

Estimation of Kinetic Parameters of Complex Reactions by MATLAB Software

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ABSTRACT:

The determination of the rate constants of chemical reactions is very difficult and time consuming process. The aims of this research were:

- 1) Develop a computer program using MATLAB 7 software to determine the rate constants for any system of complex reactions at any temperature.
- 2) Study the effect of the number of input (or experimental) points on the accuracy of predicted kinetic parameters.

Fluid catalytic cracking FCC was taken as case study. The algorithm of this research is start with a mathematical representation to generate concentration versus catalyst weight data points using six lump reaction rates model. The generated data was regarded as experimental points and would be reused to determine the reaction rate constants.

Using different number of input concentration versus catalyst weight data points, the reaction rate parameters (k values) were regressed by minimizing the sum of squares of the error between the input points and predicted ones. The sum of squares of the errors was minimized using an iterative method.

This research answered the question on every researcher mind, if reaction rate for any complex reaction can be predicted by two points (initial and final points). It was shown that using two input points will give weak kinetic model. The results showed that, the proposed programs are very efficient, fast and accurate tools to determine the rate constants of any complex reactions at any certain temperature. Also, accurate reaction kinetic could be described using 11 to 21 points.

Keywords: fluidized catalytic cracking, rate constants, kinetic, optimization, MATLAB

1. INTRODUCTION

The fluid catalytic cracking (FCC) is one of the most important chemical processes developed during the last century. Today, FCC is responsible for almost 50% of all gasoline production in the whole world. This process breaks the larger molecular weight fractions of

oil into smaller ones, such as gasoline, LPG (Liquefied Petroleum Gas) and LCO (Light Cycle Oil).

Many efforts have been made in order to develop a comprehensive mathematical model which can incorporate chemical reaction kinetic within fluid catalytic cracking (Han et al., 2001; Subramanya et al., 2005; Gupta et al., 2007; Heydari et al., 2010).

There are different kinds of laboratory reactors are available to evaluate the catalytic cracking reaction kinetics. These reactors include fixed bed, fluidized bed, stirred batch, and pulse reactors (Weekman, 1974; Sunderland, 1976). In all of these reactors the reaction rates are represented by a system of ordinary differential equations of weight or mole fractions as a function reaction time, reactor length or catalyst weight.

Parameter estimation of catalytic cracking reaction kinetics has become necessary since catalytic cracking has become an important secondary process in refineries. There are two parameter estimation methods, namely linear least square method and nonlinear least square method. The objective of both methods is to produce the best relationship, which will represent all of the experimental data with minimum average error or deviation. Linear least squares may be used to determine the best constants in a given form of equation and also for establishing the best form of equation for a given set of data. Nonlinear least squares method depends on iteration to minimize sum of squares of residuals, SSR. Due to, the most of chemical engineering processes is nonlinear therefore nonlinear least square method is appropriate for dynamic optimization and parameter estimation in chemical processes. The nonlinear least square method has been extensively used to solve the problem of rate constant optimization in complex and consecutive reactions.

A dynamic optimization technique is one of techniques available to determine trajectory because it can deal with the ordinary differential equations (ODE) which can represent a real behavior of dynamic process (Hirmajer, et al. 2009).

Brooke et al. (1997) provide a solver called NLP to solve nonlinear programming problems. NLP solver can be used to minimize the sum of squares of residuals. Ancheyta et al. (1997) presented a sequential strategy for determining the Kinetic constants of a five-lump FCC model. They divided the gas lump of the four-lump scheme into dry and wet gas lumps. Arx and Manock (1998) used a genetic algorithm technique for finding a global minimum for the error function. Genetic algorithm is adopted to optimize the parameters of the postulated mechanisms. Cai et al (1999) developed an error-compensation algorithm based on a kinetic model of detecting intermediates in consecutive first-order reactions using the non-linear least-squares method. Zamosny and Belohlav (1999) developed a useful regression analysis

software package named ERA, its input data matrix is limited to 20 independent variables and 20 responses, with up to 256 experimental points in each response and the number of model parameters is restricted to 15.

Osman (2002) developed a kinetic model to simulate the riser of a residue fluid catalytic cracking unit (RFCC) processing residue from Sudanese crude oil.

Yuceer et al. (2005) developed a parameter estimation software named PARES (PARAmeter ESTimation) coded in MATLAB 6.5 to determine the values of model parameters that provide the best fit to measured data, based on some type of least squares or maximum likelihood criterion.

Zhao et al. (2006) used a nonlinear least squares regression to fit the kinetic profiles.

Abdallah and Seoud (2010) developed a MATLAB computer program for determining the rate constants for the general form of any consecutive second order irreversible reaction at a certain temperature.

Gorjia et al. (2010) proposed a new application of the mean centering of ratio spectra method for estimation of the rate constants of second order reactions, using kinetic-spectrophotometric data. The method is based on the mean centering of the ratio spectra to obtain a kinetic profile of the product.

Di Maggio et al. (2010) formulated a parameter estimation problem for a large-scale dynamic metabolic network.

2. LUMPING OF FCC REACTIONS

The kinetics modeling of catalytic cracking has been traditionally based on using a lumping strategy: chemical species with similar behaviors are grouped together forming a smaller number of species named lump (Coxson and Bischoff, 1987).

