



Application of Monte-Carlo Simulation to Estimate the Kinetic Parameters of n-Eicosane Pyrolysis and n-Heptane Catalytic Reforming

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ABSTRACT

Pyrolysis of hydrocarbons and catalytic reforming of naphtha are important processes in petroleum refineries and petrochemical industries as they lead to production of light olefins, high octane gasoline, aromatics and so on. Thus, it is important to investigate their chemical kinetics in order to establish rate expressions or models for their reactions. In this research work, Monte-Carlo Simulation was applied to estimate kinetic parameters of two complex reactions: pyrolysis of n-Eicosane and catalytic reforming of n-Heptane. The rate models which were derived experimentally from previous work of Susu [18] were used directly as forward reaction models in the Monte-Carlo simulation model algorithm. This required the use of concentration-reaction rate data obtained from the experimental time-concentration data through a technique called Tikhonov regularization. The result revealed the values of rate constants ranging from 0.0138 – 48.301 hr⁻¹ at different temperatures of 425, 440 and 450°C with minimum objective function of 0.01730 for the 1st order kinetic of n-Eicosane pyrolysis. For the 2nd order kinetic of n-Eicosane pyrolysis, the values of rate constants ranged from 10.8348 – 261.691 cm³.gmol⁻¹.hr⁻¹ at different temperatures of 425, 440 and 450°C with minimum objective function of 0.0678. The n-Heptane catalytic reforming was examined at 460°C with rate constants ranging between 1.270 and 86.8126. The methodology used predicted accurately well as there was good agreement between the calculated values and the examined experimental values.

Keyword: Monte-Carlo simulation, Tikhonov Regularization, Catalytic Reforming, Pyrolysis, n-Heptane, n-Eicosane, Kinetics.

INTRODUCTION

Steam pyrolysis of hydrocarbons is an important process for the production of light olefins such as ethylene, propylene and butenes [1]. The catalytic reforming of naphtha is the best method for producing high octane gasoline and aromatics in petroleum refineries and petrochemical industries respectively [2]. Several research efforts have focussed on developing catalysts for pyrolysis and catalytic reforming. Limited data available on catalytic pyrolysis has been summarized elsewhere [3], [4]. However, there is need to investigate their chemical kinetics in order to establish the rate expressions or models for their reactions. The obtained rate expression relates the rate of reaction to the factors that control the reaction, namely, temperature, pressure or 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 itself [5].

There are varieties of techniques developed to estimate kinetic parameters in a rate model from experimental data. The most popular of these, being 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 very hard.

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 *et. al.* [6] 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 integrated time-concentration profiles, the parameters can be obtained with greater ease and possibly also with a higher degree of accuracy [7]. 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, Nelder-Mead simplex method, differentiation evolution and random search method [8]. 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 [9].

Monte Carlo simulation is a type of simulation that relies on repeated random sampling and statistical analysis to compute the results [10]. 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. Mathematical models are used in engineering discipline to describe the interactions in a system using mathematical expressions. 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.

The use of Monte-Carlo simulation for parameter estimation has been observed by a number of researchers. Zhang *et al.* [11] used the technique for adaptive parameter estimation for microbial growth kinetics. Marshal [12] used it for the least squares parameter estimation from multi-equation implicit models. The method was also used by Zhan *et al.* [13] for the estimation of parameters for propylene amoxidation while Agarrwal *et al.* [14] exploited the method in estimating kinetic parameters of reactive transport. Priyanka *et al.* [6] used the Monte-Carlo simulation to estimate the kinetic parameters for pyrolysis of biomass. Recently, Popoola *et al.* [15] applied artificial neural network-based Monte Carlo simulation in the expert system design and control of crude oil distillation Column of a Nigerian Refinery. In all the work 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 parameters estimation for complex reactions by Monte-Carlo simulation through Tikhonov Regularization technique.

MATHEMATICAL MODELLING

The derivation of the working equations of Tikhonov regularization is rather complicated, but the computational steps associated with the procedure are quite straightforward [16].

The Governing Equation

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

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

Equation (1) can be re-written as:

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

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 .

Given a function $f(t)$ as:

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

and integrating the RHS of equation (2) by parts as:

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

$dr(t')$ from equation (3) can be substituted into equation (4) to have

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

Combining equations (2) and (5),

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

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

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

From equation (3),

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

where r_o is the initial rate of reaction.

