

Strategic Estimation of Kinetic Parameters in VGO Cracking

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Abstract: Fluid catalytic cracking (FCC) unit plays most important role in the economy of a modern refinery that it is use for value addition to the refinery products. Because of the importance of FCC unit in refining, considerable effort has been done by scientists till now on the modelling of this unit for better understanding and improved productivity. To model a FCC unit we have to know the unknown kinetic parameters of the governing equations.

The basic aim of this paper is to prove that MATLABTM can be used as a tool to find unknown kinetic parameters of governing equations for VGO cracking. We have developed a strategic method to find the unknown kinetic parameters using MATLAB and compare the simulation results with the results obtained from methods available in literature and it was found to be the best agreement.

Keywords: Fluid Catalytic Cracking, VGO, Micro Activity Test

1 Introduction

Petroleum is our most important natural non-renewable source of energy. It is a mixture of hydrocarbon compounds such as natural gas, gasoline, kerosene, asphalt and fuel oil. We use gasoline, jet fuel, and diesel fuel to run cars, trucks, aircraft, ships, and other vehicles. Home heat sources include oil, natural gas, and electricity, which in many areas are generated by burning natural gas. Petroleum and petroleum-based chemicals are important in manufacturing plastic, wax, fertilizers, lubricants, and many other goods.

Crude oil is produced from the ground contains hydrocarbons ranging from light gases and LPG to residues boiling above 343°C (650°F). Products of various boiling ranges can be produced by atmospheric and vacuum distillation units, and then each boiling fraction is further processed by several kinds of catalytic reaction

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operation such as hydrotreating, hydrocracking, catalytic reforming and catalytic cracking; and by non-catalytic reaction operations such as thermal cracking; and by treatment operations such as the removal of impurities and fine fractionation.

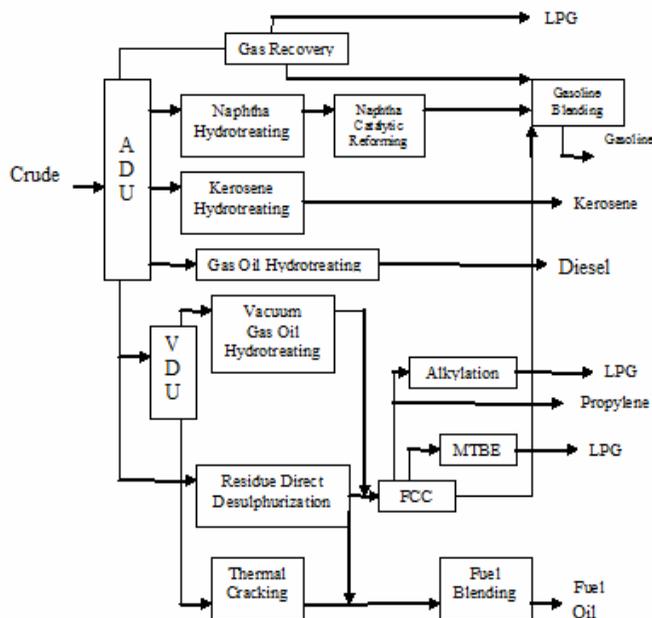


Figure 1: Role of FCC in the refining industry

Figure 1. shows that the crude oil is distilled in atmosphere distillation unit to produce LPG, naphthas, kerosene and diesel oil. The residue from the atmosphere distillation unit is fed to the vacuum distillation unit where it is separated into vacuum gas oils and vacuum residue. The heavy vacuum gas oil, which normally constitutes 25-30% of the total crude oil volume, is fed to the FCC unit where it is converted into lighter products. The heavy vacuum gas oil (VGO) has a boiling range of 343°C (650°F) to 565 °C (1050°F). In addition to the VGO a wide range of feedstock can be processed in FCC units such as hydrotreated gas oils, cracker gas oils, and deasphalted oils [11].

