NOVEL METHOD FOR ESTIMATION OF KINETIC PARAMETERS IN VGO CRACKING

Praveen Ch, Shishir Sinha[*]

*Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee-247667, INDIA, Email: sshishir@gmail.com, * author to whom all the correspondence should be addressed.*

Abstract

Considerable effort has been put by scientists on the modelling of FCC unit for better understanding and improved productivity. To model a FCC unit we have to estimate the unknown kinetic parameters in VGO cracking. In this paper authors have presented a novel method of integrating the ODE solver of MATLAB with Levenberg-Marquardt algorithm to estimate the unknown kinetic parameters.

Keywords: Fluid Catalytic Cracking; VGO; Micro Activity Test.

1. INTRODUCTION

Modelling is powerful tool in present day refineries and is used for a variety of applications. Because of the importance of FCC unit in refining, considerable effort has been done on the modelling of this unit for better understanding and improved productivity. In last fifty years, the mathematical modelling of FCC unit have matured in many ways but the modelling continues to evolve to improve the closeness of models prediction with the real process whose hardware is ever-changing to meet the needs of petroleum refining. Complexity of the FCC process because of unknown reaction mechanism, complex hydrodynamics and strong interaction between reactor and regenerator has made it almost impossible to develop a general model for the integrated process. Therefore, researchers in this field have worked on different aspects of the process separately for modelling purposes [1]. However, maximum attention has been paid on the modelling of the riser reactor which is the most important part of the FCC unit.

The level of detail of the model depends on the unit being modelled and the end use of the model. Simple linear input output models are used for inventory control, energy audit and for overall refinery optimization. On the other hand, design of a new unit may require very sophisticated models which accounts for hydrodynamics, heat and mass transfer, reaction phase equilibrium, strength of materials, corrosive properties of fluids to be handled, etc. Rating the performance of a unit or optimization of its operating conditions call for steady state models which are analytical and non linear and includes the physics of the process to a reasonable extent.

Gas oil consists of a large number of hydrocarbons normal and iso-paraffins, napthenes, aromatics, substituted (or alkyl) aromatics and condensed ring compounds. The cracking reaction kinetics will depend on the type of the hydrocarbon and the number of carbon atoms present in a molecule but due to lack of information of detailed FCC feed composition; such a detailed kinetic model is not practical. The approach followed is that the feed and products are characterized in terms of a small number of groups of hydrocarbons which are similar in nature and each of these groups of hydrocarbons which are similar in nature and each of these groups could be taken to behave like a single kinetic entity called a kinetic lump.

All these mathematical models are based on lumping scheme in which FCC feed and products are assumed to be made of a few number of the lumps and kinetic parameters

are estimated empirically for the conversion of one lump to the other. In the present work, authors used a four lump scheme and the MAT Data [2]. Different authors [2,3,4,5] used different types of regression methods to estimate kinetic parameters. But in this paper authors have estimated the kinetic parameters by integrating the ode solver in MATLAB with Levenberg-Marquardt algorithm. The Levenberg-Marquardt (LM) algorithm is an iterative technique that locates the minimum of a multivariate function that is expressed as the sum of squares of non-linear real-valued functions [6,7]. It has become a standard technique for non-linear least-squares problems, widely adopted in a broad spectrum of disciplines.

The governing equations for VGO cracking [2]:

$$-dY_1/dt = K(Y_1^2)\varphi, \text{ where } K = k_{12} + k_{13} + k_{14} \tag{1}$$
$$dY_2/dt = [k_{12}(Y_1^2) - (k_2)Y_2]\varphi, \text{ where } k_2 = k_{23} + k_{24}. \tag{2}$$
$$dY_3/dt = [k_{13}(Y_1^2) + k_{23}Y_2]\varphi \tag{3}$$
$$dY_4/dt = [k_{14}(Y_1^2) + k_{24}Y_2]\varphi \tag{4}$$
$$\varphi = e^{-at} \tag{5}$$

2. PROCEDURE FOR DEVELOPMENT OF MATLAB CODE

MATLAB is the high level computer language, which has a high computational speed. The authors have found out the kinetic parameters by writing MATLAB code and solving following function:

Minimize f= $Y_{1*}^{-2} \times \Sigma(Y_1-Y_{exp})^2 + Y_{2*}^{-2} \times \Sigma(Y_2-Y_{exp})^2 + Y_{3*}^{-2} \times \Sigma(Y_{3*}-Y_{exp})^2 + Y_{4*}^{-2} \times \Sigma(Y_4-Y_{exp})^2$

Y= Simulated value
Y_{exp} = Experimental data
Y_*= Maximum value in experimental data

To prepare the code the authors first wrote the governing equation in m-file and called it from the file which contains the minimization function. This minimization function file was finally called by a file which contains the lsqnonlin operator which is an in built code for Levenberg Marquardt method.

