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Application of Monte-carlo simulation to estimate the kinetic parameters for pyrolysis of n-Eicosane and catalytic reforming of n-Heptane

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KEYWORDS

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A B S T R A C T

The Monte-Carlo Simulation technique (MCST) was applied to estimate kinetic parameters for two complex reactions: pyrolysis of n-Eicosane and catalytic reforming of n-Heptane. Because of the complex nature of the rate models for these reactions, the required forward model by the Monte-Carlo Algorithm cannot be easily expressed as concentration-kinetic parameters /time profile by integration. Therefore, the rate models were used directly as the forward reaction models. However, this required the use of concentration-reaction rate data obtained from the experimental time-concentration data through the Tikhonov regularization technique. The combination of the rate models and Monte-Carlo Simulation technique rapidly generates huge numerical values. For the estimation of the kinetic parameters, it was found that the Monte-Carlo Simulation technique performed better than the traditional Nedler-Mead Simplex method, especially with increasing number of simulation runs (up to 2000). The MCST yielded higher than normal activation energies for the investigated pyrolysis reaction at low simulation runs, but the activation energies decreased with increasing simulation runs, until, at 2000 simulation runs where the values of the activation energies were at their lowest and in agreement with the values indicated by the Nedler-Mead simplex method. This suggest that while the MCST provides a superior model for kinetic parameter estimation, even, at low simulation runs, for a reasonable estimate of the activation energies, higher simulation runs are required. According to the results obtained in this study, Monte-Carlo Simulated data and experimental data are in reasonable agreement.

Introduction

The study of chemical kinetics is usually undertaken in order to establish the rate expression or model for any reaction. The obtained rate expression relates the rate of

reaction to the factors that control the reaction, namely, temperature, pressure, and concentration. This is accomplished by identifying the reaction mechanism through

a postulation of the sequence of elementary steps characterizing the reaction. Once a rate model is obtained for a reaction under study, it becomes necessary to determine the kinetic parameters (rate and equilibrium constants) in the model from experimental concentration - time data. Such kinetic parameters are important in sizing of reactors and pointing the direction of enhancing the reaction yield/selectivity patterns (Susu, 1997).

There are varieties of techniques developed for the estimation of kinetic parameters in a rate model from experimental data. The most popular of these techniques is the integration method where the rate equations are integrated to give the concentrations of the reactants and products as a function of time with the parameters appearing as unknowns. The unknown parameters are then obtained by matching the resulting concentration - time profile with experimental data using commercial software. However, this method suffers a setback when applied to reactions with complex rate expressions as integration becomes highly difficult. For instance, the rate expression arising from heterogeneous catalytic reactions are often formidable due to large number of elementary steps characterizing the reactions and so, obtaining concentration of any specie as a function of time and reaction parameters from such model becomes tedious.

Furthermore, integrating the rate equations generally leads to complicated concentration - time profile thereby making it difficult to determine the set of parameters to a reasonable degree of accuracy. The time - concentration profile resulting from a pyrolysis reaction studied by Priyanka and Jalal (2012) is a clear example of such cases. Interestingly, the setbacks highlighted above can be circumvented by using a technique

known as Tikhonov regularization to convert the experimental - time concentration data into concentration - reaction rate data. Since the expressions for the reaction rate models are usually simpler than for the integrated time - concentration profiles, the parameters can be obtained with greater ease and possibly also with a higher degree of accuracy (Yeow et al., 2003). Once the form of data to be used has been identified, parameter estimation would then require least square fitting of the rate equation into the concentration - reaction rate curve or concentration - time profile. Several numerical minimization techniques have been developed to perform this task. These include simulated annealing, Nedler - Mead simplex method, differentiation evolution and random search method (Press et al., 1972). All these minimization computations entail the assumption of initial guesses and can be performed using commercial software. The general objective in optimization is to choose a set of values of variables (parameters) subject to the various constraints that produce the desired optimum response for the chosen objective function (Edgar et al., 2001).

The use of Monte-Carlo simulation for parameter estimation has been used by a number of researchers. Zhang and Guay (2002) used the technique for adaptive parameter estimation for microbial growth kinetics. Marshal (2003) used it for the least squares parameter estimation from multi-equation implicit models. The method was also used by Zhan et al. (2003) for the estimation of parameters for propylene amoxidation while Agarrwal and Carrayrou (2006) exploited the method in estimating kinetic parameters of reactive transport and lastly, Priyanka and Jalal (2012) used the Monte-Carlo simulation to estimate the kinetic parameters for pyrolysis of biomass. In all the works mentioned, kinetic data

were used in their raw form (i.e. time-concentration) but in the present work, kinetic data are used in their processed form (i.e. concentration-reaction rate). This work therefore, studies the suitability and accuracy of kinetic parameter estimation for complex reactions by Monte-Carlo simulation through Tikhonov Regularization technique.

Tikhonov Regularization Technique

The derivation of the working equations of Tikhonov regularization (Engl et al., 2000) is rather complicated, but the computational steps associated with the procedure are quite straightforward.

The Governing Equation

Generally, reaction rate $r(t)$ can be expressed in terms of concentration $c(t)$ as:

$$r(t) = \frac{dc(t)}{dt} \tag{1}$$

which can be rewritten as:

$$c(t) = \int_{t'=0}^t r(t') dt' + c_0 \tag{2}$$

where c_0 is the initial concentration. Equation (2) is a Volterra integral equation for the unknown reaction rate $r(t)$ and initial concentration c_0 if this quantity is not measured directly or if the experimental measurement is considered to be unreliable. This is an integral equation of the first kind. The mathematical nature of this equation shows that the problem of obtaining $r(t)$ is an ill-posed problem in the sense that if inappropriate methods are used, the noise in the experimentally measured time-concentration data will be amplified leading to inaccurate results (Engl et al., 2000).

Instead of solving Equation (2) directly for $r(t)$, this equation can be integrated by parts as follows:

Given a function $f(t)$ such that

$$f(t) = \frac{dr(t)}{dt} \tag{3}$$

Integrating the RHS of Equation (2) by parts gives

$$\int_{t'=0}^t r(t') dt' = t' r(t') \Big|_{t'=0}^t - \int_{t'=0}^t t' dr(t') \tag{4}$$

Substituting for $dr(t')$ from Equations (3), we have

$$\int_{t'=0}^t r(t') dt' = t' r(t') \Big|_{t'=0}^t - \int_{t'=0}^t t' f(t') dt' \tag{5}$$

Combining Equations (2) and (5),

$$c^C(t) = t' r(t') \Big|_{t'=0}^t - \int_{t'=0}^t t' f(t') dt' + c_0 \tag{6}$$

where the superscripts C and M are used to distinguish between the computed concentration c^C and the experimentally measured concentration c^M .

$$c^C(t) = tr(t) - \int_{t'=0}^t t' f(t') dt' + c_0 \tag{7}$$

From Equation (3)

$$r(t) = \int_{t'=0}^t f(t') dt' + r_0 \tag{8}$$

where r_0 is the initial rate of reaction.

