23E-4	8.70E-4	9.50E-4	1.47E-3	5.12E-4	8.54E-4	9.45E-4	1.5 39E-3
K2(L/mol.min)	5.88E-4	5.94E-4	4.89E-4	2.49E-4	4.97E-4	6.25E-4	6.04E-4	6.89E-4	6.88E-4	6.49E-4	5.6E-4	3.26E-4
K3(L/mol.min)	1.98E-3	2.31E-3	2.43E-3	5.65E-3	1.69E-3	2.32E-3	1.10E-2	1.59E-2	2.497E-3	3.1 94E-3	3.0 11E-3	3.51E-3
K4(L/mol.min)	4.42	5.98	8.1	1.35	4.6	6.1	3.2	4.2	7.422E-	8.31	7.61	7.8

	E -3	E-3	8E-3	E-2	4E-3	7E-3	5E-2	1E-2	3	4E-3	4E-3	15E-3

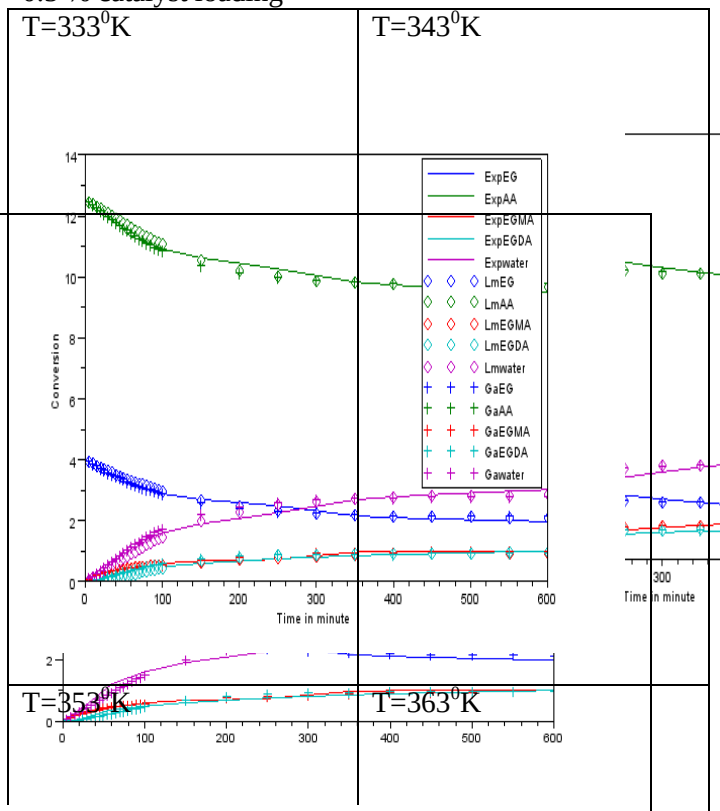
Comparison with L-M method with Genetic Algorithm
0.5 % catalyst loading

Graphs

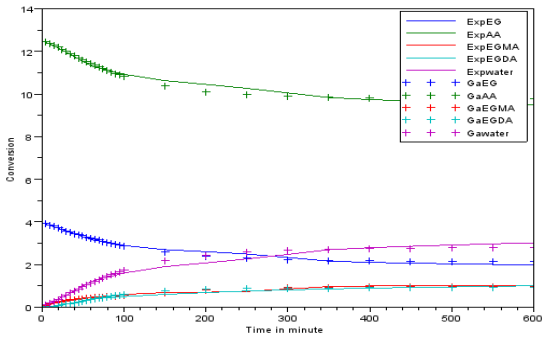
T=333^{0}K and 0.5 % catalyst loading



Graph 1 Non-linear least square method



Graph 2 Levenberg-marquardt method



Graph 3 genetic algorithm

7. Conclusion:

The empirical model for esterification of ethylene glycol with acetic acid has been developed. Genetic algorithm was used to estimate kinetic parameters. It was observed that genetic algorithm gives better fit

between the experimental data and simulated data. Error was reduced up to 50%.

8. Future Scope

A genetic algorithm is applied to get the best fit between the calculation results and the experimental data. It is time consuming process but it gives better answer comparing other methods. The proposed methodology could be used to determine the rate constants of any reaction at a certain temperature, with the possibility of expanding the program for other types of reactions. The proposed program was independent on the nature of the reaction, only the rate equations and the initial conditions had to be modified for any new reaction.

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