3. RESULTS AND DISCUSSION

Kinetic parameters for all the equations for VGO cracking were estimated using the above procedure and they are shown in table 1. The time taken to estimate these parameters was minimal. On simulating the governing equation using the estimated kinetic parameters authors found that the simulation results match well with the experimental data.

Table 1. The unknown kinetic parameters.

Temperature (°C)	k_{12} (wt.frac. x h)$^{-1}$	k_{13} (wt.frac. x h)$^{-1}$	k_{14} (wt.frac. x h)$^{-1}$	k_{23} (h^{-1})	k_{24} (h^{-1})	a (h^{-1})
550	54.2659	18.4062	0.019	3.5751	1.2424	1.2073
600	77.9531	25.4075	0.04225	5.0686	1.3703	1.6119
650	91.7508	32.3063	0.061278	8.6198	1.8791	2.1021

The simulation result at 550°C is shown in figure 1. To calculate the activation energy Arrhenius plot were plotted as shown in figure 2 . The activation energy for different reaction are shown in table 2. The activation energy for different reaction match well with literature data except for coke. The reason for this may be high coke formation due to experimental condition of MAT reactor.
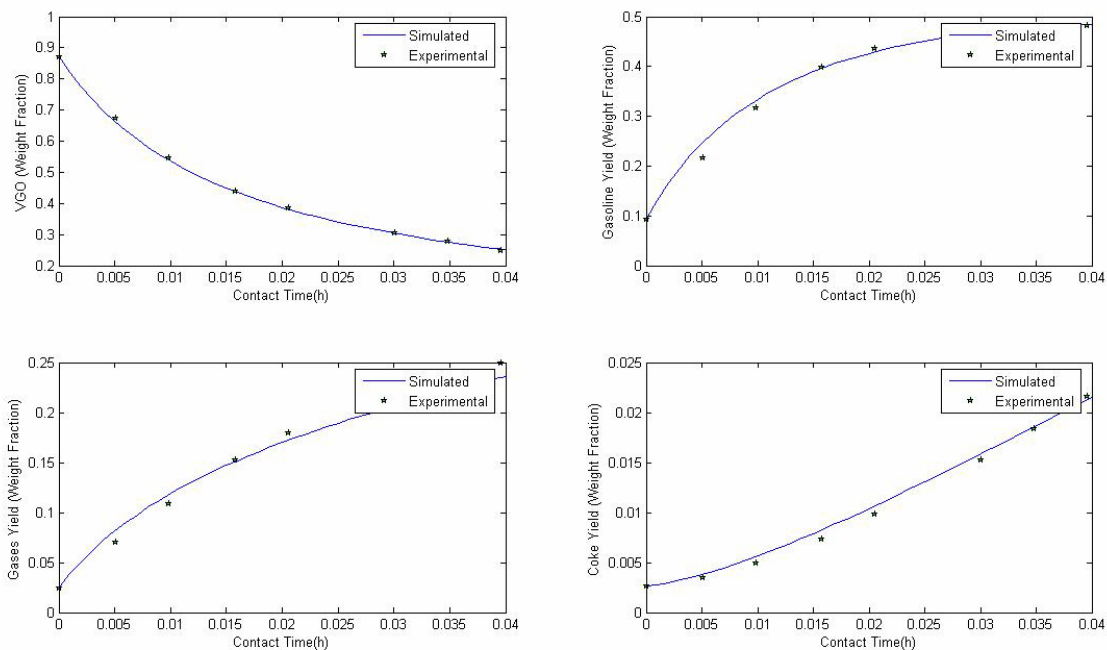
Figure 1. Yields of VGO, gasoline, gas and coke as function of contact time at 550°C
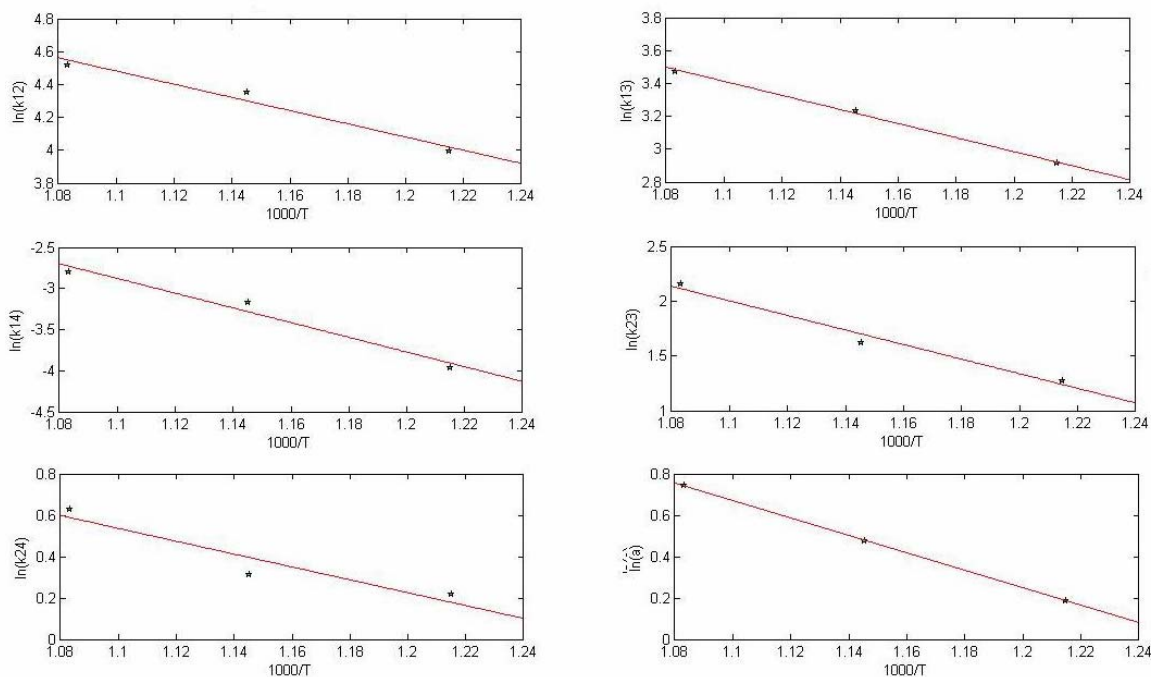