Combining Equations (7) and (8), we have

$$c^C(t) = t \left(\int_{t'=0}^t f(t') dt' + r_0 \right) - \int_{t'=0}^t t' f(t') dt' + c_0 \quad (9)$$

$$c^C(t) = \int_{t'=0}^t (t - t') f(t') dt' + c_0 + tr_0 \quad (10)$$

Equation (10) is the governing equation and the starting point of this investigation. It can be regarded as the Volterra integral equation of the first kind to be solved for the unknown function $f(t)$ and the constants c_0 and r_0 . From the way this equation was obtained it is clear that it is independent of reaction mechanism.

Given the values of $f(t)$, c_0 and r_0 , $r(t)$ and $c(t)$ can be computed by direct numerical integration. Since numerical integration does not suffer from noise amplification, the $r(t)$ thus obtained is expected to be relatively free from the influence of experimental noise (Yeow et al., 2003).

Discretization Of The Volterra Integral Equation

In discretized form Equation (10) becomes

$$c_i^C(t) = c_0 + t_i r_0 + \sum_{t'_j=0}^{t'_j=t_i} \alpha_{ij} (t_i - t'_j) f_j \Delta t' \quad (11)$$

where, $i=1,2,\dots,N_D$, and $j=1,2,\dots,N_K$, (12)

N_D is the number of data points, and N_K is the number of discretization points. $f_1, f_2, f_3, \dots, f_{N_K}$ are the discretized $f(t)$.

The independent variable $0 \leq t' \leq t_{\max}$ is divided into N_K uniformly spaced

discretization points with step size $\Delta t' = t_{\max} / (N_K - 1)$, where $t_{\max} = t_{N_D}$ is the largest t_i in the data set. α_{ij} is the coefficient arising from the numerical scheme used to approximate the integral in Equation (2.10). For Simpson's $1/3$ rule, $\alpha_{ij} = 2/3$ for odd j (except $\alpha_{i1} = 1/3$), and $\alpha_{ij} = 4/3$ for even j .

The deviation of c^C from c^M is given by

$$\delta_i = c_i^M - \left(c_0 + t_i r_0 + \sum_{t'_j=0}^{t'_j=t_i} \alpha_{ij} (t_i - t'_j) f_j \Delta t' \right) \quad (13)$$

$$= c_i^M - C_i c_0 - B_i r_0 - \sum_{t'_j=0}^{t'_j=t_i} A_{ij} f_j \quad (14)$$

where $C_i = 1$ and $B_i = t_i$ and (15)

$$A_{ij} = \alpha_{ij} (t_i - t'_j) \Delta t' \quad \text{for} \quad t_i \geq t'_j, \quad = 0 \quad \text{for} \quad t_i \leq t'_j, \quad (16)$$

$t_i, i=1,2,3,\dots,N_D$ are the times at which the concentration is measured and $t'_j, j=1,2,3,\dots,N_K$ are the uniformly spaced discretized time $0 \leq t' \leq t_{\max}$.

In matrix notation Equation (14) can be rewritten as

$$\delta = \mathbf{c}^M - \mathbf{C} c_0 - \mathbf{B} r_0 - \mathbf{A} \mathbf{f} \quad (17)$$

where,

$$\mathbf{A} = \sum_{t'_j=0}^{t'_j=t_i} \alpha_{ij} (t_i - t'_j) \Delta t' \quad (18)$$

\mathbf{C} and \mathbf{B} are $N_D \times 1$ column vectors, \mathbf{A} is a $N_D \times N_K$ matrix of coefficient of the unknown column vector $\mathbf{f} = [f_1, f_2, f_3, \dots, f_{N_K}]^T$. Since N_K generally exceeds the number of data points N_D , \mathbf{A} is not a square matrix and Equation (14) cannot be inverted to give a unique \mathbf{f} , c_0 and r_0 . Instead, these unknowns are selected to minimize the sum of squares of δ_i ,

$$\sum_{i=1}^{N_D} \delta_i^2 = \delta^T \delta = (\mathbf{c}^M - \mathbf{C}c_0 - \mathbf{B}r_0 - \mathbf{A}\mathbf{f})^T \times (\mathbf{c}^M - \mathbf{C}c_0 - \mathbf{B}r_0 - \mathbf{A}\mathbf{f}) \quad (19)$$

However, because of the noise in the experimental data, minimizing $\delta^T \delta$ will not in general result in a smooth $f(t)$. Hence, to ensure smoothness, additional conditions have to be imposed, which is the minimization of the sum of squares of the second derivative $d^2 f / dt^2$ at the internal discretization points. In terms of the column vector \mathbf{f} , this condition takes on the form of minimizing

$$\sum_{j=2}^{N_K-1} \left(\frac{d^2 f}{dt^2} \right)_j^2 = (\beta \mathbf{f})^T (\beta \mathbf{f}) = \mathbf{f}^T \beta^T \beta \mathbf{f} \quad (20)$$

where β is the tri-diagonal matrix of coefficients arising from the finite difference approximation of $d^2 f / dt^2$ (Yeow et al., 2003) and is given by

$$\beta = \begin{bmatrix} 1 & -2 & 1 & & & & & \\ & 1 & -2 & 1 & & & & \\ & & 1 & -2 & 1 & & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ & & & 1 & -2 & 1 & & \\ & & & & 1 & -2 & 1 & \end{bmatrix} \frac{1}{(\Delta t')^2} \quad (21)$$

Tikhonov Regularization

In Tikhonov regularization (Engl et al., 2000) instead of minimizing $\delta^T \delta$ and $\mathbf{f}^T \beta^T \beta \mathbf{f}$ separately, a linear combination of these two quantities $\mathbf{R} = \delta^T \delta + \lambda \mathbf{f}^T \beta^T \beta \mathbf{f}$ is minimized. λ is an adjustable weighting/regularization factor that controls the extent to which the noise in the kinetic data is being filtered out. Minimizing \mathbf{R} requires the following conditions to hold:

$$\frac{\partial \mathbf{R}}{\partial f_j} = 0, \quad j = 1, 2, 3, \dots, N_K, \quad (22)$$

$$\frac{\partial \mathbf{R}}{\partial c_0} = 0, \quad (23)$$

$$\frac{\partial \mathbf{R}}{\partial r_0} = 0, \quad (24)$$

These give rise to a set of linear algebraic equations for \mathbf{f} , c_0 and r_0 (assuming that both initial conditions are known). It can be shown (Shaw and Tigg, 1994) that the \mathbf{f} , c_0 and r_0 that satisfy Equations (22) to (24) are given by:

$$\mathbf{f}' = (\mathbf{A}'^T \mathbf{A}' + \lambda \beta'^T \beta')^{-1} \mathbf{A}'^T \mathbf{c}^M \quad (25)$$

where \mathbf{f}' denotes the column vector $[f_1, f_2, f_3, \dots, f_{N_K}, c_0, r_0]^T$ incorporating c_0 and r_0 into \mathbf{f} . \mathbf{A}' is the composite matrix $(\mathbf{A}, \mathbf{C}, \mathbf{B})$ derived from Equations (15), (16) and (18) to reflect the inclusion of c_0 and r_0 in \mathbf{f}' . Similarly, β' is the composite matrix $(\beta, \mathbf{0}, \mathbf{0})$, where $\mathbf{0}$ is a $(N_K - 2) \times 1$ column vector of 0 to allow for the fact that c_0 and r_0 play no part in the smoothness condition in Equation (20) (Yeow et al., 2003). Equation (25) is the operating equation of Tikhonov regularization computation.

