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Optimization of Industrial Fluid Catalytic Cracking Unit having Five Lump Kinetic Scheme using Genetic Algorithm

Shishir Sinha[1] **and Praveen Ch.**

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 on the modeling of this unit for better understanding and improved productivity. The process is characterized by complex interactions among feed quality, catalyst properties, unit hardware parameters and process conditions.

The traditional and global approach of cracking kinetics is lumping. In the present paper, five lump kinetic scheme is considered, where gas oil crack to give lighter fractions (like gasoline, LPG, dry gas) and coke. There are present nine kinetic parameters and one catalyst deactivation activity. The integrated reactor-regenerator steady state model makes gross assumption about the hydrodynamics, using Runga Kutta method.

The Genetic Algorithm (GA) is a stochastic global search method that mimics the metaphor of natural biological evolution. GA operates on a population of potential solution applying the principle of survival of the fittest to produce better and better approximations to a solution. At each generation, a new set of approximations is created by the process of selecting individuals according to their level of fitness in the problem domain and breeding them together using operators borrowed from natural genetics. In the present work, the multi objective binary coded elitist non-dominated sorting genetics algorithm (NSGA-II) is studied, and for the new code, NSGA-II JG is used to obtain optimal solution. In the present paper, the optimal solutions are compare which obtained by NSGA-II JG and NSGA-II performance.

Keyword: Fluid catalytic cracking, Mathematical modeling, Five lump Kinetic scheme, Non-dominated sorting genetics algorithm (NSGA-II), Jumping genes.

1 Introduction

The fluid catalytic cracking is called FCC, and is one of the most important units. The FCC technology was initially developed and put into practical use in the United States in early 1930s, and the first commercial unit was ready by 1942. After the improvements in catalysts and process technologies have been made. The FCC unit is known to contribute approximately 45% of the total revenue in a typical petroleum refinery (Wilson, 1997). Its main function is to convert atmosphere residue (AR) from the crude distillation unit (CDU) into several value added products such as gasoline, middle distillates and light alkenes. FCC is a process for splitting large, low valuable products molecules in the gas oil feedstock into smaller, more valuable products. In spite of its commercial importance optimization of the FCC unit is still largely empirical due to complex interactions between a large number of dependent and independent parameters. Determine optimal operating parameters for different mode of operation by changing process conditions on a commercial FCC is neither feasible nor advisable.

There are approximately 400 catalytic crackers operating present in worldwide and a total processing capacity over the 45,000 m^3/day (12 million barrels per day). Several oil companies such as Exxon, Shell, and TOTAL, have their own designs; however, most of the current operating

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[1] Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee-247667, Email: sshishir@gmail.com

units have been designed or revamped by three engineering companies: UOP, M.W. Kellogg, and Stone & Webster. Although the mechanical configuration of individual FCC units may be different, their common objectives are to be upgrading low value feedstock to more valuable products.

Several studies have been reported in the open literature that deals with various aspects of FCC units. These include their kinetics, modeling, and simulation, multiplicity of steady states, chaotic behavior, online optimization and control. Avidan and Shinnar (1990) reviewed the developments and commercialization of catalytic cracking in detail. Different workers have discussed the kinetics (Weekman, 1969; Jacob et al., 1976; Ancheyta et al., 1999) in the reactor and the regenerator and have modeled (Errazu et al., 1979; Krishna and Parkin, 1985) these units separately, where as few (Arbel et al., 1995; Han et al., 2000; Arandes et al., 2000; Elnashaie and El-Hennawi, 1979; Elshishini and Elnashaie, 1990; Elnashaie et al., 1995)) have developed an integral model for the reactor regenerator system.