The products of gasoline cracking can include a wide distribution of molecular weights, from C_1 to C_{20} . Thus, lumping of species is important to make the kinetic modeling. The number of lump in the fluid catalytic cracking differs from 3 to 34.

2.1 Three Lump Model

The first proposed lumping model was the three lump model advanced by Weekman and Nace (1970). The three lump model consists of one feedstock lump (gas oil, VGO or any other heavy feed) and two product lump: a) gasoline b) coke + light gases. The three lump model can be represented in figure (1):

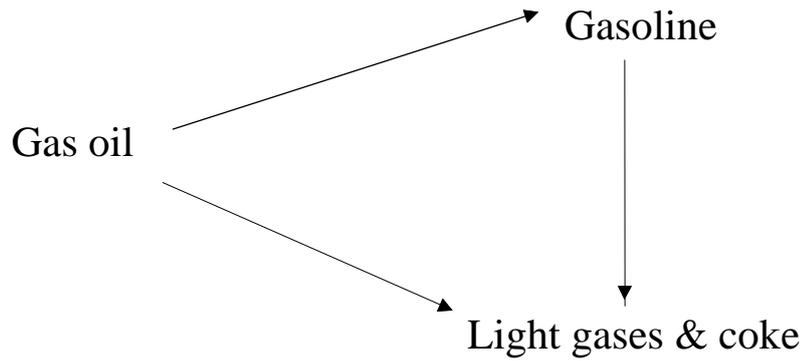


Figure (1) Three lump model

2.2 Four Lump Model

Yen et al. (1987) introduced the four lump model. With four lump the coke and gases were separated. Figure (2) represent four lump model:

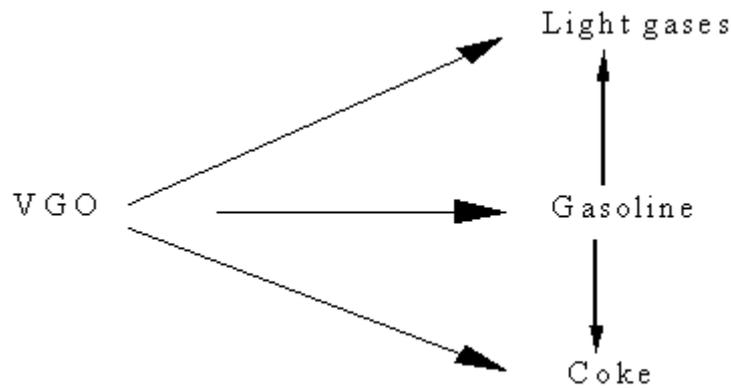


Figure (2) Four lump model

2.3 Five Lump model

Ancheyta et al. (1997) extended the four lump model to five lump who divided the gases lump into two different lump: a) liquefied petroleum gas (LPG), b) dry gas. LPG can be formed either directly from gas oil or as a secondary product from gasoline over-cracking. On the other hand, dry gas (H_2 , C_1 , C_2) can be formed either directly from gas oil cracking or as a secondary product from gasoline and LPG cracking. The five lump model can be schematically represented as in figure (3):

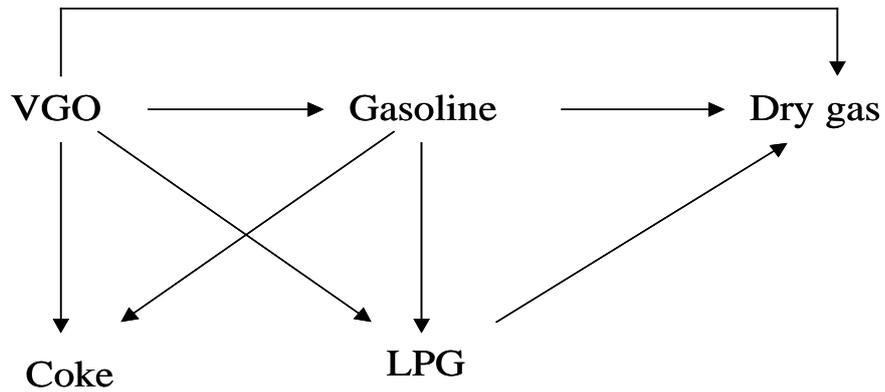


Figure (3) Five lump model

2.4 Six Lump Model

Takatuska et al (1987) used a six lump model including heavy feedstock (vacuum residue), vacuum gas oil (VGO) and heavy cyclic oil (HCO), light cyclic oil (LCO), gasoline, light gases, and the coke.

2.5 Other Lump Model

In 1990 Kraemer et al. proposed an eight lump model. The feedstock was separated into heavy and light fractions: a) heavy paraffins, heavy naphthenes and heavy aromatics with boiling point greater than 343°C and b) light paraffins, light naphthenes, and light aromatics with boiling points in the range 220°C to 343°C. The eight lump model can be represented in figure (4) (Meng et al 2006):