Monte-Carlo Simulation

Monte - Carlo simulation is a general method to compute statistical characteristics of an output Y which is a function of a random variable set X:
$$y = f(x) \quad (26)$$

It is a type of simulation that relies on repeated random sampling and statistical analysis to compute the results. This method of simulation is very closely related to random experiments, experiments for which specific result is not known in advance. In this context, Monte Carlo simulation can be considered as a methodical way of doing so - called what-if analysis. We use mathematical model in engineering discipline to describe the interactions in a system using mathematical expressions (Wikipedia, 2008). The models typically depend on a number of input parameters which when processed through the mathematical formula in the model, result in one or more outputs. The Monte Carlo Simulation is a user - friendly technique and can be used to numerically represent a physical problem based on the deterministic

model. This is achievable by utilizing random numbers generated on the basis of probable distribution of parameters as inputs. In Equation (26), every random sample x of the random variable set X, yields a sample y of Y. Solving Equation (26) N times yield a data set (y_1, y_2, \dots, y_n) of samples of Y.

Steps Involved In Monte-Carlo Simulation of Physical Process

Static model generation

Every Monte-Carlo simulation starts off with developing a deterministic model which closely resembles the real scenario. In this deterministic model, we apply mathematical relationships which use the values of the input variables, and transform them into the desired outputs.

Input Distribution Identification

When we are satisfied with the deterministic model, we add the risk components to the model. Since risks originate from the stochastic nature of the input variables, we try to identify the underlying distributions, if any, which govern the input variable. There are standard statistical procedures to identify input distributions.

Random Variable Generation

After we have identified the underlying distributions for the input variables, we generate a set of random numbers from these distributions. One set of random numbers, consisting of one value for each of the input variables, will be used in the deterministic model, to provide one set of output values. We then repeat this process by generating more sets of random numbers, one for each input distribution, and collect different sets of possible output values.

Application To Kinetic Parameter Estimation

When there exists a number of experimentally observed values of input variables from a kinetic study of a particular reaction, the Monte-Carlo simulation can be used to obtain the kinetic parameters (rate and equilibrium constants) that appear in a rate model if the Monte-Carlo algorithm incorporates the objective function (target function) which in this case, will be to minimize the sum of square of errors between the experimentally observed values of input variables and their calculated values.

Monte-Carlo simulation software

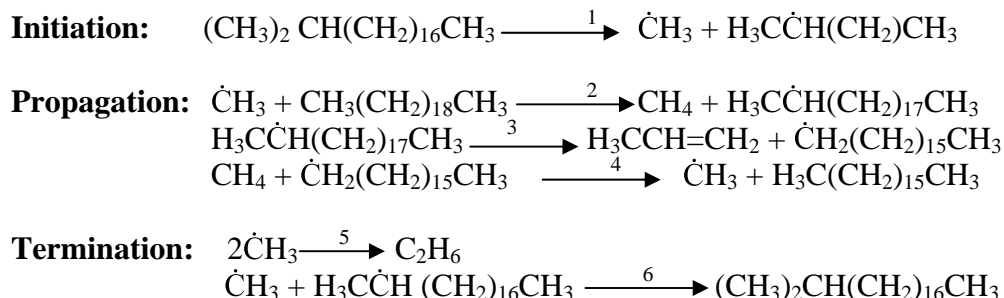
Various options are available to use Monte Carlo simulations on computers. One can use any high level programming language

like C, C++, Java, or one of the .NET programming languages introduced by Microsoft to develop a computer program for generating uniform random numbers, generating random numbers for specific distributions and output analysis. This program will possibly be tailor made for specific situations. Finally, MC simulations can also be performed using add-ins to popular spreadsheet software like Microsoft Excel.

Application to Specific Reactions

Pyrolysis of n-Eicosane

For the initial first-order chain sequence the following free radical mechanism was proposed by Susu (1982) for the decomposition of n-eicosane with a C-C bond scission at the α -isomer of iso-eicosane as the initiation step.

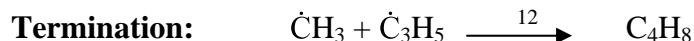
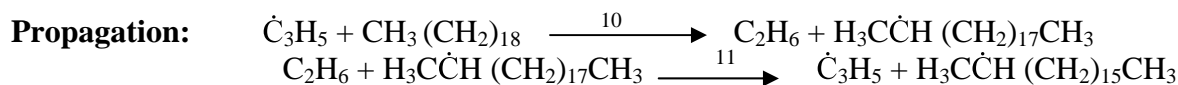
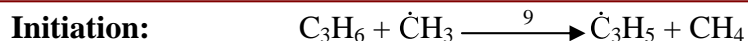


Based on this mechanism the overall reaction rate was given by Susu (1982) as:

$$\frac{d[\text{nC}^{20}]}{dt} = -k^2 \left(\sqrt{\frac{k^1}{k^5}} \right) \sqrt{[\text{iC}^{20}]} [\text{nC}^{20}] \quad (27)$$

This rate expression is considered as first order because the concentration of iso-eicosane $[\text{iC}^{20}]$ was constant throughout the decomposition reaction. The k s are the rate constants in hr^{-1} .

To account for the autocatalysis of this pyrolysis reaction, a second sequence of chain reactions was proposed for the acceleration of the first-order reaction. For the new second-order chain sequence resulting from the production of alkyl radicals from propylene the following mechanism was proposed by Susu (1982).



The overall rate expression for this new mechanism was given by Susu (1982) as:

$$\frac{d[nC^{20}]}{dt} = -\frac{k^{10}k^{12}}{k^9[C^3H^6][nC^{20}]} \quad (28)$$

This is a second-order rate model where the ks are the rate constants in $cm^3 \cdot gmol^{-1} \cdot hr^{-1}$. In terms of fractional conversion of n-Eicosane $[nC_{20}]$ the two rate models can be written as:

$$\frac{dX}{dt} = k^2 \left(\sqrt{\frac{k^1}{k^2}} \right) \sqrt{[nC^{20}]} [1 - X] \quad (29)$$

and

$$\frac{dX}{dt} = \frac{k^{10}k^{12}}{k^9[C^3H^6][1 - X]} \quad (30)$$

The experimental data for this reaction were reported by Susu (1982) at three different temperatures, 425, 440 and 450°C and given in Table 1.

Table 1 Experimental data for the pyrolysis of n-Eicosane

Temperature (°C)	Time (hr)	Conversion of n-Eicosane (X)	Yield of C ₃ H ₆ (mol C ₃ H ₃ /mol n-C ₂₀)
425	0.50	0.06	0.078
	0.75	0.14	0.088
	1.00	0.20	0.118
	1.25	0.32	0.046
	1.50	0.42	0.050
	1.75	0.45	0.047
440	0.25	0.08	0.044
	0.50	0.34	0.049
	0.75	0.40	0.093
	1.00	0.53	0.139
450	0.50	0.29	0.056
	0.75	0.58	0.063
	1.00	0.72	0.086

The reaction rate versus conversion curves obtained by Tikhonov regularization for n-eicosane pyrolysis at reaction temperatures 425⁰C, 440⁰C and 450⁰C were taken from the work of Omowunmi and Susu (2011) and are presented in Figures 1, 2 and 3 respectively.

