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Optimization of Gasoline Yield in FCC riser unit Using RSM.

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ABSTRACT

The aim of this study is maximization of gasoline production in an industrial fluid catalytic cracking unit in steady state. The reactions in the riser occur in a transported bed with the fluid and the solids in ideal plug flow. One of the main advantages of the model is that it does not include any partial differential equations. This facilitates the solution of the equations and makes the model particularly suitable for control studies. The present work aims to apply optimization in an industrial FCC converter unit, using the four-lump model involved gas oil, gasoline, light gas and coke (to predict the Gas oil conversion and the product distribution) and to carry out a numerical and graphical analysis of the solution procedure. The results demonstrate the effect of changing various process variables, such as temperature, catalyst to oil rate and mass of gasoil. The calculated data of the product distribution were agreed well with the experimental results.

Keywords: FCC, riser reactor, four-lump kinetic model, catalytic cracking.

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INTRODUCTION

The Fluid Catalytic Cracking (FCC) unit is one of the most important processes in the petroleum refining industry. Heavy petroleum fractions are catalytically cracked to lower molecular weight products. In the FCC riser, lift steam pushes the dense catalyst bed upward from the riser base to the feed injection point. The feed enters as liquid droplets along with atomizing steam, contact the hot catalyst and rapidly evaporates. As the suspension of catalyst powder in reactant gases rises upward, the gas is cracked to lighter hydrocarbons (gasoline and light gases) and coke. The coke is deposited on the catalyst, which is transported out of the riser and into the regenerator, where the coke is burned off the catalyst in a combustion environment. The hot regenerated catalyst is then reinjected into the base of the riser (Berry *et al*., 2004). In this way similar components are grouped into a few "cuts" or "lumps. The number of lumps of the proposed models for catalytic cracking reactions has been consecutively increasing to obtain a more detailed prediction of product distribution (Bollas *et al*., 2007). In the first kinetic model (3-lump), proposed by Weekman (1968), reactants and products were lumped into three major groups: Gas oil, gasoline and light gas plus coke. Lee *et al*. (1989b) and Lee *et al*. (1989a) took one step forward by dividing the light gas plus coke lump into two different lumps C_1-C_4 gas and coke, developing the first 4-lump models for fluid catalytic cracking Advancing the lumping methodology, Corella and Frances (1991) developed a 5-lump models, in which the gas-oil lump was divided into its heavy and light fractions. Dupain *et al*. (2006) simplified the 5- lump model of Corella and Frances (1991) for the specific case of the catalytic cracking of aromatic gas oil, by reducing the reactions involved in the lumping scheme. Another 5-lump model was developed by Kraemer *et al*. (1991) in which the 3-lump model of Weekman (1968) was modified by splitting the gas oil lump into aromatic, paraffinic and naphthenic lumps. Ancheyta-Juarez *et al*. (1999) followed a different approach in their 5-lump models development, in which they considered the gas oil as one lump, but divided the gas lump into two lumps (liquefied product gas and dry gas). Hagelberg *et al*. (2002) expanded the 5-lump model of Ancheyta-Juarez *et al*. (1999) to an 8-lump model by dividing the gasoline fraction into paraffins, olefins, naphthenes and aromatics. With presence of the high efficiency feed injection system in modern FCC units cause all cracking in the riser occur during the short time (about 1-5 sec). Therefore based on this fact, it is explainable that many of the models found in the literature (Arandes and de Lasa, 1992; Arbel *et al*., 1995; Han and Chung, 2001; Ali and Rohani, 1997; Bollas *et al*., 2007), describe the riser reactor, with one-dimensional mass, energy and chemical species balances, so in the present research, a one-dimensional, adiabatic model for the FCC unit riser has been developed that combines predicative riser hydrodynamic model with a four-lump kinetic model.

MATERIALS AND METHODS

The model is based on the schematic flow diagram presented in Fig. 1. It is assumed that gas oil is converted to gasoline range hydrocarbons, light gases and coke in the riser reactor, which is considered to be a transported bed. The upper fluidized bed immediately above the riser acts as a disengaging chamber where vapor products and heavy components are separated from the catalyst using stripping steam. The only effect of the stripping process is to remove hydrocarbon gases adsorbed inside the pellets before the spent catalyst is sent to the regenerator. Fresh gas oil is brought into contact with the hot regenerated catalyst at the entrance of the riser which leads to the vaporization of gas oil. The inlet zone is considered to be the most complex part of the riser.