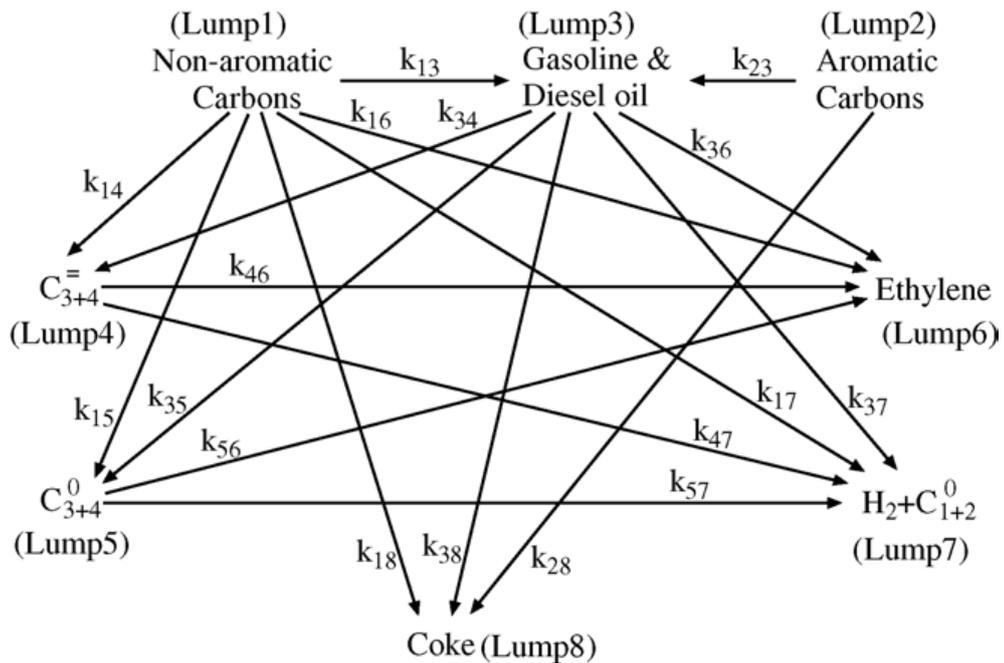


Figure (4) Eight lump model

Jacob et al., (1976) proposed a more complicated and detailed lump model (10-lump) describing in more detail the feedstock. Figure (5) shows the 10-lump model.

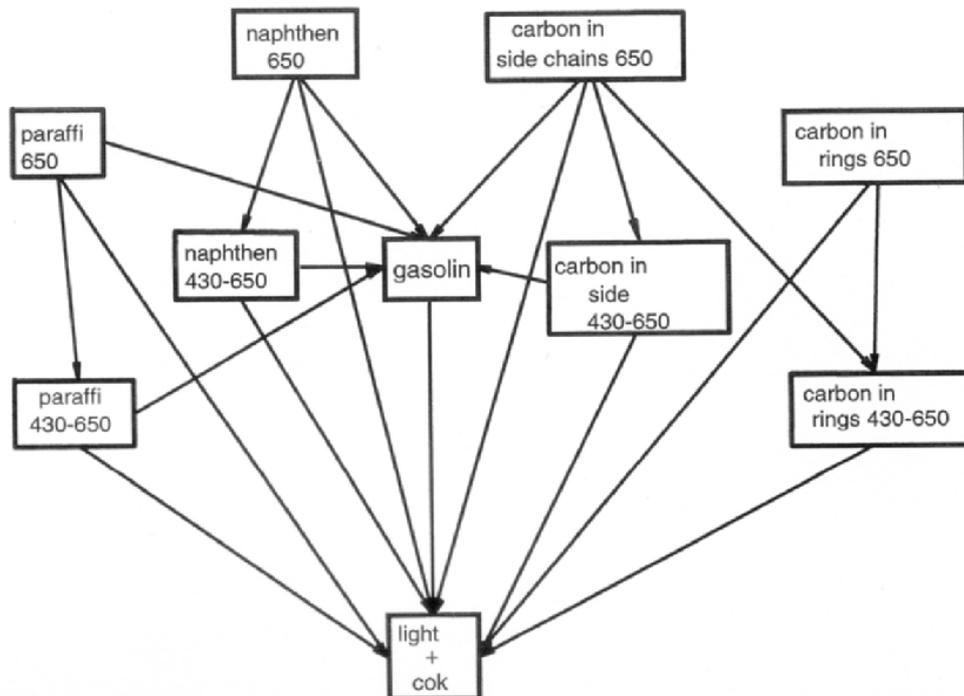


Figure (5) Ten lump model

Meier et al., (2001) used more complicated model containing 34 lumps to describe FCC.

3. MATHEMATICAL REPRESENTATION

3.1 The Kinetic model

The kinetic modeling of the catalytic cracking reactions is essential for the mathematical model. In this study six lump model was used to represent the reaction kinetics, as shown in Figure (6) (Ancheyta and Sotelo, 2002). Ancheyta and Sotelo, (2002) obtained experimental data about catalytic cracking of vacuum gas oil in microactivity reactor at reaction temperature of 773 K and WHSV between 6-48 hr⁻¹ using a commercial equilibrium catalyst. They also calculated the kinetic parameters of six lump kinetic model.