2 Overview of the industrial FCC unit

The simplified schematic of the reactor regenerator section of the FCC unit is shown in Fig. 1; the main components of this section are the riser, the regenerator, and the catalyst cooler. The FCC unit in the refinery is designed to crack AR from the CDU, which is fed with AR and other feedstocks such as heavy vacuum gas oil (HVGO) and light sulfur fuel oil (LSFO). The feed to the reactor (often known as riser) is preheated in a series of heat exchangers to the required temperature and then injected at the bottom of the riser, though feed nozzles into the moving regenerated catalyst at high temperature. The cracking of the feed takes place in the riser. At the top of the riser, the catalyst and hydrocarbon vapor disengage from each other. The catalyst flows down the riser, where they are stripped free of hydrocarbon by saturated steam (Fig.1). The stripped catalyst is then sent to the regenerator for the catalyst regeneration. The hydrocarbon vapors pass through vertical pipes which discharge near the inlets of the four stage cyclones inside the upper section of the reactor. The entrained catalyst in the vapor is collected by the cyclones and flows down to the riser. The effluent vapor leaves the cyclones and flows to the separator section for separating into valuable products.

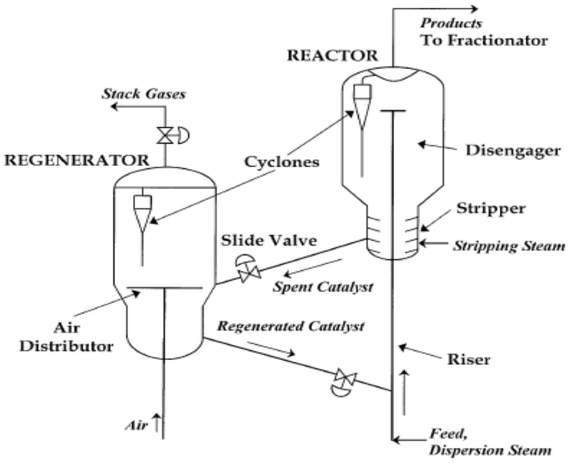

Figure 1: The simplified schematic of the reactor regenerator section of the FCC unit (Han et al. 2001)

During the process of catalytic cracking in the riser, coke is deposited on the catalyst. The spent catalyst is sent to the regenerator. The catalyst is fluidized in the regenerator, and the flows of the spent and regenerated catalysts (Fig.1) are controlled by the slide valves. The spent catalyst is regenerated by burning the coke with combustion air in the regenerator via the lift line controlled by the plug valve. The catalyst cooler helps to keep the temperature within a controlled range in the regenerator especially during the processing of feed with a higher percentage of carbon. It is expected that the coke on the catalyst would have almost been burnt off in the regenerator and enters the riser, where the hydrocarbon feed is injected at the bottom of the riser through fresh feed nozzles. A small amount of purge steam keeps the nozzles clear of any catalyst. As the fresh feed passes through the nozzles, it is finely atomized and dispersed in the steam injected in the feed nozzles.

3 Previous Studies

Because of the importance of FCCU in refining, considerable effort has been put into the modeling of this unit. In last six decades, the mathematical modeling of FCC units has matured in many ways but the modeling continues to evolve to improve the closeness of models predictions to the real process whose hardware is ever-changing to meet the needs of petroleum refining. The 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.

Process models are must for the design, optimization and control of commercial plants. In addition they provide guidance in the development of a new process and can reduce both time and capital requirements. The utility of a process model depends strongly on its predictive capabilities. The predictions should be reliable over wide ranges of charge stock compositions and process conditions. The result will provide an understanding of the chemical reactions involved and lead to the development of improved catalysts and processes. Therefore researchers in this field have worked on different aspects of the process separately for modeling purposes.