In fluidized catalytic cracking processes, high molecular weight hydrocarbon liquids and vapours are contacted with hot, finely-divided, solid catalyst particles, either in a fluidized bed reactor or in an elongated transfer line reactor, and maintained at an elevated temperature in a fluidized or dispersed state for a period of time sufficient to effect the desired degree of cracking to lower molecular weight

hydrocarbons of the kind typically present in motor gasoline and distillate fuels (Gupta et al (2005)).

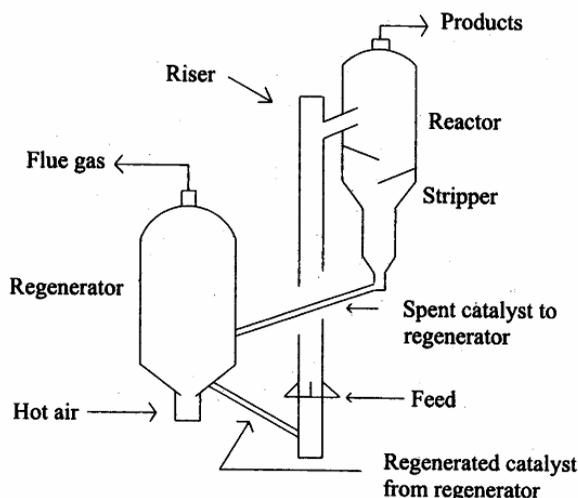


Figure 2: Schematic of FCC unit (Gupta et al (2005))

In the past, microactivity test (MAT) unit was used by scientists throughout the world to determine the activity and selectivity of either equilibrium or laboratory deactivated fluid catalytic cracking (FCC) catalysts. The activity is evaluated on the basis of wt% conversion of gas oil to gasoline, light gases, and coke. The selectivities are evaluated on the basis of wt% yields of specifically defined products resulting from the catalytic cracking of gas oil. Over the years, the scope of the MAT test has been extended to include the evaluation of the feedstock with respect to its crackability under specified conditions. Currently, the MAT unit is widely accepted as a tool to perform laboratory scale FCC research and testing because of its simple operation and cost effectiveness. The unit only requires small quantities of catalyst and gas oil for each MAT test, compared with barrels of materials needed for a pilot scale riser run.

The bench-scale MAT unit consists of a fixed-bed quartz reactor, a fluidized-bed stainless steel reactor, a liquid product receiver and a series of traps controlled at various temperatures, and a gaseous product collection system including a Ruska gasometer. Generally each reactor is heated by a three-zone electric furnace. Feed oil is delivered into the reactor by a constant drive syringe pump through a syringe which can be heated at high temperature if required. After cracking, the unit is capable of simultaneously regenerating spent catalyst in situ and determining coke

yield by both photometric and gravimetric methods. This capability is facilitated by an air delivery system, a CO catalytic converter, an on-line infrared CO₂ analyzer, a series of traps to absorb moisture and carbon dioxide, and a wet test meter. Alternatively, the coke yield can also be determined externally by the conventional carbon analysis on spent catalyst. The unit is fully automated, using PC-based control package FIX for system control, historical trend recording and retrieving, and data acquisition and processing [Ng].

There has been a trend now a days to use micro-activity test data to develop governing equations for VGO cracking for the FCC process as described by **Hamayel et al (2003)**. The authors used the MAT data of **Hamayel et al (2003)** and developed a MATLAB program to estimate the kinetic parameters of the governing equations for VGO cracking which would help in modelling the FCCU. The accuracy of the results obtain form MATLAB is demonstrated in this paper.