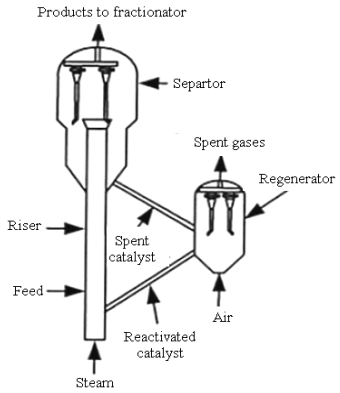


Figure 1: Schematic diagram of catalytic cracking unit

This is attributed to the presence of high turbulence, high temperature and concentration gradients and flow in homogeneity.

Vaporization of the feed, according to plant data (Ali and Rohani, 1997) it takes about 0.1 sec to fully vaporize the feed. Therefore, it is justifiable to assume instantaneous vaporization of the feed. In this study, all the cracking reactions are considered to take place in the riser. This assumption is reasonable since the zeolite catalysts, the reaction promoters and the multifunction catalyst additives highly accelerate the cracking reactions rates. Furthermore, the coke formation will sharply decrease the catalyst activity towards the exit of the riser. The four-lump model involved gas oil, gasoline, light gas and coke has been shown in Fig. 2. The advantage of this scheme is that the coke and light gases are represented by two separated lumps. Where A, B, C and D represent gasoil, gasoline, coke and light hydrocarbon gases, respectively. According of this scheme, a part of gasoline is also converted to light gases and coke. It is assumed that the cracking of gas oil is a second-order reaction but the cracking of gasoline is a first-order reaction and the reactions take place only in the gas phase. The deactivation of catalyst due to coke deposition has been the subject of many research work. In this study, the deactivation kinetic model due to Weekman (1968) is chosen because of its implicity, popularity in FCC modeling and abundance of data available in the literature. In this scheme, the decay of the catalyst activity due to coke deposition is represented by a function ϕ_i,

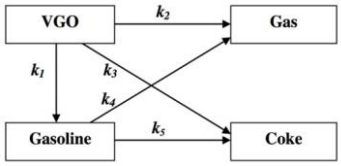
$$\phi_i = \frac{B+1}{B+\exp\left(A.C_{coke,i}\right)}$$

Where, A= 4.29 and B= 10.4,

In order to develop a mathematical model for this system the following assumptions are introduced:

- One-dimensional transported plug flow reactor prevails in the riser without radial and axial dispersion and the riser wall is adiabatic
- Feed viscosity and heat capacities of all components are constant
- In each section of riser, the catalyst and gas have a same temperature
- Instantaneous vaporization occurred in entrance of riser
- All cracking reactions are considered to take place in the riser

Figure 2: Four-lumped model



Steady state mass and energy balance:

Applying the conservation principles and assuming plug flow in the riser, the mass and heat balances in dimensionless form are:

For VGO:

$$r_{gasoline,i} = -\phi_i\left(k_1\frac{\left(\rho_{gi}y_{C_{1,i}}\right)^2}{\rho_{VGO}} - (k_4+k_5)\rho_{gi}y_{C_{2,i}}\right)V_{cat,i}$$

$$r_{VGO,i} = -\phi_i(k_1+k_2+k_3)\frac{\left(\rho_{gi}y_{C_{1,i}}\right)^2}{\rho_{VGO}}V_{cat,i}$$

Gas:

$$r_{gas,i} = -\phi_i\left(k_2\frac{\left(\rho_{gi}y_{C_{1,i}}\right)^2}{\rho_{VGO}} + k_4\rho_{gi}y_{C_{2,i}}\right)V_{cat,i}$$

Coke:

$$r_{coke,i} = -\phi_i\left(k_3\frac{\left(\rho_{gi}y_{C_{1,i}}\right)^2}{\rho_{VGO}} + k_5\rho_{gi}y_{C_{2,i}}\right)V_{cat,i}$$

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Gasoline:

The dependence of kinetics on temperature is described by a modified Arrhenius expression shown as.

$$k_j(T_i) = k_{j,756K} exp\left[-\frac{E_j}{R}\left(\frac{1}{T_i} - \frac{1}{756}\right)\right]$$

The material balance equations can be combined with kinetics and mass transfer models and solved for concentrations in cluster phase.

For VGO, a quadratic equation can be obtained as follows:

$$a_i\, y_{C_{VGO,i}}^2 + b_i y_{C_{VGO,i}} + c_i = 0$$

Where,

$$a_i = \frac{(k_{1,i}+k_{2,i}+k_{3,i})V_{cat,i}\phi_i(\rho_{gi}/\rho_{VGO})}{a_{pi}k_{m,i}}$$

$$b_i = \frac{M_g}{M_g + k_{m,i}a_{P_i}\rho_{gi}}$$

RESULTS

We consider the four lumped model in which the four variable factor A, B, C, and D represents M_{VGO} , T_{VGO} , T_{CAT} and Cp. The ranges of variables in M_{VGO} is 18 to 22, in T_{VGO} is 400 to 500, in T_{CAT} is 800 to 1100 and in Cp is 2 to 4 .