Ford et al. (1976) developed a distributed parameters model of the regenerator in an FCC unit using a detailed kinetic combustion model. Lee and Grove (1985) presented a model of an FCC unit based on macroscopic models of the reactor and regenerator. Monga and Georgakis (1987) developed a dynamic model of an FCC unit and used it to examine the dynamic behavior of the process. McFarlane et al. (1993) developed a dynamic FCC unit model with constraints that was posted as a challenge problem for the chemical process control community. The used a distributed parameters model of the regenerator but used only a continuous stirred tank reactor (CSTR) for the reactor section, which did not include a yield model. The FCC simulator used in this work is based on a modified version of the McFarlane FCC model. Theologos and Markatos (1993) developed a mathematical empirical model to describe the three dimensional two phase flow and the heat transfer analysis of the particle and gases, as well as predicting the products distribution in the riser reactor. Theologos et al. (1997) used a three dimensional fluid flow and reaction yield model of the FCC reactor to investigate the effects of injection geometry on the yield of the desired products.

Krishna and Parkin (1985) presented a modeling attempt to simulate the behavior of the commercial FCC regenerator reactor. Elnashaie and El-Hennawi (1979) and Elshishini and Elnashaie (1990) described the kinetics of cracking and recognized the two phase nature of the reactor and regenerator fluidized beds. The cracking reactor investigated in the models is a fluidized bed instead of transported bed (riser) as exists in most of the modern FCC units. Arandes and de-Lasa (1992) incorporated the kinetics of coke combustion valuable tools for the simulation and investigation of the multiplicity behavior of the FCC units over their operating range.

Zheng (1994) presented dynamic model for the riser type FCC unit. This model simulates the startup, shutdown and routine operation of the unit. Ancheyta et al. (1999) developed a five lump kinetic model, to describe the gas oil catalytic cracking (FCC) process. The model contains eight kinetic constants, including one for catalyst deactivation, taking into account LPG(combined $C_3 - C_4$), dry gas(C_2 and lighter)and coke yields separately from other lumps (unconverted gas oil and gasoline).

Blasetti and de-Lasa (2001) described the multicrackex unit constituted by a riser reactor with an upflow catalyst suspension exchanging heat with a surrounding fluidized bed regenerator. A statistical based analysis is developed to establish a semiempirical correlation able to describe the heat transport phenomena between a bundle of riser reactor tubes and fluidized bed regenerator. The proposed correlation is tested and developed under reaction and realistic conditions for fluidized catalytic cracking (FCC) units.

Peixoto and de Medeiros (2001) used the concept of continuous description of catalytic cracking of petroleum fractions. They are characterized the petroleum fractions using multi indexed concentration distribution function (CDF) developed by Aris (1989). Author used the twelve lump schemes, combined with instantaneous adsorption hypothesis of Cerqueira (1996) and deactivation hypothesis of Oliveira (1987) in their model.

Bidabehere and Sedran (2001) developed a model to analyze the simultaneous effects of diffusion, adsorption, and reaction at high temperature inside the particles of commercial FCC catalysts. Authors also experimentally established the relative importance of diffusion, adsorption and reaction using two equilibrium catalysts and n-hexadecane as a test reactant in a riser simulator reactor.

Martignoni et al. (2001) developed the heterogeneous reaction model for FCC riser units. A mathematical model is considered to describe the importance of hydrocarbon species in FCC risers. Results show that both hydrodynamic and the reaction kinetics are strongly influenced by adsorption phenomena. The proposed heterogeneous reaction model predicts increases in catalyst and vapor residence times and consequently higher gas oil conversions.

Hagelberg et al. (2002) described the kinetics of catalytic cracking with short contact times. A novel isothermal pulse reactor was used to study the kinetics of gas oil cracking on a FCC equilibrium catalyst with short contact times. The feed was lighter gas oil than typically used in FCC-units.

Dupain et al. (2003) discussed the aromatic gas oil cracking under realistic FCC conditions in a micro-riser reactor. The conversion by cracking reactions is limited to the paraffinic fraction of the feed and the alkyl groups associated with the benzene ring in aromatic compounds; the aromatic probes did not crack under the applied conditions, and in fact an additional amount of naphthalene was formed by complex dealkylation and hydrogen transfer reactions.