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

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

Collecting like terms, we have

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

Equation (10) is referred to as the Volterra integral equation which can be solved for the unknown function $f(t)$ and the constants c_o and r_o . This equation is independent of reaction mechanism. Given the values of $f(t)$, c_o and r_o ; $r(t)$ 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 [7].

Discretization of the Volterra Integral Equation

The discretized form of equation (10) is given thus:

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

$$\text{where } i = 1, 2, \dots, N_D \text{ and } j = 1, 2, \dots, N_K. \quad (12)$$

N_D is the number of data points, N_K is the number of discretization points and $f_1, f_2, f_3, \dots, f_{N_K}$ 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

(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

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

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

$$\text{where } C_i = I \text{ and } B_i = t_i \quad (15)$$

$$A_{ij} = \alpha_{ij} (t_i - t'_j) \Delta t' \quad \text{for}$$

$$t_i \geq t'_j = \mathbf{0} \quad \text{and} \quad t_i \leq t'_j \quad (16)$$

$t_i, i = 1, 2, 3, \dots, N_D$ 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

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

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

\mathbf{C} and \mathbf{B} are $N_D \times I$ 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_o and

r_o . Instead, these unknowns are selected to minimize the sum

of squares of δ_i ,

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

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 $d^2 f/dt^2$ and is given by

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

Tikhonov Regularization

In Tikhonov regularization 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 that the \mathbf{f} , c_0 and r_0 that satisfy equations (22) to (24) are given by [17]:

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

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). 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:

$$y = f(x) \quad (26)$$

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. The following steps are involved in Monte-Carlo simulation of physical processes.

- **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.

The algorithm used for the process was developed using commercial software MATLAB and it is shown in Figure 1.

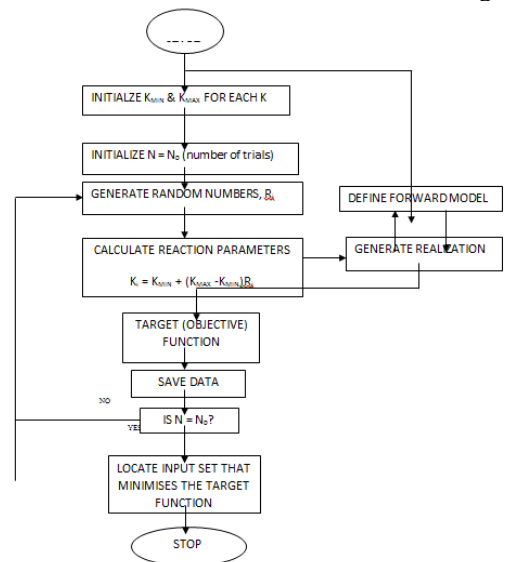


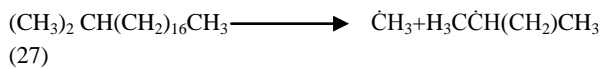
Figure 1: Flow Diagram of Model Algorithm
APPLICATION TO KINETIC PARAMETERS ESTIMATION

When there exist a number of experimentally observed values of input variables from a kinetic study of a particular reaction, Monte-Carlo simulation can be used to obtain the kinetic parameters (rate and equilibrium constants) that appear in a rate model. However, Monte-Carlo algorithm should incorporate the objective 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.

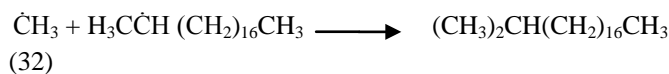
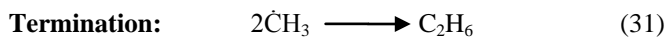
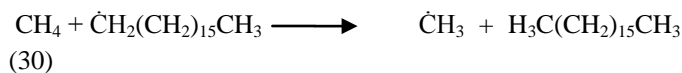
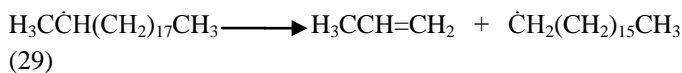
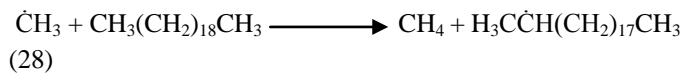
Application to Pyrolysis of n-Eicosane

For the initial first-order chain sequence the following free radical mechanism was proposed by Susu [18] for the decomposition of n-eicosane with a C-C bond scission at the α -isomer of iso-eicosane as the initiation step.