Figure 2. Arrhenius plots of rate constants k_{12}, k_{13}, k_{14}, k_{23}, k_{24} and a

Table 2. Comparison of activation energies

Reaction step	E(kcal/mol) (present work)	E(kcal/mol) (literature [5])
VGO to gasoline	8.1023	10-36
VGO to gas	8.5441	12-21
VGO to coke	17.8830	7-15
Gasoline to gas	13.3129	13-15
Gasoline to coke	6.2535	16-27

4. CONCLUSION

Most of the conventional methods of estimating kinetic parameters in VGO cracking are complex and consume more CPU time compared to the novel method of integrating

the ode solver of MATLAB with Levenberg-Marquardt algorithm. Also the results obtained by simulation of these equations using unknown parameters obtained from MATLAB code were found to be much closer to experimental data. Also the activation energies compare well with literature values.

Nomenclature

A	deactivation constant	k_{24}	rate constant for gasoline to coke
Φ	deactivation function	t	contact time (h)
k_{12}	rate constant for VGO to gasoline	Y_1	weight fraction of vacuum gas oil
k_{13}	rate constant for VGO to gas	Y_2	weight fraction yield of gasoline
k_{14}	rate constant for VGO to coke	Y_3	weight fraction yield of gases
k_{23}	rate constant for gasoline to gas	Y_4	weight fraction yield of coke

REFERENCES

[1]   Gupta,R., Kumar,V., Srivastava, V.K.: Reviews in Chemical Engineering ,21(2005), p. 95.
[2]   Mohammad,A.: Fuel, 82(2003), p. 1113.
[3]   Larocca,M.: Ind. Engng. Chem. Res., 29(1990), p.17.
[4]   Olivera,L.L., Biscaia,E.C.: Ind Engng Chem Res, 28(1989), p. 264.
[5]   Ancheyta-Juarez, Ind. Engg. Chem. Res., 36(1997), p. 5170.
[6]   Levenberg,K.: Quarterly of Applied Mathematics, 2(1944), p. 164.
[7]   Marquardt,D.W.: SIAM Journal of Applied Mathematics, 11(1963), p. 431.
[8]   Sadeghbeigi,R.: Fluid Catalytic Cracking Handbook. 2nd edition, Gulf Publishing Company, 2000.
[9]   Kumar,S., Chadha,A., Gupta,R., Sharma,R.: Ind. Eng. Chem. Res.,34(1995)., p. 3737.
[10]   Takatsuka,T.: Int. Chem. Engng., 27(1987), p. 107.
[11]   Jacob,S.M.: AICHE J., 22(1976), p. 701.
[12]   Lee,L.S., Can. J. Chem. Engg., 67(1989), p. 615.
[13]   Weekman,V.M.: Ind. Eng. Chem. Prod. Res. Dev., 7(1968), p. 90.