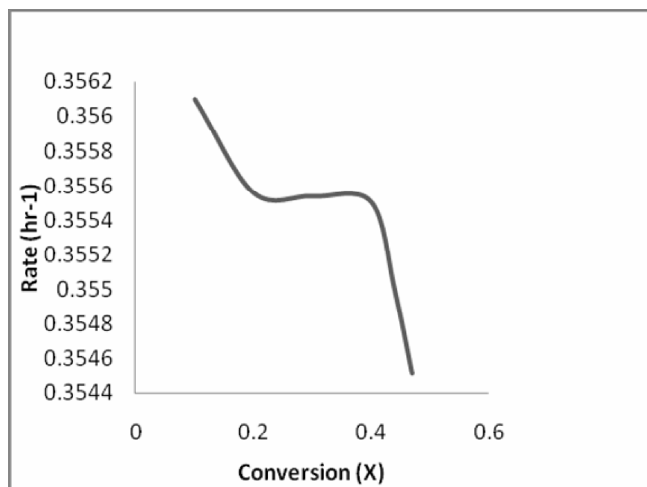


Figure.1 Rate versus Conversion curve for n-Eicosane pyrolysis at 425⁰C

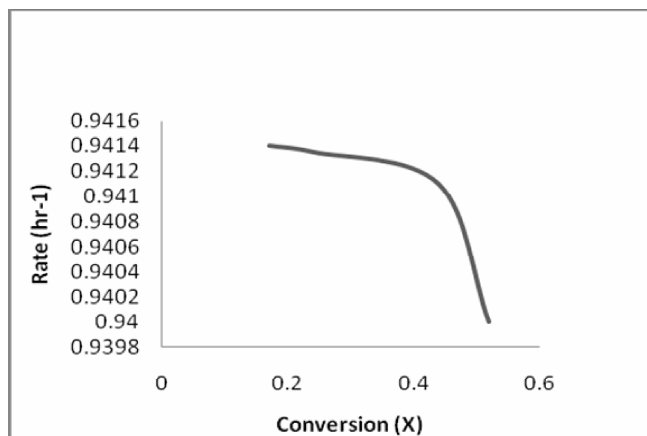


Figure.2 Rate versus Conversion curve for n-Eicosane pyrolysis at 440⁰C

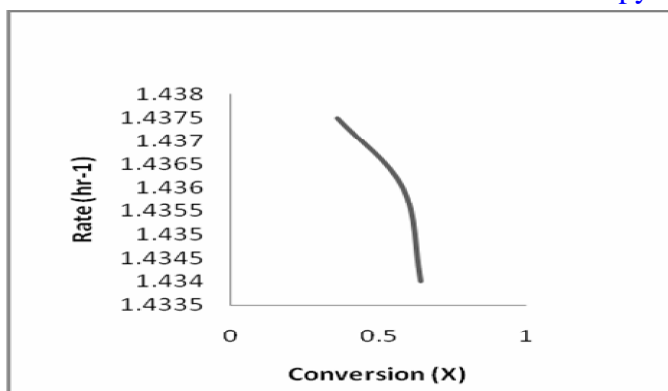


Figure.3 Rate versus Conversion curve for n-Eicosane pyrolysis at 450⁰C

In order to obtain the reaction parameters (rate constants), the rate models and reaction rate-concentration data obtained through Tikhonov regularization technique were used to conduct a Monte Carlo simulation. The algorithm used for the process was developed using commercial software MATLAB and it is shown in Figure 4.

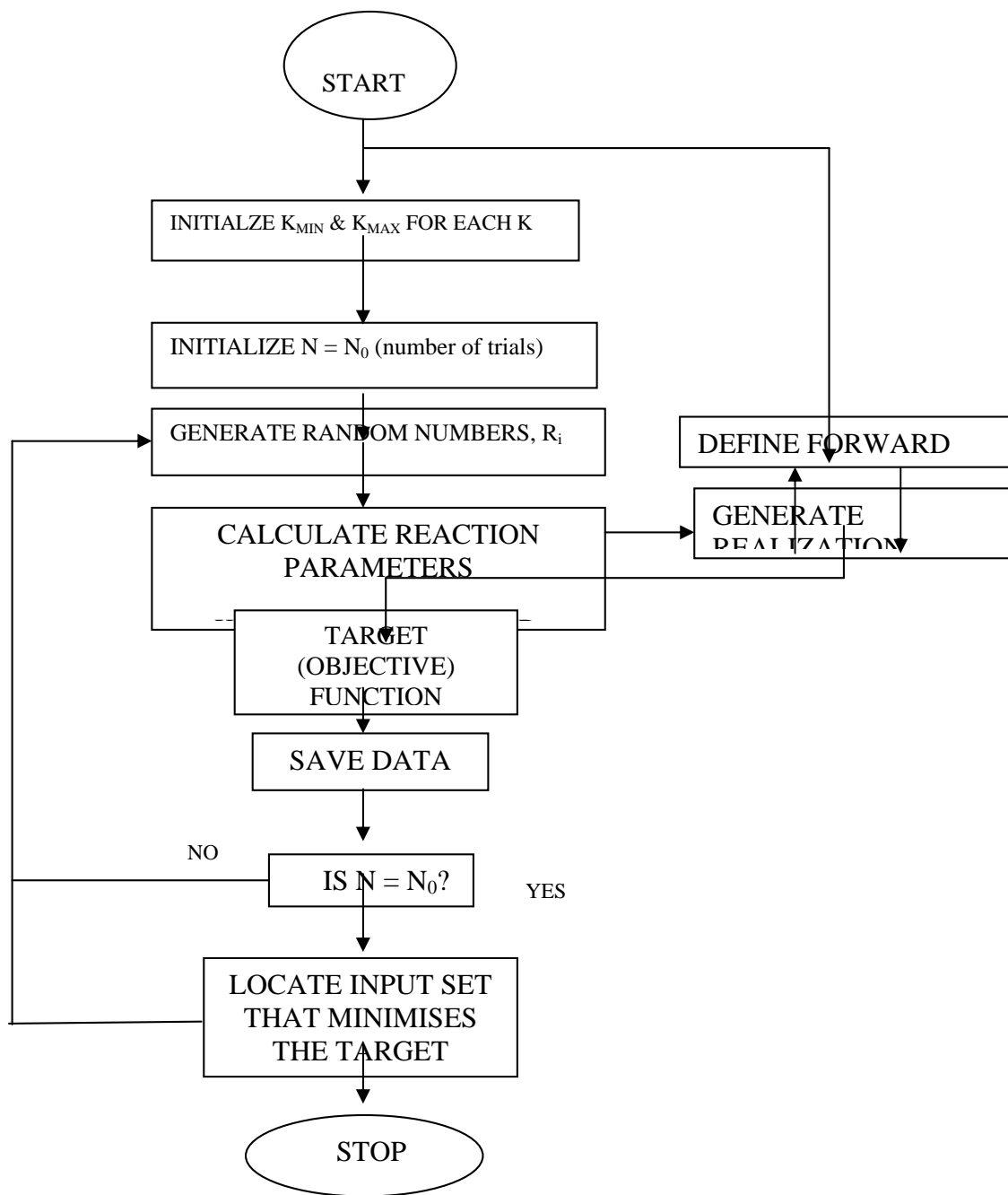


Fig.4 Flow diagram of model algorithm

The computer program was run on MATLAB. The minimum and maximum values for the rate parameters were specified by series of initial guesses. For example, some of the minimum and maximum initial guesses for rate parameters of the 1st order kinetics are: k_1 (40-100, 30-40, 0-10), k_2 (100-200, 50-100, 20-50) and k_5 (10-30, 5-10, 1-5). We also considered the range of values that have been reported in previous works on the same reaction. This has in no small measure reduced our task to a more manageable level as indiscriminate guessing can make the work very tedious.