Initiation:



Propagation:



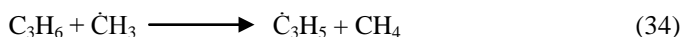
Based on this mechanism the overall reaction rate is given as (Susu, 1982):

$$\frac{d[nC_{20}]}{dt} = -k_2 \left(\frac{k_1}{k_5} \right) \sqrt{[iC_{20}]} [nC_{20}] \quad (33)$$

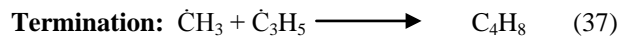
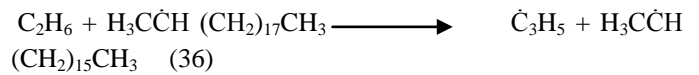
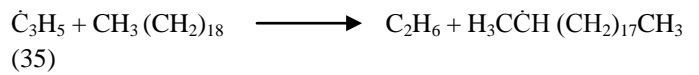
This rate expression is considered as first order because the concentration of iso-eicosane $[iC_{20}]$ was constant throughout the decomposition reaction. The ks are the rate constants in hr^{-1} .

For the new second-order chain sequence resulting from the production of alkyl radicals from propylene the following mechanism was proposed [18].

Initiation:



Propagation:



The overall rate expression for this new mechanism is given as [18]:

$$\frac{d[nC_{20}]}{dt} = -\frac{k_{10}k_{12}}{k_9} [C_3H_6] [nC_{20}] \quad (38)$$

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 $[nC_{20}]$, equation (33) can be written as:

$$\frac{dX}{dt} = k_2 \left(\frac{k_1}{k_5} \right) \sqrt{[iC_{20}]} [1 - X] \quad (39)$$

Since $\sqrt{[iC_{20}]}$ in equation (39) is a constant, the expression can be re-written as

$$\frac{dX}{dt} = K_2 \left(\frac{k_1}{k_5} \right) [1 - X] \quad (40)$$

Where $K_2 = k_2 \times \sqrt{[iC_{20}]}$ and $k_1, k_2,$ and k_5 are in hr^{-1}

In terms of fractional conversion, equation (38) can be written as:

$$\frac{dX}{dt} = \frac{k_{10}k_{12}}{k_9} [C_3H_6] [1 - X] \quad (41)$$

The experimental data for this reaction reported by Susu [18] at three different temperatures of 425, 440 and 450^oC are given in table 1. 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).

$$\sum_{i=1}^n (r_i^{calc} - r_i^{obs})^2 \quad (42)$$

The reaction rate versus conversion curves obtained by Tikhonov regularization for n-eicosane pyrolysis at reaction temperatures 425^oC, 440^oC and 450^oC were presented elsewhere [19].

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

Application to N-Heptane reforming on Platinum/Alumina Catalyst

Susu [5] investigated the kinetics of reforming n-heptane on Platinum/Alumina catalyst. Six rate models were proposed based on two possible rate controlling steps and 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°C. The rate model that best described the process is given as:

$$R = \frac{k_4 K_1 K_2 C_N - k_4 r \frac{K_2^2}{K_3 K_{12}} C_H C_T}{[1 + K_1 C_N (1 + K_3) + K_2 \sqrt{C_H} (1 + \frac{C_T}{K_3 K_{12}}) + \frac{C_T}{K_{12}} + \frac{C_B}{K_{10}} + \frac{C_{cp}}{K_{11}} + \frac{C_m}{K_{14}}]^2} \quad (43)$$

Where: C_N=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
 k_{4f}&k_{4r}=rate constants for forward&backward reactions of rate determining step

The reaction rate – concentration data obtained from the time – concentration data for this reaction at various temperatures shown in table 2 was presented elsewhere [20].

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/d m ³)	CH ₃ (gmol/d m 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

The rate model stated as equation (43) 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. Thus, the concentration-reaction rate data obtained from the original concentration-time data through Tikhonov regularization technique by Omowunmi *et. al.* [20] was used. The concentration-reaction rate data and the rate model can directly be used as forward model in the Monte Carlo algorithm. The target function for this reaction is as stated as equation (42).