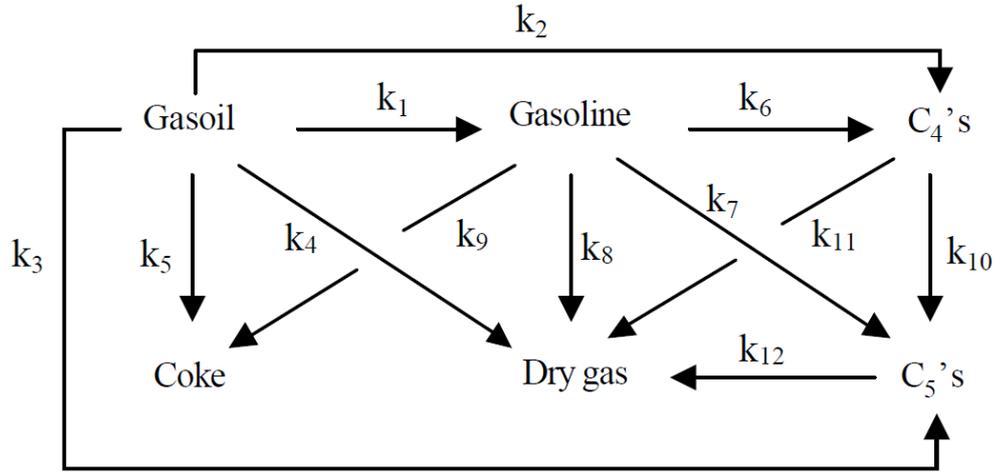


Figure (6) Six lump model

For each reaction, a kinetic expression (r_i) was formulated as a function of weight fraction (y_i), deactivation function (ϕ) and kinetic constants (k_i). According to the kinetic model, the weight fraction of each of these six lumps could be described by the following system of equations:

$$\text{Gas oil: } r_1 = -(k_1 + k_2 + k_3 + k_4 + k_5)y_1^2\phi \quad (1)$$

$$\text{Gasoline: } r_2 = (k_1y_1^2 - k_6y_2 - k_7y_2 - k_8y_2 - k_9y_2)\phi \quad (2)$$

$$\text{C4's: } r_3 = (k_2y_1^2 + k_6y_2 - k_{10}y_3 - k_{11}y_3)\phi \quad (3)$$

$$\text{C5's: } r_4 = (k_3y_1^2 + k_7y_2 + k_{10}y_3 - k_{12}y_4)\phi \quad (4)$$

$$\text{Dry gas: } r_5 = (k_4y_1^2 + k_8y_2 + k_{11}y_3 + k_{12}y_4)\phi \quad (5)$$

$$\text{Coke: } r_6 = (k_5y_1^2 + k_9y_2)\phi \quad (6)$$

Table (1) contain the values of the kinetic constants. A rate law is a differential equation, describes the rate of change of a reactant (or product) concentration with catalyst weight.

3.2 Catalyst Deactivation

Catalyst deactivation in FCC process can take place due to several factors. But coke formation is the most important factor affecting catalyst activity. As catalytic reactions proceed coke deposits on the catalyst surface. Coke covers the catalyst active sites leading to catalyst activity decay. Weekman (1968) employed exponential decay law to describe catalyst deactivation, the following simple relations;

$$\phi = e^{-k_d t_c} \quad (7)$$

3.3 Concentration-Catalyst Weight Data

Due to the lack in the experimental data concerning with fluid catalytic cracking, a mathematical representation was build to generate concentration-catalyst weight data points using six lump reaction rates. The following assumptions were used:.

- 1- Plug flow within the reactor.
- 2- Axial dispersion in the reactor is negligible.
- 3- All reactions are first order except gas oil cracking reaction which assumed to be second order.
- 4- Catalyst activity decay according to exponential decay law.
- 5- The feed does not contain a coke.
- 6- Isothermal reactor temperature.

The simultaneous first order differential equations (1 to 6) with catalyst deactivation equation (7), were integrated numerically using fourth order Runge-Kutta method with the following initial boundary conditions.

$$y_1 = 1, y_2 = 0, y_3 = 0, y_4 = 0, y_5 = 0, y_6 = 0$$

In the mathematical model, the reaction temperature was taken as 773 K and WHSV 48 hr⁻¹. Table (2) contains the generated concentrations versus catalyst weight data of six lump fluidized catalytic cracking reactions.

3.4 Parameter Identification

Different number of data points was used to predict parameters of reaction kinetic. The kinetic model was predicted using data obtained in table (2) at a significant temperature 773 K. The following steps were used to calculate parameters of reaction kinetic:

1. The first step is determining the rate constants of the reactions by getting the concentration difference for each catalyst weight interval depending on selected number of points using the following equation:

$$-r_i = \frac{\Delta y_i}{\Delta Wc} \quad (8)$$

2. Choose an initial guess for the k values.
3. Depending on assumed k values and using equations (1-7), simulation of the kinetic reactions is performed.
4. Updating the values of the assume k values using simplex search method.

5. The predicted values are compared with experimental ones at each measured point. All deviations between experimental and calculated values are squared and summed up to form an objective function F:

$$F = \sum_{i=1}^n \sum_{j=1}^N (y_{exp\ i} - y_{cal\ i})^2 \quad (9)$$

Where the $y_{exp\ i}$, $y_{cal\ i}$ are the input (or experimental) and concentration values of species i at catalyst weights W_c , n is the number of species and N is the number of input data points. For each set of input points, the new value of F is calculated. The rate constants corresponding to the minimum F are stored and considered as improved rate constants.