As the number of trials (simulation runs) increases, the number of set of random values generated for the parameters increases and we can thus, expect more accurate result from the simulation because the probability of obtaining lower objective functions would then increase. For instance, an initial one hundred and fifty simulation runs performed for n-Eicosane pyrolysis (1st order kinetics) resulted in the following least objective functions: 0.2760 (at reaction temperature 425^oC) and 0.3605 (at reaction temperature 440^oC) but for this work we performed three hundred simulation runs for each task and the corresponding values of the least objective functions mentioned earlier are 0.0173 and 0.2381 respectively.

The generation of random variable sets was achieved by assuming a uniform distribution of values in the underlying population from which the values were drawn. This gave each value equal chance of being chosen from the population. The forward model is the rate model and is defined for each regularized concentration and reaction rate obtained from the experimental time-concentration data. Note that since $\sqrt{[iC^{20}]}$ in Equation (29) is a constant the

expression, it can be re-written as

$$\frac{dX}{dt} = K^2 \left(\sqrt{\frac{k^1}{k^5}} \right) [1 - X] \quad (31)$$

Where $K^2 = k^2 \times \sqrt{[iC^{20}]}$ and $k^1, k^2, \text{ and } k^5 \text{ are in } hr^{-1}$

Note also that the values used for the concentration of C_3H_6 in Equation (30) are tabulated in the tables of experimental data above in the dimensionless form – yield of

$C_3H_6 \left(\frac{mol C^3H^6}{mol nC^{20}} \right)$, as a result the units of $k^9, k^{10} \text{ and } k^{12}$ will be $\frac{gmol nC^{20}}{gmol C^3H^6 hr^{-1}}$.

These ks can easily be converted into their physical equivalents in $cm^3 \cdot gmol \cdot hr^{-1}$ by dividing by the initial concentration of n-eicosane. The target function is an optimization procedure whose objective function is to minimize the sum of square of the errors (the difference between the calculated and observed rate values at each of the regularized concentration).

$$\sum_{i=1}^n (r_{obs} - r_{calc})^2$$

(Target function)

n-Heptane reforming on Platinum/Alumina catalyst

Susu and Adewusi (1997) investigated the kinetics of reforming n-heptane on Platinum/Alumina catalyst. Six rate models were proposed based on two possible rate controlling steps with three different assumptions of hydrogen adsorption. The experimental data (time-concentration) were obtained using a pulse micro-catalytic reactor at a total pressure of 3918kpa and a temperature range of 420-500^oC. Out of the six rate models obtained, rate model number VI emerged the best when all models were

subjected to various analyses. The rate model number VI is given by:

$$R = \frac{k^4 K^1 K^3 C_M - k^4 r \frac{K^{12}}{K^8 K^{12}} C_H C_T}{\left[1 + K^1 C_M (1 + K^3) + K^2 \sqrt{C_H} \left(1 + \frac{C_T}{K^8 K^{12}} \right) + \frac{C_T}{K^{12} + \frac{K^{10}}{K^{11}} + \frac{K^{14}}{K^{14}}} \right]}$$

k⁴ & k⁴r = rate constants for forward & backward reactions of rate determining step

Where:

- C_M* = concentration of n – heptane
- C_H* = concentration of Hydrogen
- C_T* = concentration of Toluene
- C_B* = concentration of Benzene
- C_{cp}* = concentration of cracked products
- C_m* = concentration of Methane
- K_s* = equilibrium constants

Omowunmi and Susu (2012) obtained the concentration data from the reaction rate – concentration data for this reaction at various temperatures. Table 2 and Figure 5 show their results (i.e the regularized concentrations of each species in the exit stream at various residence times and reaction rate- concentration curve for n-heptane at reaction temperature 460°C respectively).

Table.2 Regularized concentrations of reaction species in exit stream at different residence times

Residence Time (mg.min/ml)	n-C ₇ H ₁₇ (gmol/dm ³)	Cracked products (C ₂ – C ₆) (gmol/dm ³)	C ₆ H ₅ CH ₃ (gmol/dm ³)	C ₆ H ₆ (gmol/dm ³)	CH ₃ (gmol/dm ³)	H ₂ (gmol/dm ³)
0.8333	0.1350	0.2480	0.2620	0.0118	0.0118	66.2017
1.250	0.1256	0.2517	0.2661	0.0127	0.0127	66.2017
1.580	0.1200	0.2539	0.2685	0.0131	0.0131	66.2017
1.875	0.1115	0.2572	0.2721	0.0139	0.0139	66.2017
2.500	0.0975	0.2628	0.2782	0.0151	0.0151	66.2017
3.750	0.0694	0.2738	0.2904	0.0175	0.0175	66.2017

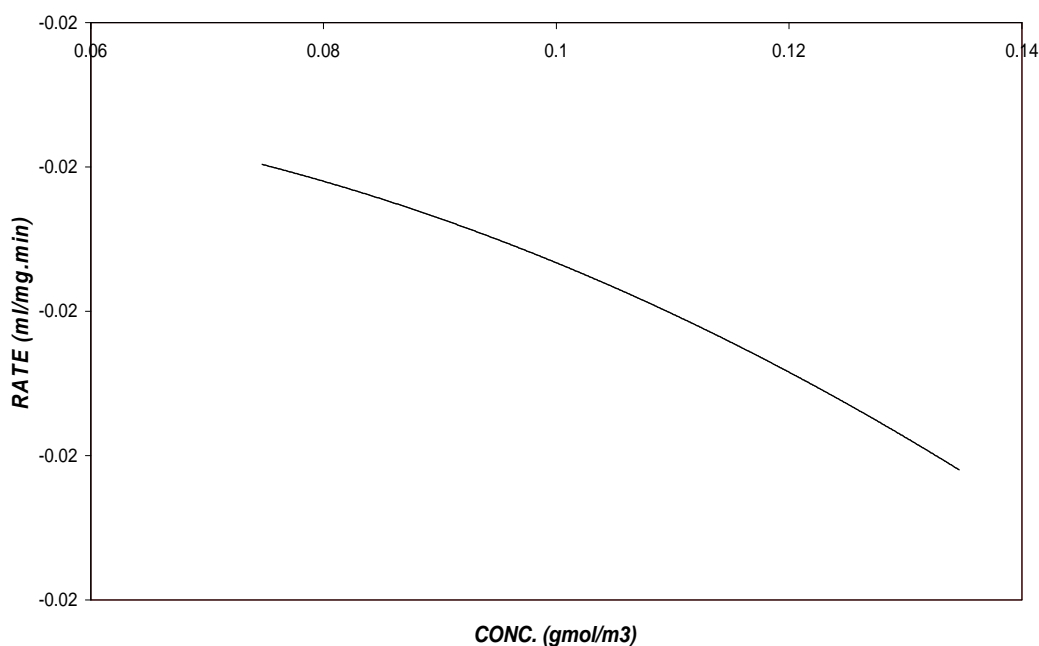


Figure.5 Concentration-Reaction rate profile for n-Heptane reforming on platinum/alumina at 460°C