RESULTS

Table 3 shows the results of parameter estimation for 1st order kinetic of n-eicosane pyrolysis while table 4 indicates the results for its 2nd order kinetics. The results of parameters estimation and objective functions for n-heptane catalytic reforming are presented in table 5. Figures 2, 3 and 4 represent comparison between Monte-Carlo simulated data and experimental data for 1st order kinetics of n-eicosane pyrolysis at 425°C, 440°C and 450°C respectively. Boldface figures are parameter values obtained by Monte-Carlo simulation while lightface figures are experimental values obtained by Omowunmi *et. al.* [19] using the Nedler-Mead simplex method. Figures 5 and 6 represent the plots of rate constants versus

Table 3: Results of Parameter Estimation for 1st Order Kinetic of N-Eicosane Pyrolysis

Rate Constants (hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
k_1	0.0138 4.091	0.0521 5.486	0.1097 6.490	349.07 77.09
k_2	5.6349 18.045	9.6349 46.763	13.4877 48.301	146.41 171.63
k_5	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	- -

temperature for n-Eicosane pyrolysis for its 1st order and 2nd order kinetics respectively. Figures 7 and 8 represent Arrhenius

plot for n-Eicosane pyrolysis for its 1st order and second order kinetics respectively.

Table 4: Results of Parameter Estimation for 2nd Order Kinetic of N-Eicosane Pyrolysis

Rate Constants (cm ³ .gmol ⁻¹ .hr ⁻¹)	Temperature (°C)			Activation Energy (KJ/gmol)
	425	440	450	
k_9	13.3937 55.684	18.3937 59.910	24.0014 104.946	143.17 98.79
k_{10}	15.3024 138.795	20.6047 145.432	38.0033 241.187	94.77 85.65
k_{12}	10.8348 138.184	20.4174 144.838	29.0067 261.691	162.28 98.83
<i>OBJ.F</i>	1.2404 0.0678	0.4636 1.8792	0.0913 1.6055	- -

Table 5: Results of Parameter Estimation for n-Heptane Catalytic Reforming at 460oC

k_{4f}	K_1	K_2	K_3	K_5	K_{10}	K_{11}	K_{12}	K_{14}	k_{4r}
13.9193	1.8826	86.8126	61.6266	59.9638	53.2567	85.8923	52.9638	15.5236	4.1088
13.630	1.270	85.840	67.600	56.810	53.660	85.960	57.100	15.840	4.755

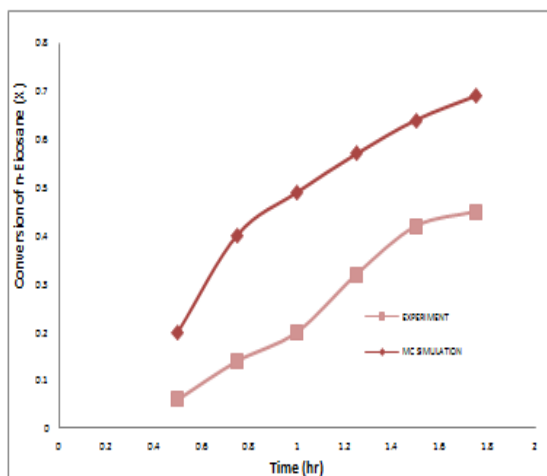


Figure 2: Comparison between Monte-Carlo Simulated Data and Experimental Data for 1st Order Kinetics of n-Eicosane Pyrolysis at 425oC

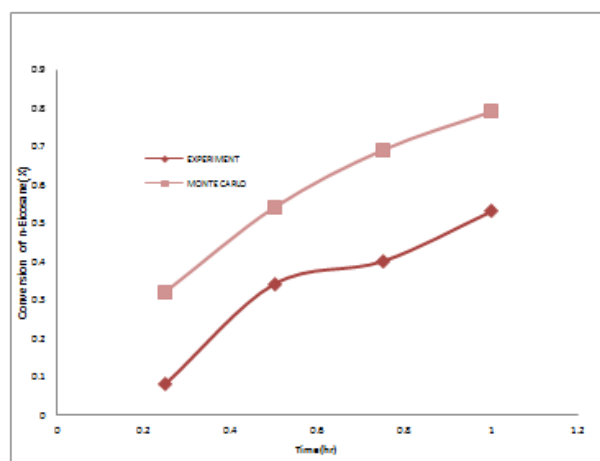


Figure 3: Comparison between Monte-Carlo Simulated Data and Experimental Data for 1st Order Kinetics of n-Eicosane Pyrolysis at 440oC