The Arrhenius equation represents the dependence of the reaction rate constant k on the temperature. With this equation from two measuring points in different temperatures the activation energy (E_A) of the reaction could be calculated.

$$k = k_0 \cdot \exp\left[-\frac{E_A}{R.T}\right] \quad (10)$$

3.5 Software

All calculations in this paper were performed using Matlab 7.0 software. The *ode23* command was used to integrate simultaneous ordinary differential equations numerically using fourth-order Runge-Kutta algorithm, while *fmincon* command was used to estimate the kinetic parameters based on minimization the objective function F , which subject to a nonlinear constraint in which k values must be positive (greater than 0).

4. RESULTS AND DISCUSSION

4.1 Reaction Kinetic

Table (3) contains the predicted reaction rate constants using different number of points. It's clear from table (3) that, increasing the number of input data points will decrease the error between model k values and predicted k values. The predicted reaction rate constants in Table (3) were used in simulation and the simulation results were compared with input data points. Figures (8, 9, 10, 11, 12 and 13) represent the predicted results using different input points (2, 3, 5, 6, 11 and 21 respectively).

In Figure (8), it's clear that using two data points (initial and final) will show fair representation to input points. Increasing the number of data points such as in figures (9 to 13), enhanced the representation of input points.

Figure (10) shows that acceptable predicted results could be reached out in spite of huge difference in Table (3) between the model k values and predicted k values that depending on 5 points.

Using 11 data points such as in figure (12) shows that the observed data fits the input data very well.

Further increasing of input data points to 21 points such as in Figure ((13) shows excellent agreement between the model predictions and input data points.

Finally, it can be concluded that, higher than 11 to 21 data points are required for good representing of the reaction kinetic in any complex system.

5. CONCLUSION

In this study, constrained non linear least square method with the aid of quasi-Newton method was used for determining the rate constants of six lump fluidized catalytic cracking reactions. The results showed that:-

- Increasing the number of input data points will enhance the accuracy of predicted kinetic parameters. Accurate reaction kinetic could be described using 11 to 21 points.
- The lower accuracy reaction rate could be determined depending on two points (initial and final).
- The same concentration behavior could be obtained using different values of the rate constants.
- Also the results showed that the proposed programs are very efficient, fast and accurate tools to determine the rate constants of any complex reaction at a certain temperature.

The proposed program could be modified to simulate any kinetic reaction, of any number of components or lump such as reforming reaction kinetic.

Nomenclature

E: Activation energy (j/mol)

k_i : Rate constant (wt% /hr)

k_0 : Pre-exponential factor (wt% /hr)

k_d : Deactivation constant (hr⁻¹)

R: Gas law constant (8.314 J/mol·K)

r_i : Rate of reaction (wt%/hr.gm catalyst)

T: Temperature (K)

tc: Catalyst residence time (hr)

Wc: Catalyst weight (k)

y₁: Weight fraction of residual oil (wt%)

y₂: Weight fraction of heavy fuel oil (wt%)

y₃: Weight fraction of light fuel oil (wt%)

y₄: Weight fraction of gasoline (wt%)

y₅: Weight fraction of liquefied petroleum gas (wt%)

y₆: Weight fraction of dry gas (wt%)

φ: Deactivation function (-)

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Table (1). Kinetic parameters of the used model at 773 K(Ancheyta and Sotelo (2002))

	Reaction	k
$k_1(\% \text{ wt}^{-1} \text{ h}^{-1})$	Gas oil→Gasoline	3166.61
$k_2(\% \text{ wt}^{-1} \text{ h}^{-1})$	Gas oil→C4's	322.44
$k_3(\% \text{ wt}^{-1} \text{ h}^{-1})$	Gas oil→C3's	152.18
$k_4(\% \text{ wt}^{-1} \text{ h}^{-1})$	Gas oil→Dry gas	75.00
$k_5(\% \text{ wt}^{-1} \text{ h}^{-1})$	Gas oil→Coke	219.98
$k_6(\text{ h}^{-1})$	Gasolne→C4's	100.02
$k_7(\text{ h}^{-1})$	Gasolne →C3's	54.96
$k_8(\text{ h}^{-1})$	Gasolne →Dry gas	25.46
$k_9(\text{ h}^{-1})$	Gasolne →Coke	0.915
$k_{10}(\text{ h}^{-1})$	C4's →C3's	18.631
$k_{11}(\text{ h}^{-1})$	C4's →Dry gas	8.889
$k_{12}(\text{ h}^{-1})$	C3's →Dry gas	203.88
$k_d(\text{ h}^{-1})$	Deactivation constants	1786.71