This rate model (equation (32)) is a very complex one which cannot be integrated analytically to obtain the concentration of n-heptane as a function of the kinetic parameters and time which will then be incorporated as a forward model in the Monte-Carlo algorithm. We therefore, used the concentration-reaction rate data obtained from the original concentration-time data through Tikhonov regularization technique by Omowunmi and Susu (2012). We can then use the concentration-reaction rate data and the rate model directly (as forward model) in the Monte Carlo algorithm.

$$\sum_{i=1}^n (r_{i,exp} - r_{i,model})^2 \quad \text{(Target function)}$$

Results

Tables 3 and 4 show the results of parameters estimation for n-eicosane pyrolysis. Boldface numbers are parameter values obtained by Monte-Carlo simulation (150 simulations) while lightface numbers are parameter values obtained by Omowunmi and Susu (2011) using the Nedler-Mead Simplex method. The results of parameter estimation and objective functions for

Table 8 Results 300 Simulation runs for n-Heptane Catalytic reforming at 460⁰C

Rate Constants (hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
<i>k</i> ₁	0.0187 4.091	0.0597 5.486	0.4210 6.490	502.33 77.09
<i>k</i> ₂	9.0014 18.045	9.8176 46.763	27.8911 48.301	175.07 171.63
<i>k</i> ₅	0.8003 4.773	1.9809 7.782	2.8164 9.278	212.48 112.48
<i>OBJ. F</i>	0.2760 0.1471	0.3605 0.5935	0.5012 0.614	-- --

Rate Constants (hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
<i>k</i> ₉	14.7465 55.684	19.7546 59.910	32.5234 104.946	132.18 98.79
<i>k</i> ₁₀	16.7982 138.795	20.7409 145.432	38.6409 241.157	127.55 85.65
<i>k</i> ₁₂	10.0782 138.184	20.8630 144.838	28.8630 261.691	177.06 98.83
<i>OBJ.F</i>	1.9807 0.0678	1.3803 1.8792	0.2101 1.6055	-- --

Table.5 Result of 150 Simulation Runs for n-heptane catalytic reforming n-heptane catalytic reforming are shown in Table 5.

<i>k</i> _{4f}	<i>K</i> ₁	<i>K</i> ₂	<i>K</i> ₃	<i>K</i> ₅	<i>K</i> ₁₀	<i>K</i> ₁₁	<i>K</i> ₁₂	<i>K</i> ₁₄	<i>k</i> _{4r}
13.1629 13.630	1.8829 1.270	83.8267 85.840	67.4561 67.600	59.4385 56.810	59.4015 53.660	82.0492 85.960	57.2675 57.100	15.2430 15.840	4.3363 4.755
OBJ. F	0.0632 0.0429								

Table.6 Results of 300 Simulation runs for n-Eicosane pyrolysis(1st order kinetics)

Rate Constants (hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
<i>k₁</i>	0.0138 4.091	0.0521 5.486	0.1097 6.490	349.07 77.09
<i>k₂</i>	5.6349 18.045	9.6349 46.763	13.4877 48.301	146.41 171.63
<i>k₅</i>	0.9296 4.773	1.9296 7.782	2.8154 9.278	187.07 112.48
<i>OBJ.F</i>	0.0173 0.1471	0.2381 0.5935	0.3969 0.614	- -

Table.8 Results 300 Simulation runs for n-Heptane Catalytic reforming at 460°C

<i>k_{4f}</i>	<i>K₁</i>	<i>K₂</i>	<i>K₃</i>	<i>K₅</i>	<i>K₁₀</i>	<i>K₁₁</i>	<i>K₁₂</i>	<i>K₁₄</i>	<i>k_{4r}</i>
13.9193 13.630	1.8826 1.270	86.8126 85.840	61.6266 67.600	59.9638 56.810	53.2567 53.660	85.8923 85.960	52.9638 57.100	15.5236 15.840	4.1088 4.755
OBJ.F 0.0251 0.0429									

Table.10 Result of 2000 simulation runs for n-eicosane pyrolysis (2nd order kinetics)

Rate Constants (hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
<i>k₉</i>	59.979 104.802 55.684	59.344 59.910		85.54 98.79
<i>k₁₀</i>	104.946			95.09 85.65
<i>k₁₂</i>	130.641 240.484 241.187	140.860 138.795	145.432	107.08 98.83
<i>OBJ.F</i>	130.656 260.310 138.184 261.691	140.270 144.838		- -
	0.0541 0.0678	0.1412 1.8792	0.0231 1.6055	

Table.11 Summary of activation energies for n-eicosane pyrolysis (1st order kinetics)

Method	Activation Energy (kJ/gmol)			
	Rate Constants	k ₁	k ₂	k ₅
Nedler-Mead		77.09	171.63	112.42
Monte-Carlo Simulation		502.23	175.07	
<i>150 simulation runs</i>	212.48			
<i>300 simulation runs</i>		349.07	146.41	
<i>2000 simulation runs</i>	187.07			
		71.75	93.43	93.89

Table.12 Summary of activation energies for n-eicosane pyrolysis (2nd order kinetics)

Method	Activation Energy (kJ/gmol)			
	Rate Constants	k ₉	k ₁₀	k ₁₂
Nedler-Mead		98.79	85.65	
	98.83			
Monte-Carlo Simulation		132.18	127.55	
<i>150 simulation runs</i>	177.06			
<i>300 simulation runs</i>		143.17	94.77	
<i>2000 simulation runs</i>	162.28			
		85.54	95.09	
	107.08			

It is noteworthy to consider the results of the very important activation energies as functions of the strategies used for the simulation. Tables 11 and 12 present summaries of this comparison. The activation energies reported for the Nelder-Mead method for both the 1st order and 2nd order kinetics of the n-eicosane pyrolysis reaction are the lowest recorded. Although the Monte-Carlo simulation was found superior, no matter the value of the simulation runs, the values of the activation energies predicted were excessively high at the lowest simulation run investigated (150).

However, as the number of simulation runs increased, the value of the activation energy decreased considerably, until at a simulation run of 2000, the values of the activation energies were as low as were obtained for the Nelder-Mead simulations. The possible conclusion reachable from this observation is that the superiority of the Monte-Carlo simulation in predicting kinetic parameters could only be obtained at very high simulation runs to ensure reasonable values of both the activation energies and the parameters themselves.

The Monte-Carlo simulation technique has been used to obtain the model parameters for the pyrolysis of n-eicosane and catalytic reforming of n-heptane. Table 3 shows the values of rate constants for n-eicosane (1st order) kinetics. It is seen that the values of k_1 ranges from 0.0138 at 425^oC to 0.1097 at 450^oC while the values for k_2 ranges from 5.6349 at 425^oC to 13.4877 at 450^oC. The values for k_5 ranges from 0.9296 at 425^oC to 2.8154 at 450^oC. Generally, it is observed that the values for k_2 are much higher than those for k_1 and k_5 at all temperatures reported. The least value of objective function is 0.1730 and it is reported for parameter estimation at 425^oC. This means parameter values obtained at 425^oC are most reliable.