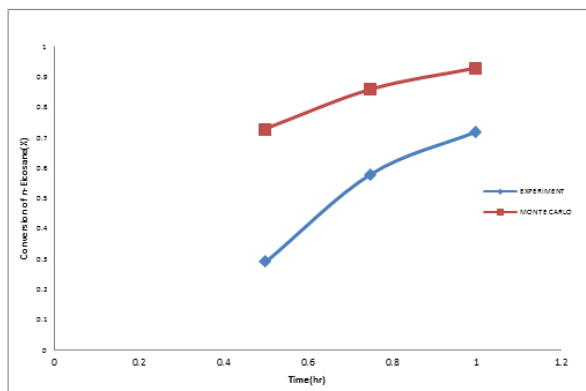


Figure 4: Comparison between Monte-Carlo Simulated Data and Experimental Data for 1st Order Kinetics of n-Eicosane Pyrolysis at 450°C

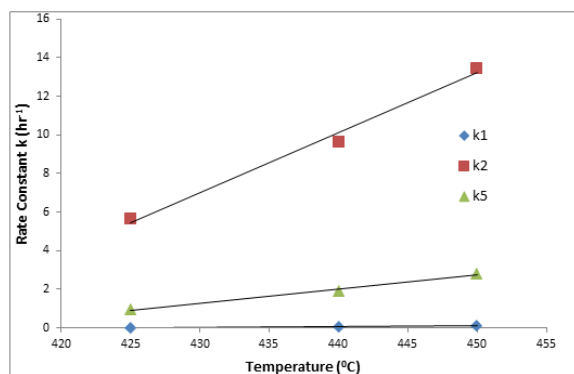


Figure 5: Rate Constants Versus Temperature for 1st order Kinetics of n-Eicosane pyrolysis

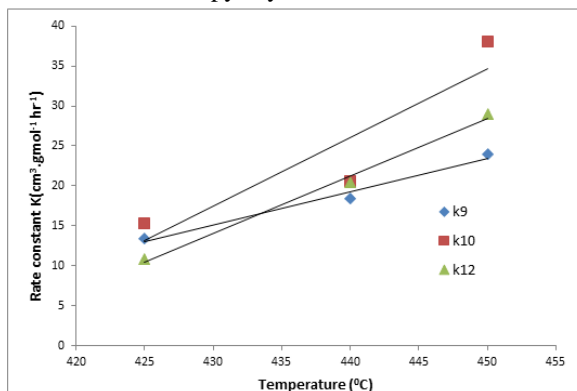


Figure 6: Rate Constants Versus Temperature for 2nd order Kinetics of n-Eicosane pyrolysis