The governing equations for VGO cracking:

$$dY_1/dt = K(Y_1^2)\phi \quad (1)$$

Where $K = k_{12} + k_{13} + k_{14}$.

$$dY_2/dt = [k_{12}(Y_1^2) - (k_2)Y_2]\phi \quad (2)$$

where $k_2 = k_{23} + k_{24}$.

$$dY_3/dt = [k_{13}(Y_1^2) + k_{23}Y_2]\phi \quad (3)$$

$$dY_4/dt = [k_{14}(Y_1^2) + k_{24}Y_2]\phi \quad (4)$$

$$\phi = e^{-\alpha t} \quad (5)$$

2 Procedure for development of MATLAB code

MATLAB is short for **matrix laboratory**. It is a user friendly computer software which helps in performing simulations and carrying out scientific calculations. We have developed the code with MATLAB which is a high-level language and interactive environment that enables to perform computationally intensive tasks faster than with traditional programming languages such as C, C++, and Fortran. This can be used as a tool find out unknown kinetic parameters of governing equations if experimental data is available.

The procedure is a simple three step procedure in which we have to create three m-files.

In the first step a function file was created by the authors in which the governing differential equations for VGO cracking are written.

In the second step another function file was created to solve the differential equations which were written in step one using ODE Solver. Here initial condition was supplied to solve the differential equations and a trial value was assumed for the unknown kinetic parameters. The differential equations were solved and the results were compared with experimental data. Their error was stored in a variable say E.

In the third step lsqnonlin operator (based on Levenberg-Marquardt algorithm) was used. Error variable E was supplied to the lsqnonlin operator and iterations were performed by MATLAB by repeating all the three steps to get the final values of the unknown kinetic parameters.

3 Solution of governing differential equations for VGO cracking

A MATLAB code was written by authors to solve the differential equations by using the kinetic parameters.

In the first step we created a function file in which the governing differential equations for VGO cracking are written.

```
function dy = fcc ( t , y )

dy = zeros ( 4 , 1 );

k12 = ; k13= ; k14= ; k23= ; k24= ; \% enter kinetic constants
-dy(1) = ( k12 + k13 + k14 ) * y(1)^2 * exp(-a*t);

dy(2) = (k12 * y(1)^2 - ( k23 + k24 ) * y(2) ) * exp(-a*t);

dy(3) = (k13 * y(1)^2 + k23 * y(2) ) * exp(-a*t);
dy(4) = (k14 * y(1)^2 + k24 * y(2) ) * exp(-a*t);
```

ODE Solver was used to solve the set of differential equations using the kinetic parameters and then the simulation results were plotted.

```
function e = fcc1( t , y)

t = [Time span];

odeoptions = [ ];
[t,y] = ode23 ( @fcc , t , [intial conditions] , odeoptions )

yd = [ experimental data ]
```

```

plot ( t , y(:,4) ) \% plot of simulated results
hold on
plot (td , yd(:,4) , 'r') \% plot of experimental data

```

4 Results and discussion

Table 1 presents the kinetic constants for the reactions VGO to gasoline (k_{12}), VGO to gas (k_{13}), VGO to coke (k_{14}), gasoline to gas (k_{23}) and gasoline to coke (k_{24}) estimated by the authors. The authors also found that the kinetic parameters were estimated in less than a minute using this code.

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) | α (h ⁻¹) |
|---------------------|--|--|--|--------------------------------|--------------------------------|--------------------------------|
| 550 | 54.2426 | 18.6074 | 0.01986 | 3.8488 | 1.198 | 1.1888 |
| 600 | 77.8778 | 25.5316 | 0.03 | 5.4814 | 1.4936 | 1.5226 |
| 650 | 91.7257 | 32.1742 | 0.059476 | 8.5808 | 3.007 | 2.1373 |

Using the method specified above simulation curves were plotted for the kinetic parameters and these simulation results were compared with the experimental results. **Figure 3** clearly shows that the kinetic parameters obtained from MATLAB code by the authors give simulation results which are very close to experimental results.

Table 2: Comparison of activation energies

| Reaction step | E(kcal/mol) (present work) | E(kcal/mol) (literature Ancheyta et al 1997) |
|------------------|-------------------------------|---|
| VGO to gasoline | 9.22 | 10-36 |
| VGO to gas | 8.88 | 12-21 |
| VGO to coke | 14.56 | 7-15 |
| Gasoline to gas | 11.4 | 13-15 |
| Gasoline to coke | 16.57 | 16-27 |

Activation energies of the reactions involved were calculated from the Arrhenius plot of respective rate constants. This plot is shown in **Figure 2**. **Table 2** compares the activation energies determined in this work with those found in the literature [1]. The Activation energies calculated by authors using MATLAB Code are reasonably close to the values found in the literature (1;3;6;7;13;14).