Table 4 reveals the values of rate constants obtained for n-eicosane pyrolysis (2nd order kinetics). Rate constant k_9 has values ranging from 13.3937 to 24.0014 while k_{10} value ranges from 15.3024 to 38.0033. Rate constant k_{12} also has values ranging from 10.8348 to 29.0067. It is observed that values for rate constant k_{10} are generally higher than those for k_9 and k_{12} at all temperatures. The least value of objective function is 0.0913 which is lower than the least obtained for the 1st order kinetics and it is reported for parameter estimation at 450^oC. This means that parameter values obtained at highest temperature 450^oC are most reliable.

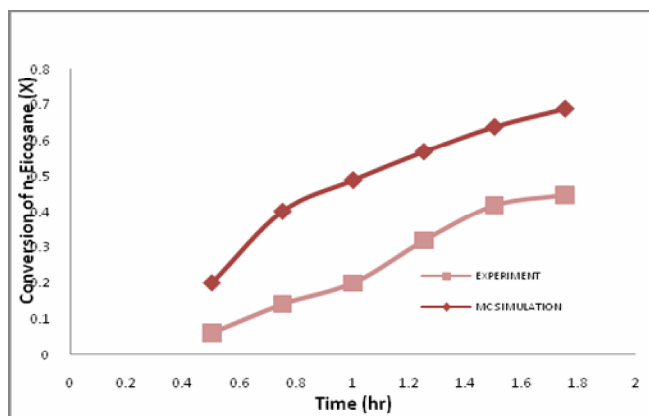


Figure 6
Carlo simulated data for n-Eicosane kinetics) at 425^oC

Comparison of Monte-data with Experimental pyrolysis (1st order

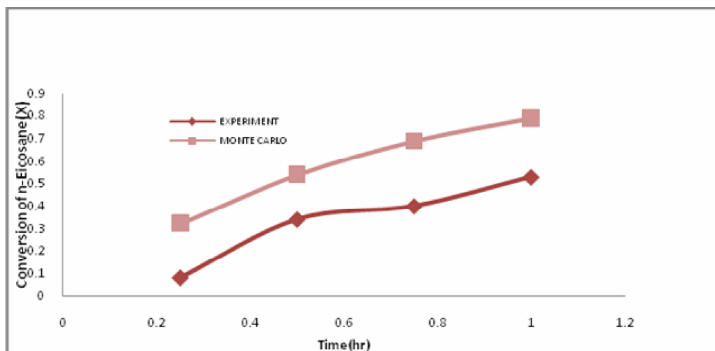


Figure 7 Comparison of Monte-Carlo simulated data with Experimental data for n-Eicosane pyrolysis (1st order kinetics) at 440^oC

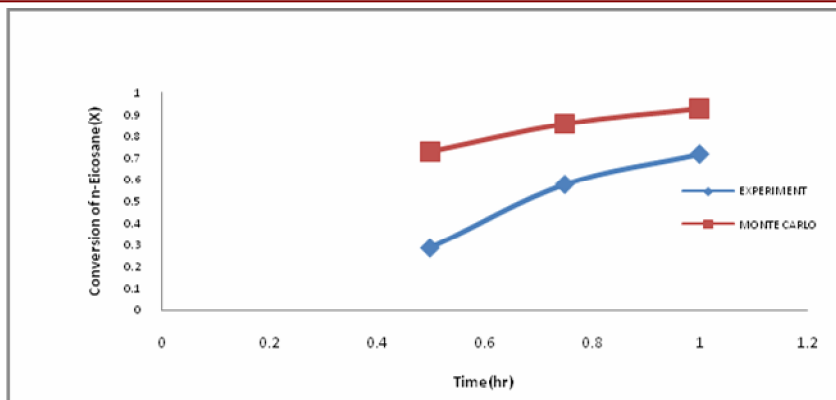


Figure 8 Comparison of Monte-Carlo simulated data with Experimental data for n-Eicosane pyrolysis (1st order kinetics) at 450°C

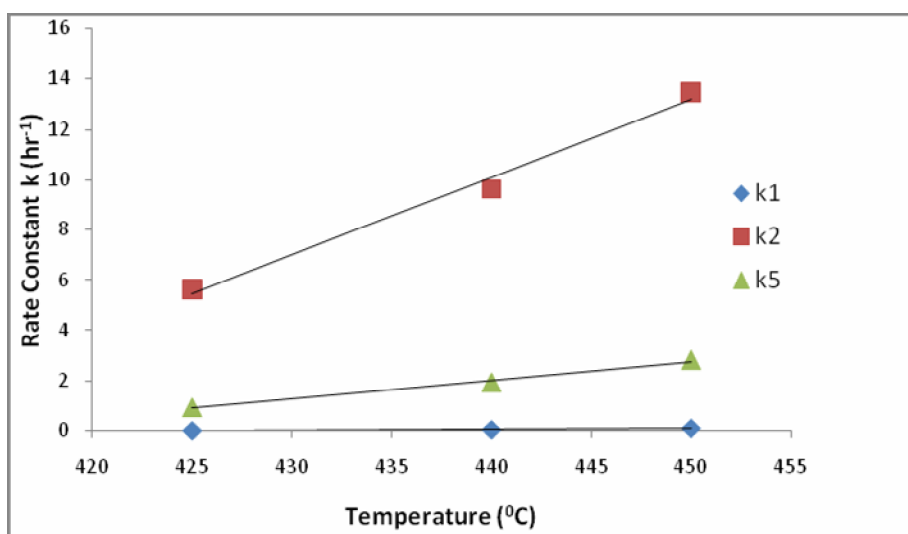


Figure 9 Rate Constant versus Temperature for n-Eicosane pyrolysis (1st order kinetics)

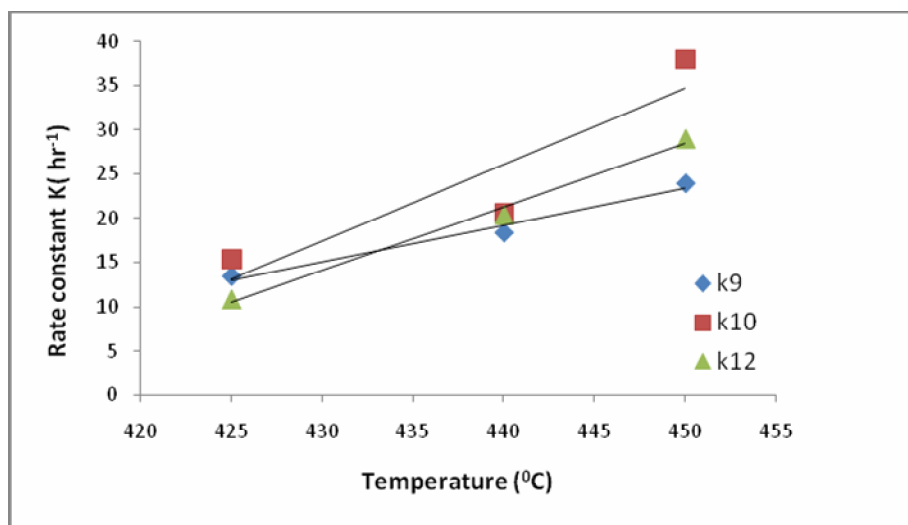


Figure 10 Rate constant versus Temperature for n-Eicosane pyrolysis (2nd order kinetics)