Table (2) Result of fluidized catalytic cracking using 6 lump model

Dimensionless catalyst weight (-)	Weight fraction					
	Gas oil	Gasoline	C4's	C5's	Dry gas	Coke
0	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.05	0.6714	0.2610	0.0287	0.0136	0.0069	0.0184
0.10	0.5053	0.3871	0.0463	0.0219	0.0116	0.0277
0.15	0.4051	0.4582	0.0596	0.0281	0.0156	0.0333
0.20	0.3382	0.5011	0.0709	0.0334	0.0193	0.0371
0.25	0.2901	0.5282	0.0810	0.0380	0.0228	0.0399
0.30	0.2541	0.5451	0.0903	0.0423	0.0263	0.0420
0.35	0.2260	0.5553	0.0991	0.0462	0.0298	0.0436
0.40	0.2035	0.5608	0.1076	0.0499	0.0333	0.0449
0.45	0.1850	0.5629	0.1157	0.0534	0.0369	0.0460
0.50	0.1697	0.5626	0.1235	0.0568	0.0405	0.0469
0.55	0.1567	0.5604	0.1312	0.0599	0.0442	0.0477
0.60	0.1455	0.5568	0.1386	0.0629	0.0478	0.0484
0.65	0.1358	0.5520	0.1458	0.0658	0.0516	0.0490
0.70	0.1274	0.5465	0.1528	0.0685	0.0553	0.0496
0.75	0.1199	0.5402	0.1596	0.0711	0.0591	0.0500
0.80	0.1132	0.5335	0.1663	0.0736	0.0630	0.0505
0.85	0.1073	0.5263	0.1728	0.0759	0.0669	0.0509
0.90	0.1019	0.5188	0.1791	0.0782	0.0708	0.0512
0.95	0.0971	0.5111	0.1853	0.0803	0.0747	0.0515
1.00	0.0927	0.5032	0.1913	0.0823	0.0787	0.0519

Table (3) Predicted reaction kinetic parameters using different number of points.

No. of points	Model k values	2		3		5		6		11		21	
		Cal. k values	% Relative error										
k ₁	3166.61	813.16	74.32	1445.68	54.35	2143.01	32.32	2346.09	25.91	2824.72	10.80	3056.08	3.49
k ₂	322.44	180.87	43.90	220.46	31.63	259.88	19.40	271.92	15.67	301.06	6.63	315.36	2.19
k ₃	152.18	86.85	42.93	115.85	23.87	130.01	14.57	134.98	11.30	145.64	4.30	150.08	1.38
k ₄	75.00	71.31	4.92	63.48	15.36	73.09	2.55	74.39	0.81	75.98	-1.30	75.46	-0.61
k ₅	219.98	69.83	68.26	110.64	49.71	155.39	29.36	168.43	23.44	199.09	9.50	213.82	2.80
k ₆	100.02	91.39	8.63	95.96	4.06	95.19	4.83	95.84	4.18	98.18	1.84	99.57	0.45
k ₇	54.96	36.75	33.14	23.68	56.92	42.82	22.08	43.88	20.15	49.64	9.67	53.28	3.06
k ₈	25.46	32.54	-27.80	28.95	-13.69	11.46	54.99	12.55	50.72	17.39	31.69	22.44	11.87
k ₉	0.92	0.00	100.00	0	100.00	0	100.00	0	100.00	0	100.00	0	100.00
k ₁₀	18.63	0.38	97.97	19.73	-5.89	0.02	99.88	0.05	99.76	37.21	-99.72	31.42	-68.63
k ₁₁	8.89	0.33	96.30	24.59	-176.67	42.36	-376.56	42.07	-373.31	0	100.00	0	100.00
k ₁₂	203.88	51.49	74.75	53.80	73.61	150.34	26.26	150.88	26.00	244.59	-19.97	233.19	-14.37

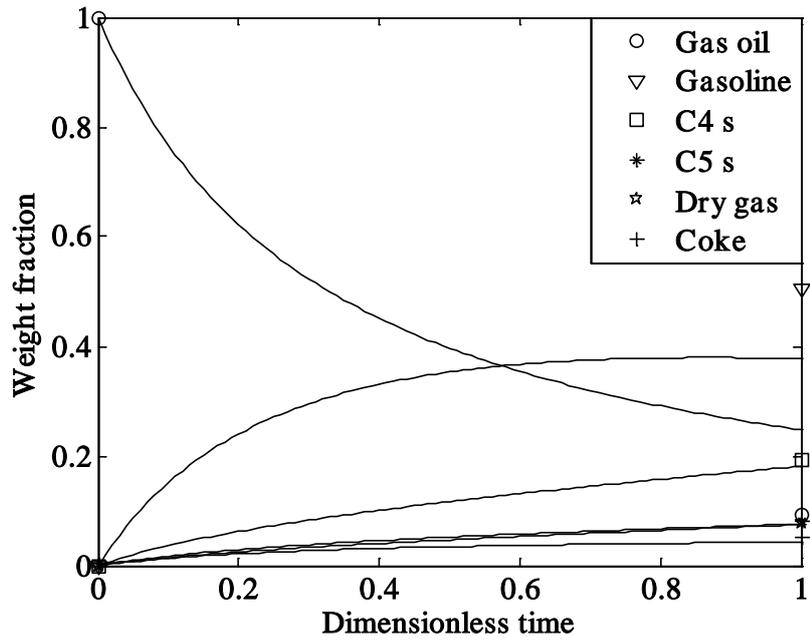


Figure (8) Predicting weight fractions depending on 3 point
(Solid lines indicate predicted concentration and dots indicate input points).