Chang et al. (2003) described the simulation of FCC riser with multiphase heat transfer and cracking reaction. A validated CFD code ICRK-FLO was developed for simulation of three dimensional three phase reacting flows in fluid catalytic cracking (FCC) riser reactors.

Pareek et al. (2003) developed a non isothermal model for the riser reactor which was in corporate in CATCRACK for obtaining the temperature and conversion profiles within the riser reactor. Authors predicted a temperature drop of about 30-40 °C in the riser.

Berry et al. (2004) described the two dimensional reaction engineering model of the riser section of a fluid cracking unit. A two dimensional model that predicts conversion and yield pattern in the riser section of a fluid catalytic cracking unit has been developed. The riser hydrodynamics have been described by the two dimensional model of Malcus and Pugsley (2002). The hydrodynamic model has been modified to make it predictive by incorporating the slip factor for calculation of the cross-sectionally averaged voidage. The model has been coupled with the four-lump kinetic model of Gianetto et al. (1994). To predict how riser operating conditions affect profiles of conversion, yield, temperature, and pressure in the riser.

Monroy et al. (2006) described the modeling and simulation of an industrial FCC riser reactor using a lump kinetic model for a distinct feedstock. A process model for an industrial FCC reactor is an important tool for predicting the flexibility to operate with different feedstock within the expected range of conversion, yield of gasoline, and coke production.

Huang et al. (2006) described the dynamic model of the riser in circulating fluidized bed. The author focuses on modeling the transient behavior of large CFB units, whose flow characteristics were shown to yield C-shaped voidage profiles using cork as the fluidizing material and air at ambient conditions.

Bollas et al. (2006) described the Five-lump kinetic model with selective catalyst deactivation for the prediction of the product selectivity in the fluid catalytic cracking process. The catalyst deactivation may affect each one of the reactions in different ways, which creates an additional reason for different variation with time-on-stream of the yield to each product.

Ramachandran et al. (2007) described the data analysis, modeling and control performa cement of an industrial FCC unit. Considerable fluctuations were observed in the riser temperature. The undesired occurrence has an adverse effect on the performance of the process unit.

Several studies have also been carried out on the optimization of FCC units. Most of them use some type of a profit-function as the objective. Some of the commonly used decision variables in these studies are the regenerator temperature, reactor temperature, catalyst circulation rate and the air supply rate. These studies use a single objective function. In the past several years, more detailed optimization studies using multiple objective functions and constraints have been reported in the chemical engineering literature using a variety of mathematical algorithms. These are reviewed by Bhaskar et al. (2000). Besides being more realistic (several noncommensurate objective function need not be clubbed together, by scalarization / parameterization, into a single profit function), these studies the added advantage that they do not miss out the optimal solutions when a duality gap is encountered due to the nonconvexity of the objective function (Bhaskar et al., 2000; Chankong and Haimes, 1983). In such multiobjective studies, we often obtain a Pareto set of non-dominating (equally good) solutions, and a decision-maker needs to use his intuition or additional information to decide upon the preferred solution. We use a recent adaptation of genetic algorithm (referred to herein as NSGA-II) as developed by Deb and co-workers (Deb et al., 2000) to optimize industrial FCC units using more than one objective where more than a single objective function. This is also the first attempt in FCC unit optimization where more than a single objective function has been used.

4 Riser Kinetics

In the modeling of riser, the hydrodynamics characteristics of riser of a FCC plant are considered the gas and solid velocity profiles by using a plug flow model with radian dispersion. The hydrodynamics proposed by Pugsley and Berruti (1996) and Gupta and Subba Rao (2001). Since a large number of complex cracking reactions are involved, calculation of the exact value of the heat of estimate of the heat of reaction may be made by taking the microscopic difference between the enthalpies of the products and the reactants.