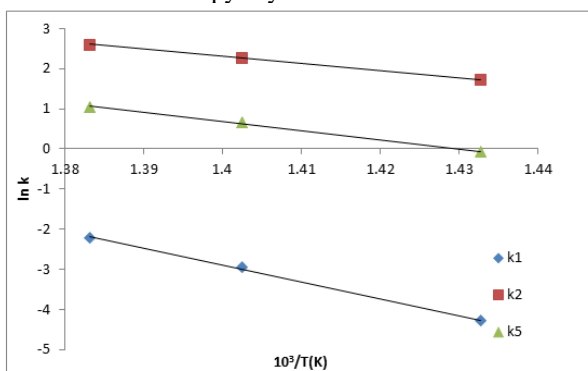


Figure 7: Arrhenius Plot for 1st Order Kinetics of n-Eicosane Pyrolysis

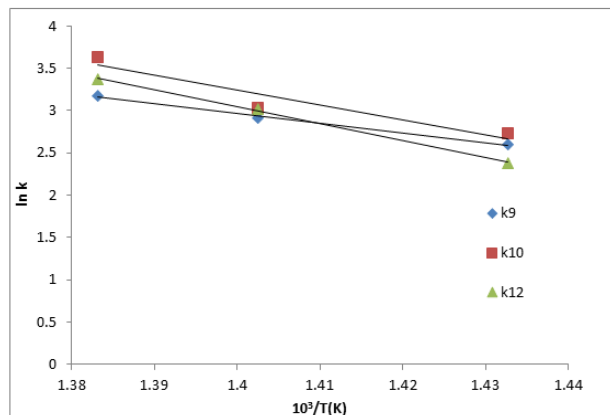


Figure 8: Arrhenius Plot for 2nd Order Kinetics of n-Eicosane Pyrolysis

DISCUSSION OF RESULTS

The Monte-Carlo simulation technique had been used to obtain the model parameters for the pyrolysis of n-eicosane and catalytic reforming of n-heptane. It was seen from the results presented in table 3 that the values of k_1 ranges from 0.0138 at 425°C to 0.1097 at 450°C while the values for k_2 ranges from 5.6349 at 425°C to 13.4877 at 450°C. The values for k_5 ranges from 0.9296 at 425°C to 2.8154 at 450°C. Generally, it was 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 was 0.01730, reported for parameter estimation at 425°C. This means parameter values obtained at 425°C are most reliable as minimum sum of square errors were obtained at this temperature.

The results from table 4 revealed the values of rate constants obtained for 2nd order kinetics of n-eicosane pyrolysis. Rate constant k_9 had values ranging from 13.3937 to 24.0014 while k_{10} value ranged from 15.3024 to 38.0033. Rate constant k_{12} also had values ranging from 10.8348 to 29.0067. It was observed that values for rate constant k_{10} were generally higher than those for k_9 and k_{12} at all temperatures. The least value of objective function was 0.0913, lower than the least obtained for the 1st order kinetics and it was reported for parameter estimation at 450°C. This means that parameter values obtained at highest temperature 450°C were the most reliable. For n-heptane catalytic reforming, the parameters were reported in table 5 only at one reaction temperature of 460°C. The rate constants for the forward and backward reactions of the rate determining step were 13.9193 and 4.1088 respectively. On the other hand, the values for the equilibrium constants ranged from 1.8826 for K_1 to 86.8126 for K_2 . The value of the objective function was estimated to be 0.0251.

When the rate parameters obtained by Monte-Carlo simulation were compared with those reported by Omowunmi *et. al.* ([19], [20]) for 1st order kinetics of n-eicosane pyrolysis, significant difference was observed. The least difference between parameters was 68.8% for k_2 at 425°C for 1st order kinetics while for 2nd order kinetics, the least difference between parameters was 69.3% for k_9 at 440°C. This significant difference might be due to the superiority of Monte-Carlo

Simulation to Nedler-Mead simplex method. However, there was a good agreement between parameters obtained for n-heptane catalytic reforming with the largest difference being 10% for K_3 .

Figures 2, 3 and 4 show the plots of conversion of n-eicosane against time at different temperatures for its 1st order kinetics. These plots compared the model prediction to experimentally obtained conversion values for the pyrolysis of n-eicosane for its 1st order kinetics. It was observed that very little agreement existed between the n-eicosane conversion values. However, this little agreement could be taken as good in view of the values of the objective functions obtained. If more random value sets were generated, we could be sure of getting very small error (least objective function value) which would enhance the accuracy of the parameters obtained. Similar plots 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 did not permit easy integration. The plots of rate constants against reaction temperature for n-eicosane pyrolysis were shown in figures 5 and 6 while the Arrhenius plots for the same reaction were shown in figures 7 and 8. The activation energies obtained from the Arrhenius plots were displayed in tables 3 and 4. Since the data for n-heptane catalytic reforming were given only at one reaction temperature (460°C), we did not consider plotting an Arrhenius plot for the reaction.

CONCLUSION

The Monte-Carlo simulation technique had been applied to estimate kinetic parameters for pyrolysis of n-eicosane for both 1st and 2nd order kinetics at different temperatures; and catalytic reforming of n-heptane. This methodology provides a reliable way of estimating the kinetic parameters of complex rate models via the Tikhonov regularization technique. MATLAB computer program was written for the model algorithm to perform multiple simulation procedure. The kinetic parameters of n-eicosane pyrolysis and n-Heptane catalytic reforming were estimated with relative ease and good accuracy. There was good agreement between experimental and calculated parameters for both pyrolysis of n-eicosane and catalytic reforming of n-heptane.

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