The Aim of the project is to maximize the yield of Gasoline For this goal; we have conducted twenty nine experiments by changing variable factor (M_{VGO} T_{VGO}, T_{CAT} and Cp) with the help of Design Expert Software. Through this Software we calculated different values gasoline on putting different values of M_{VGO}, T_{VGO}, T_{CAT} and Cp.

Gas:

$$y_{C_{2,i}} = \frac{\frac{M_g \times y_{g_{3,i-1}}}{M_g + k_{m,i}a_{P_i}\rho_{gi}} + \frac{\left(k_{1,i}y_{C_{1,i}}^2\left(\frac{\rho_{gi}}{\rho_{VGO}}\right) + k_{4,i}y_{C_{2,i}}\right)\phi_i V_{cat,i}}{a_{pi}k_{m,i}}}{\frac{M_g}{M_g + k_{m,i}a_{P_i}\rho_{gi}}}$$

The study of Relation of response described as with input parameters is named as Response Surface Methodology (RSM). It is used to find optimum operating condition and comprises of various statistical techniques to find better operating condition in terms of product quality and energy requirement.

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$$c_i = \frac{-M_g \times y_{g_{1,i-1}}}{M_g + k_{m,i} a_{P_i} \rho_{gi}}$$

Gasoline:

$$y_{C_{2,i}} = \frac{\frac{M_g \times y_{g_{2,i-1}}}{M_g + k_{m,i} a_{P_i} \rho_{gi}} + \frac{k_{1,i} V_{cat,i} \phi_i \left(\frac{\rho_{gi}}{\rho_{VGO}}\right)}{a_{pi} k_{m,i}}}{\frac{(k_{4,i} + k_{5,i}) V_{cat,i} \phi_i}{a_{pi} k_{m,i}} + \frac{M_g}{M_g + k_{m,i} a_{P_i} \rho_{gi}}}$$

RSM is a useful method in the selection of such factors which affect the responses with statistical significance and also to establish regression models. RSM can be useful for optimizing a response.

Box–Behnken designs are experimental designs for response surface methodology,

Tcatalyst	Tvgo	Cpfeed	Mvgo	Gasoline yield
800.00	381.61	3.09	18.00	56.9607

Table 1: Optimized model for Gasoline

This Project has done on the Design Expert software by the use ANOVA method for finding the statistical variance to maximize gasoline yield.

Analysis of variance table [Partial sum of squares]

This statistical model is used to analyze the differences between group means and their associated procedures. Here we have taken the variable M_{VGO} , T_{VGO} , T_{CAT} and Cp which is denoted by A,B, C and D. These variables have been taken either alone or their groups (with two different variable and with same variable) which is shown below. For maximization of the gasoline, we find the Sum of squares(SS), Degree of freedom (DF), Mean square, F-test and the probability of given source model. By comparing all the models we get optimized results of gasoline (table-2).

Table 2: ANOVA for Optimization

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	274.0820	14	19.5772	11.2895	< 0.0001	significant
A	169.6211	1	169.621	97.8149	< 0.0001	
B	13.52351	1	13.5235	7.79856	0.0144	
C	25.08520	1	25.0852	14.4658	0.0019	
D	8.818530	1	8.81853	5.08535	0.0407	
A^2	34.15084	1	34.15084	19.6936	0.0006	
B^2	0.307321	1	0.307321	0.1772	0.6802	
C^2	2.321856	1	2.321856	1.3389	0.2666	

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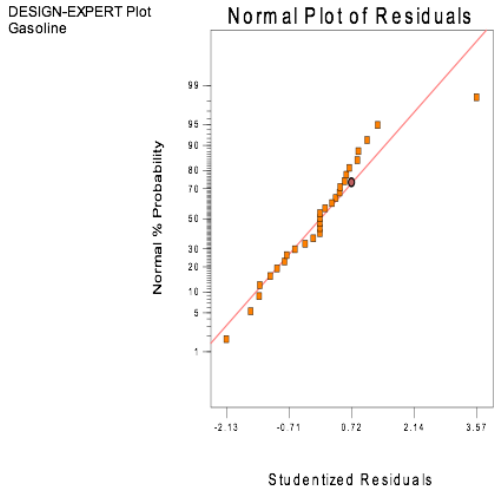
D^2	1.272487	1	1.272487	0.7338	0.4061	
AB	3.296040	1	3.29604	1.9007	0.1896	
AC	17.10236	1	17.102	9.8623	0.0072	
AD	0.992015	1	0.992015	0.5720	0.4620	
BC	0.531440	1	0.531440	0.3064	0.5886	
BD	0.228483	1	0.228483	0.1317	0.7220	
CD	0.143262	1	0.143262	0.0826	0.7780	
Residual	24.27744	14	1.734103			
Lack of Fit	24.27744	10	2.427744			
Pure Error	0	4	0			
Cor Total	298.3594	28				