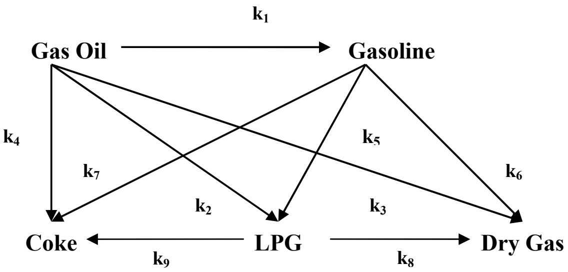

Figure 2: Schematic diagram of the five-lump model examined

The present kinetic scheme is differ from that used by Ancheyta et al. (1999) in that the latter did not allow cracking of gasoline and LPG to coke which have been included in the present study. So in the present kinetic model, nine kinetic constant are estimated by experimental and theoretically approach. The model parameters are estimated by minimizing the error between the data obtained from the steady state process model and those from the hypothetical process model.

In the model development of riser reactor, the commonly used assumptions are follows below:

1. At the riser inlet hydrocarbon feed comes into contact with the hot catalyst coming from the regenerator and instantly vaporizes (taking latent heat and sensible heat from the hot catalyst). The vapor thus formed move upwards in thermal equilibrium with the catalyst.
2. There is no loss of heat from the riser and the temperature of the reaction mixture (hydrocarbon vapors and catalyst) falls only because of the endothermicity of the cracking reactions.
3. Gas phase velocity variation on account of gas phase temperature and molar expansion

due to cracking is considered. Ideal gas law is assumed to hold.

4. Heat and mass transfer resistances are assumed as negligible.
5. There are no radial temperature gradient in the gas and solid phase.
6. Conradson carbon residue of feed is zero.
7. Catalyst deactivation is non-selective and related to coke on catalyst only.
8. Gas oil cracking is a second order reaction but cracking of gasoline and LPG are first order reactions.
9. Dry gas produces no coke.
10. Heat capacities and densities are constant through the length of the reactor.

5 Kinetic expression

For each reaction, a kinetic expression (r_i) was formulated as a function of product yield (y_i), deactivation function (ϕ) and kinetic constants (k_i). Gas oil cracking was considered as a second order reaction and gasoline and LPG as first order (Blanding, 1953). The use of first order reaction for cracking of LPG has been discussed in the literature (Landeghem et al., 1996). The exponential law was assumed for catalyst decay (ϕ) which depends on the time on stream (t_c). A non-selective deactivation model, which is based on the hypothesis that ϕ is the same for all reactions, was used to simplify the overall kinetic model and parameter estimation (Corella et al., 1994). A selective deactivation model would approximate more the reality and would give slightly better results, however it would need more accurate deactivation kinetic data (Corella et al., 1998). Based on these assumptions, the reaction rates of the proposed model are:

Gas oil:

$$(r_1) = -(k_1+k_2+k_3+k_4)y_1^2\phi \tag{1}$$

Gasoline:

$$(r_2) = (k_2y_1^2-k_5y_2-k_6y_2-k_7y_2)\phi \tag{2}$$

LPG:

$$(r_3) = (k_2y_1^2+k_5y_2-k_8y_3-k_9y_3)\phi \tag{3}$$

Dry gas:

$$(r_4) = (k_3y_1^2+k_6y_2+k_8y_3)\phi \tag{4}$$

Coke:

$$(r_5) = (k_4y_1^2+k_7y_2+k_9y_3)\phi \tag{5}$$

6 Riser Modeling

On the basis of above assumption, the mole balance for the jth lump over a differential element can be written as follows (Dave et al. 2001)

$$\frac{dF_j}{dh} = A_{ris}H_{ris}(1-\varepsilon)\rho_c\sum_{i=1}^{9}\alpha_{ij}r_i \quad j=1,2,\ldots,5 \tag{6}$$

Where j = 1 to 5 represents gas oil, gasoline, LPG, dry gas, and coke respectively. i = 1 to 9 represents the reactions as shown in fig. 2.