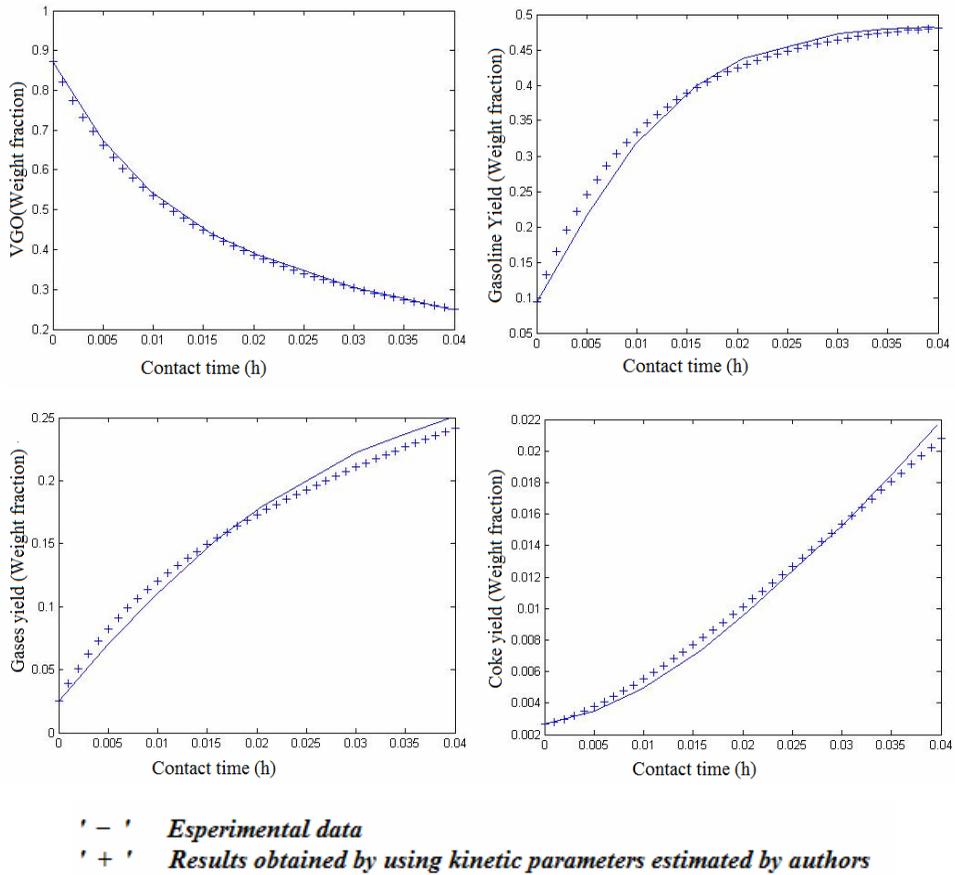


Figure 3: Yields of VGO, gasoline, gas and coke as a function of contact time at 550 °C. (Experimental data taken from Hammayel et al (2003))

5 Conclusion

The results obtained by simulation of these equations using unknown parameters obtained from MATLAB code were found to be much closer to experimental data. The author found the method to be time efficient which gave results with reasonable accuracy when compared to the methods found in the literature which are time consuming. Also the activation energies compare well with literature values.