Normal Plot of Residuals for Gasoline

ANOVA analysis confirmed that the form of the model chosen to explain the relationship between the factors and the response was correct. ANOVA results for the maximization of gasoline yield with a model F-value of 11.2895 implying that the model is significant. From the ANOVA analysis, it is clear that the structural variables for the gasoline are not significant and that only the process variables –M_{VGO}, T_{VGO}, T_{CAT} and C_P are highly significant for the optimum result.



A normal probability plot and a dot diagram of the residuals are shown in Fig. below. The data points on this plot lie reasonably close to a straight line, which exemplifies that the underlying assumptions of the analysis were satisfied. Here the graph shows the variation of Gasoline with M_{VGO}, T_{VGO}, T_{CAT} and C_P .where the optimum point of gasoline is 56.9607 which are shown in the graph.

Graph between T_{VGO}, M_{VGO} and Gasoline: In this graph we have considered the variables are D (M_{VGO}), B (T_{VGO}) and Gasoline where A has been represented at X-axis, B at Y-axis and Gasoline at Z-axis. Here actual factor is A (T_{CAT}) and C (Cp). When we put the different value M_{VGO} and T_{VGO} and get the yield of Gasoline on design expert plot which is shown.

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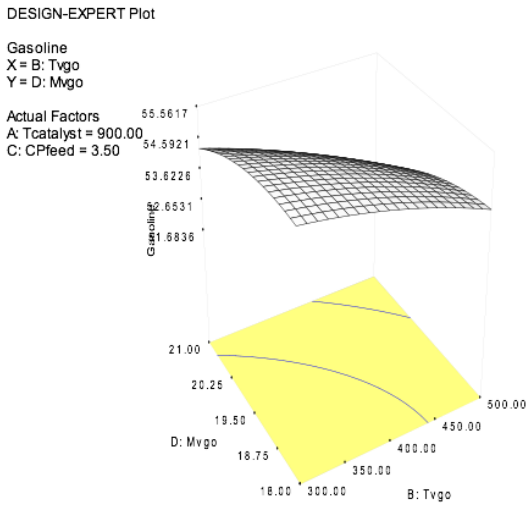
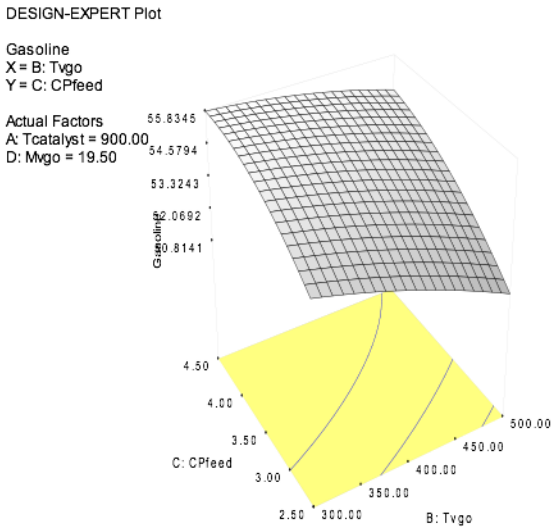


Graph between T_{VGO}, C_P and Gasoline: In this graph we have considered the variables are B (T_{VGO}), C (C_p) and Gasoline where B has been represented at X-axis, D at Y-axis and Gasoline at Z-axis. Here actual factor is D (M_{VGO}) and A (T_{CAT}). When we put the different value T_{VGO} and C_P and get the yield of different value of Gasoline which is shown.



Graph between Tcatalyst, T_{VGO} and Gasoline: In this graph we have considered the variables are B (T_{VGO}), A (Tcatalyst) and Gasoline where B has been represented at X-axis, A at Y-axis and Gasoline at Z-axis. Here actual factor is D (M_{VGO}) and C (C_p). When we put the different value T_{VGO} and Tcatalyst and get the yield of different value of Gasoline which is shown.