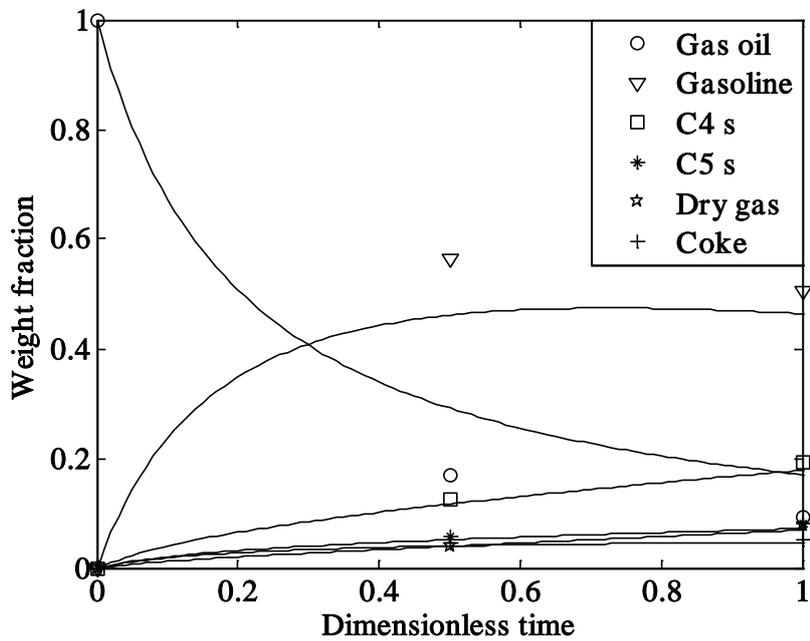


Figure (9) Predicting weight fractions depending on 3 point
(Solid lines indicate predicted concentration and dots indicate input points).

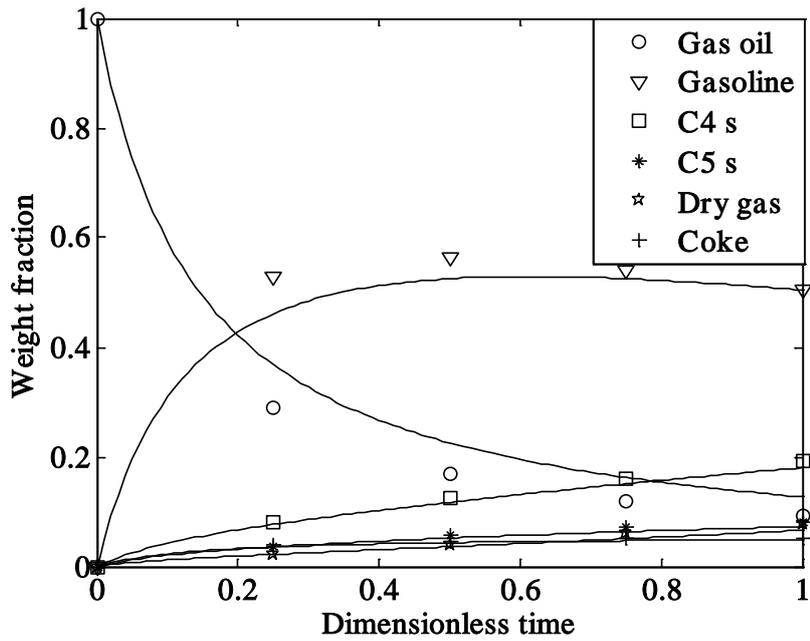


Figure (10) Predicting weight fractions depending on 5 point
(Solid lines indicate predicted concentration and dots indicate input points).

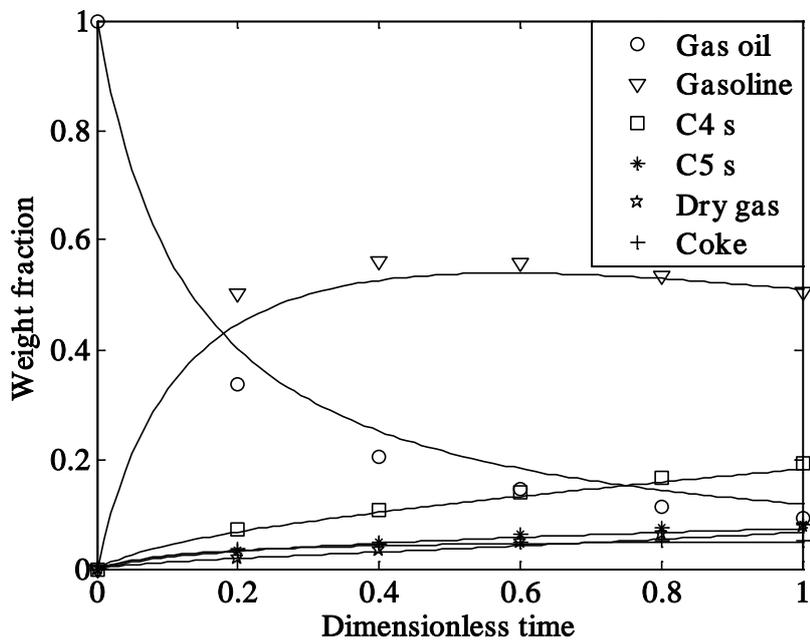


Figure (11) Predicting weight fractions depending on 6 point
(Solid lines indicate predicted concentration and dots indicate input points).