Nomenclature

- α deactivation constant
 ϕ deactivation function

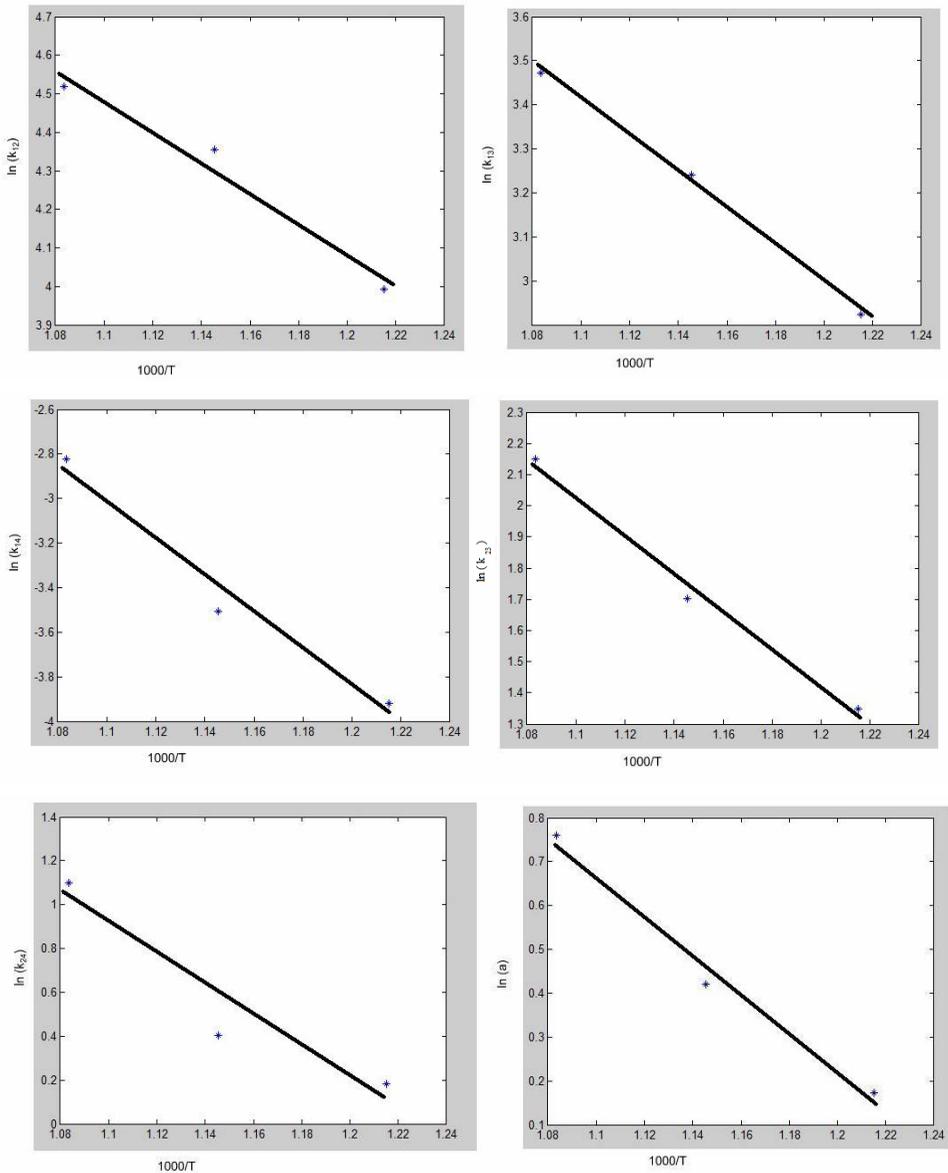


Figure 4: Arrhenius plots of rate constants k_{12} , k_{13} , k_{14} , k_{23} , k_{24} and α

- k_{12} rate constant for VGO to gasoline
- k_{13} rate constant for VGO to gas
- k_{14} rate constant for VGO to coke
- k_{23} rate constant for gasoline to gas

| | |
|----------|------------------------------------|
| k_{24} | rate constant for gasoline to coke |
| t | contact time (h) |
| Y_1 | weight fraction of vacuum gas oil |
| Y_2 | weight fraction yield of gasoline |
| Y_3 | weight fraction yield of gases |
| Y_4 | weight fraction yield of coke |

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