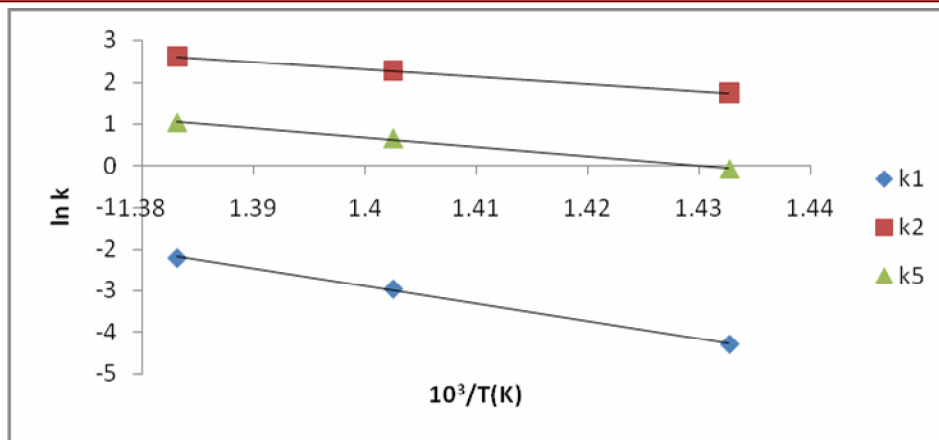


Figure 11 Arrhenius plot for n-Eicosane pyrolysis (1st order kinetics)

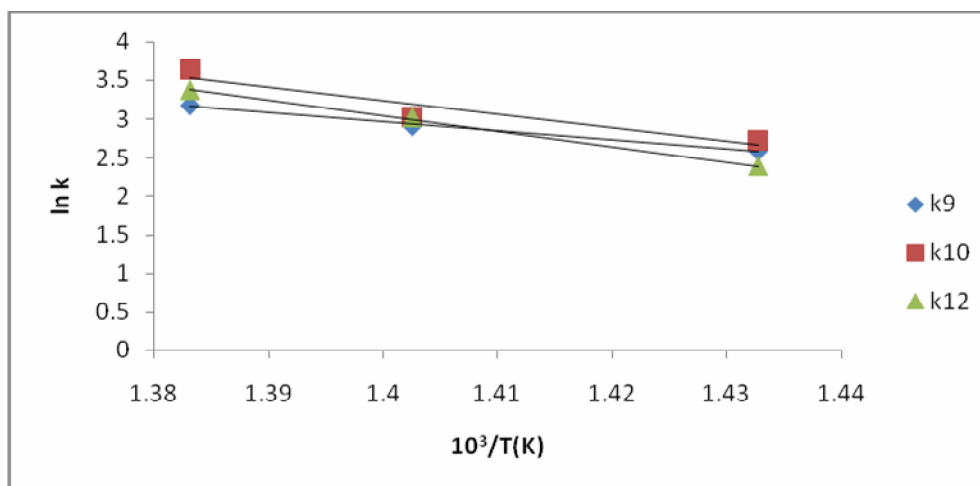


Figure 12 Arrhenius plot for n-Eicosane pyrolysis (2nd order kinetics)

In the case of n-heptane catalytic reforming, the parameters are reported in Table 5 only at one reaction temperature 460⁰C. The rate constants for the forward and backward reactions of the rate determining step are 13.9193 and 4.1088 respectively. On the other hand, the values for the equilibrium constants range from 1.8826 for K_1 to 86.8126 for K_2 . The value of the objective function is 0.0251.

We can compare the kinetic parameters obtained through Monte-Carlo simulation and those obtained from Nelder-Mead simplex method by considering the objective functions obtained and activation energies calculated from the Arrhenius plot in each

case. It is seen that objective functions from the Monte-Carlo simulation are generally lower than their corresponding values obtained through the Nelder-Mead method with an exception in the case of n-eicosane pyrolysis (2nd order kinetics) at 425⁰C. For the activation energies however, the reverse is the case (i.e. activation energies from Monte-Carlo are much higher than those from the Nelder-Mead method). When the rate parameters obtained by Monte-Carlo simulation were compared quantitatively with those reported by Omowunmi and Susu (2011 & 2012) for n-eicosane pyrolysis (1st order kinetics), a sharp contrast was observed. The least difference between parameters is 68.8% (in k_2) at 425⁰C while

for the 2nd order kinetics, the least difference between parameters is 69.3% (in k_9) at 440^oC. In view of the objectives functions obtained for both methods, this significant difference may be due to the superiority of Monte-Carlo Simulation to Nelder-Mead simplex method. However, there is a good agreement between parameters obtained for n-heptane catalytic reforming with the largest difference being 10% (in K_3). From the results of parameter estimation for an initial one hundred and fifty simulation runs presented in Tables 6 and 7 for n-eicosane pyrolysis at 425^oC and 440^oC and in Table 8 for n-heptane catalytic reforming at 460^oC, it is observed that the set of values for the objective functions recorded for parameter estimation when three hundred (300) simulation runs were performed are significantly lower than their corresponding values recorded with one hundred and fifty (150) simulation runs. This shows that the more simulation runs we perform the lower the objective function we get and thus the more accurate the kinetic parameter values are. It is also noticed that the parameter values obtained with one hundred and fifty simulation runs show high deviations from the values obtained by Omomwunmi and Susu (2011) using Nelder Mead Simplex approach in the case of n-eicosane pyrolysis. Deviations are however, low in the case of n-heptane reforming.

Figures 6 - 8 show the plots of conversion of n-eicosane against time. These plots compare the model prediction to experimentally obtained conversion values for the pyrolysis of n-eicosane (1st order kinetics) at three different temperatures. It is observed that there exists very little agreement between the n-eicosane conversion values. However, this little agreement can be taken as good in view of the values of the objective functions obtained. If more random value sets are

generated for more simulation runs we can be sure of getting very small error (least objective function value) which will enhance the accuracy of the parameters so obtained as shown in the case of one hundred and fifty (150) and three hundred (300) simulation runs above. To buttress this point, another 2000 simulation runs was conducted and the result is shown on Tables 8 and 9 for pyrolysis of n-eicosane (1st and 2nd order kinetics respectively). In this new result, a much lower objective functions is obtained which result in better parameter estimates and lower activation energies. Plots of conversion against time were not considered for pyrolysis of n-eicosane (2nd order kinetics) and n-heptane catalytic reforming because of the complex nature of their rate models which do not permit easy integration.

The plots of rate constants against reaction temperature for n-eicosane pyrolysis are shown in Figures 9 and 10 while the Arrhenius plots for the same reaction are shown in Figures 11 and 12. The activation energies obtained from the Arrhenius plots are displayed in Tables 2 and 3. Since the data for n-heptane catalytic reforming are given only at one reaction temperature (460^oC) we did not consider plotting an Arrhenius plot for the reaction.

Conclusion

The Monte-Carlo simulation technique provides a reliable way of estimating the kinetic parameters of complex rate models via the Tikhonov regularization technique. The kinetic parameters of n-Eicosane pyrolysis and n-Heptane catalytic reforming were estimated with relative ease and good accuracy by the use of a computer algorithm developed to perform multiple simulation procedure. The MCS technique was found superior to the traditional Nelder-Mead Simplex method for the generation of kinetic

parameters, especially for large iterations of the MCST.

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