$$MW_g = \sum_{j=1}^{5}x_jMW_j \tag{7}$$

$$\rho_v = \frac{P_{ris}MW_g}{RT} \tag{8}$$

$$\varepsilon = \frac{\frac{F_{feed}}{\rho_v}}{\frac{F_{feed}}{\rho_v}+\frac{F_{rgc}}{\rho_c}} \tag{9}$$

$$\alpha_{ij} = \frac{MW_i}{MW_j} \tag{10}$$

The molecular weights of different lumps used for the calculation of $\alpha_{ij}$are given in table. 3. The rate equation in (kmol)/ (kg cat.) (s) are given by following expressions:

$$r_i = k_{0,i}\exp(-\frac{E}{RT})C_1^2\phi \quad \text{for } i=1,2,3,4 \tag{11}$$

$$r_i = k_{0,i}\exp(-\frac{E}{RT})C_2\phi \quad \text{for } i=5,6,7 \tag{12}$$

$$r_i = k_{0,i}\exp(-\frac{E}{RT})C_3\phi \quad \text{for } i=8,9 \tag{13}$$

Where, C_1, C_2 and C_3 are concentration of gas oil, gasoline and LPG respectively.

Table 1: Kinetic and Thermodynamic Parameters used for the Reactor Modeling (obtained from the Dave, 2001)

Rate Constant	**Reaction**	**Frequency Factor**	**Activation Energy (kJ/kmol)**	**Heat of Reaction (kJ/kmol)**
k1	Gas Oil to Gasoline	19584.55*	57540	45000
k2	Gas Oil to LPG	3246.45*	52500	159315
k3	Gas Oil to Dry Gas	559.90*	49560	159315
k4	Gas Oil to Coke	41.44*	31920	159315
k5	Gasoline to LPG	65.40	73500	42420
k6	Gasoline to Dry Gas	0.00	45360	42420
k7	Gasoline to Coke	0.00	66780	42420
k8	LPG to Dry Gas	0.32	39900	2100#
k9	LPG to Coke	0.19	31500#	2100#

* Values determined from the plant data by regression (m^6/ (kg catalyst) (kmol gas oil) (s) for the reactions 1 to 4, (m^3/ (kg catalyst) (s) for reactions 5 to 9

\# Estimated

Table 2: Kinetic Parameters used for Regenerator Modeling (Obtained from the Arbel et al. (1995))

Kinetic Parameter	**Frequency Factor**	**Activation energy (E/R, K)**
β_c	2512	6795
K_c (1/(atm)(s))	1.069×10^8	18890
K_{3c} ((kmol CO)/ (kg cat.)(s) (m^3))	117	13890
K_{3h} ((kmol CO)/ (m^3) (atm)^2 (s)	5.07×10^{14}	35555

For the modeling of the catalyst deactivation, the function proposed by Yingxun (1991) for the catalytic cracking of vacuum gas oil was used. Thus, the function ϕ was related to coke on catalyst as follows:

$$\phi = (1+51C_c)^{-2.78} \tag{14}$$

Due to the endothermic cracking reactions in the riser, there is a temperature drop along the height of the riser. The enthalpy balance across a differential element of height dh of the riser can be represented as follows:

$$\frac{dT}{dh} = \frac{A_{ris}H_{ris}(1-\varepsilon)\rho_c}{F_{rgc}C_{P_C}+F_{feed}C_{P_{fv}}}\sum_{i=1}^{9} r_i(-\Delta H_i) \tag{15}$$