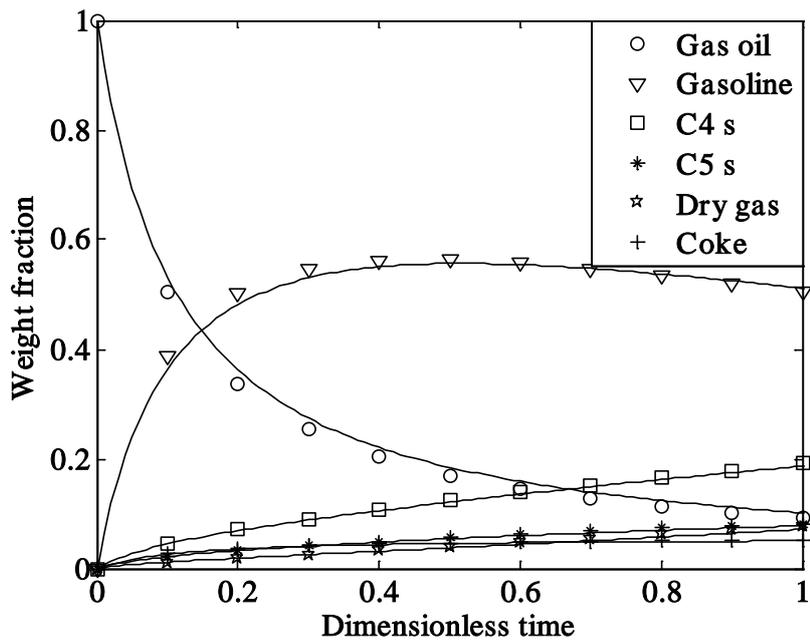


Figure (12) Predicting weight fractions depending on 11 point
(Solid lines indicate predicted concentration and dots indicate input points).

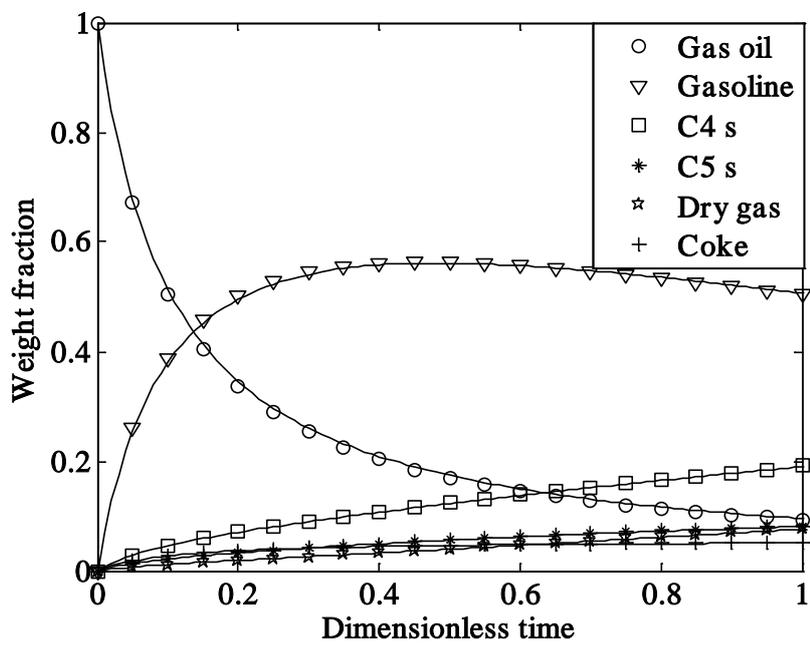


Figure (13) Predicting weight fractions depending on 21 point
(Solid lines indicate predicted concentration and dots indicate input points).

حساب ثوابت ميكانيكية التفاعلات المعقدة باستخدام لغة ماتلاب

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الخلاصة :

عملية حساب ثوابت التفاعلات الكيماوية تكون عملية معقدة ومستهلكة للوقت. الهدف من هذا البحث هو:

● تطوير برنامج باستخدام لغة ماتلاب لحساب ثوابت التفاعلات لاي نظام معقد من التفاعلات ولاي درجة حرارة.

● دراسة تأثير عدد النقاط المدخلة للبرنامج على دقة حساب ثوابت التفاعلات.

في هذا البحث تم دراسة تفاعلات التفسير المحفز. حيث تم عمل موديل رياضي لأيجاد تراكيز المواد مع وزن العامل المساعد باستخدام ميكانيكية تفاعل من ستة مواد. هذه البيانات تم اعتبارها كبيانات عملية وتم استخدامها لاحقا لأيجاد ثوابت التفاعلات.

باستخدام عدد مختلف من النقاط لكل مرة تم حساب ثوابت معدل التفاعل بطريقة تقليل مجموع مربع الخطأ بين النقاط المدخلة للموديل والنقاط المحسوبة من الموديل. حيث تم تقليل مجموع مربع الخطأ باستخدام طريقة التكرار والتحقق. هذا البحث اجاب عن التساؤل الموجود لدى اي باحث وهو هل يمكن حساب معدل التفاعل لاي تفاعل معقد بالاعتماد على نقطتين (بداية ونهاية)؟ . حيث كانت الاجابة انه يمكن ايجاد وصف ضعيف لمعدلات التفاعلات بالاعتماد على نقطتين. وتبين ان البرنامج الرياضي المطور فعال وسريع ودقيق في حساب ثوابت معدلات التفاعلات لاي نظام من التفاعلات المعقدة وباية درجة حرارية. وللحصول على وصف جيد لميكانيكية اي تفاعل يجب الحصول على عدد من النقاط العملية يتراوح بين 11 الى 21 نقطة.

الكلمات الداله : التفسير الحراري المحفز ، معدل التفاعل، ثوابت، افضل، ماتلاب