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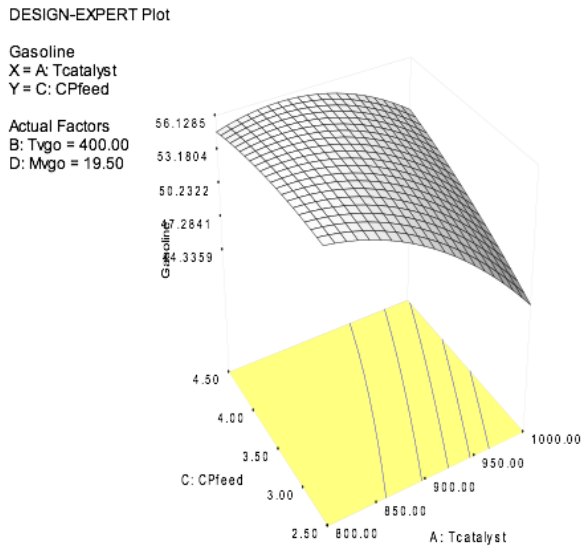
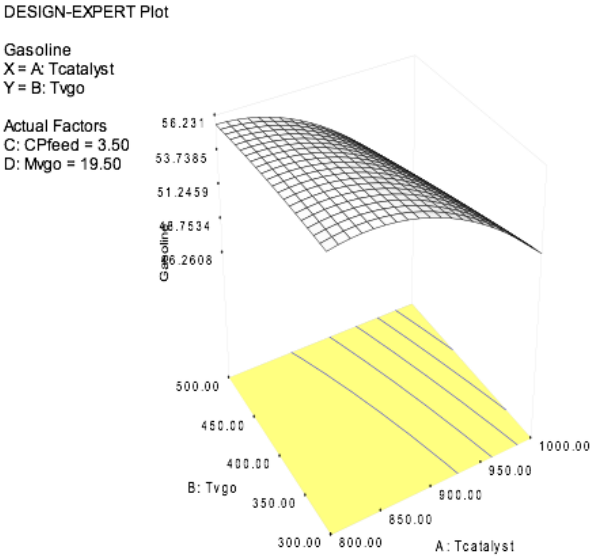


Graph between Tcatalyst, C_P and Gasoline: In this graph we have considered the variables are A (Tcatalyst), C (C_p) and Gasoline where A has been represented at X-axis, C at Y-axis and Gasoline at Z-axis. Here actual factor is D (M_{VGO}) and B (T_{CAT}). When we put the different value Tcatalyst and C_P and get the yield of different value of Gasoline which is shown.



Graph between M_{VGO}, C_P and Gasoline: In this graph we have considered the variables are C (C_p) , D (M_{VGO}) and Gasoline where C has been represented at X-axis, D at Y-axis and Gasoline at Z-axis.

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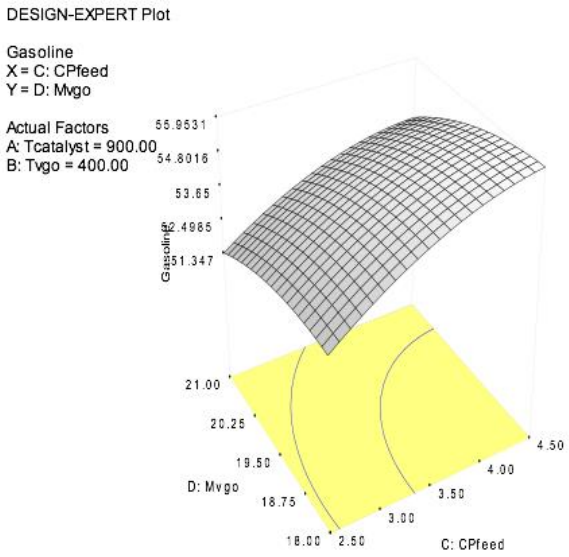

Here actual factor is A (T_{CAT}) and B (T_{VGO}). When we put the different value T_{VGO} and C_P and get the yield of different value of Gasoline which is shown.

CONCLUSION

This project has been done on the Design Expert Software by using Box-Behken Design and Response Surface Methodology for finding the optimized result of Gasoline. In this system we have considered the four lumped system.

The result shows the significant variation in the yield of coke and gasoline as compared to plant data. The increase in yield of gasoline and decrease in yield of coke can be very useful in the profitability of refineries. The table below shows the optimized results of coke and gasoline,

	Plant data	Optimized result	% Variation
Gasoline	46.981034	57.9607	18.94% rise

Table 3: % optimization of gasoline

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