The regenerated catalyst and the preheated feed are mix at the base of the riser. Temperature at this zone can be determined from enthalpy balance. Assuming a 10°C drop in temperature of the regenerated catalyst during its journey in transfer line, the riser bottom temperature is calculated as follows:

$$T(h=0) = \Big[F_{rgc}C_{P_c}(T_{rgn}-10)+F_{feed}C_{P_{fl}}T_{feed} - \Delta H_{evp}F_{feed} - Q_{loss,ris}\Big] \Big/ \Big[F_{rgc}C_{P_c}+F_{feed}C_{P_{fv}}\Big] \tag{16}$$

where,

$$\begin{aligned} Q_{loss,ris} =& 0.019[F_{rgc}C_{p_c}(T_{rgn}-10) \\ &+F_{feed}C_{P_{fl}}T_{feed}-\Delta H_{evp}F_{feed}] \end{aligned}$$

To match the riser base temperature with the plant value, so the empirical term $Q_{loss,ris}$ can be incorporated.

7 Stripper Modeling

Due to the lack of required design and operating data the performance of the stripper has been idealized. The temperature drop across the industrial stripper was observed to be 8-12°C. So the temperature drop across the stripper was assumed to be 10°C by Dave and Saraf (2002) and 13.88°C by

Table 3: Thermodynamics and other Parameters used for Simulation (obtained from the Dave, 2001)

Parameter	Numerical Value
$C_{P,c}$ (kJ/kg K)	1.003
$C_{P,fl}$(kJ/kg K)	3.430
$C_{P,fv}$(kJ/kg K)	3.390
$C_{P,N2}$(kJ/kg K)	30.530
$C_{P,O2}$(kJ/kg K)	32.280
$C_{P,H2O}$(kJ/kg K)	36.932
$C_{P,CO}$(kJ/kg K)	30.850
$C_{P,CO2}$(kJ/kg K)	47.400
ΔH_{evp} (kJ/kg)	350.0
H_{CO} (kJ/kg)	1.078×10^5
H_{CO2}(kJ/kg)	3.933×10^5
H_{H2O}(kJ/kg)	2.42×10^5
X_{Pt}	0.10
ρ_c (kg/m^3)	1089.0
C_H (kg H_2/kg coke)	0.165
D_P (ft)	2.0×10^{-4}
MW_{gasoil}	350
$MW_{gasoline}$	114
MW_{LPG}	52
MW_{drygas}	30
MW_{coke}	12
Gas oil lump Boiling range ˚C	221
Gasoline lump Boiling range ˚C	30-220

Table 4: Design data for FCC unit (Dave and Saraf, 2003)

Parameter	Value
Riser length (m)	37.0
Riser diameter (m)	0.68
Regenerator length (m)	19.34
Regenerator diameter (m)	4.52
Catalyst hold up in the regenerator (vol %)	40.5

Arbel et al. (1995). The temperature of the spent catalyst entering the regenerator is calculated by following equation:

$$T_{sc} = T_{ris,top} - \Delta T_{st} \tag{17}$$

8 Regenerator Modeling

The development of the steady state model is based on the following assumptions:

1. Gas is in the plug flow throughout the bed and in thermal equilibrium with surrounding bed.
2. Catalyst in dense bed is well mixed and isothermal with uniform carbon on the catalyst particles.
3. Kinetics of the coke combustion assumes catalyst particles to be 60 μm sizes.
4. Resistance to mass transfer from gas to catalyst phase is negligible.
5. Mean heat capacities of gases and catalyst are assumed to remain constant over the temperature range encountered.
6. All entrained catalyst is returned via cyclones.

9 Regenerator Kinetics

The following combustion reactions are considered to be taking place in the regenerator.

$$C + \frac{1}{2}O_2 \xrightarrow{k_1} CO \tag{18}$$

$$C + O_2 \xrightarrow{k_2} CO_2 \tag{19}$$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_{3c}} CO_2 \quad \text{(Heterogeneous CO combustion)} \tag{20}$$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_{3h}} CO_2 \quad \text{(Homogeneous CO combustion)} \tag{21}$$

$$H_2 + \frac{1}{2}O_2 \xrightarrow{k_4} H_2O \tag{22}$$

The coke combustion in the reaction (18) and (19) are proportional to C_{rgc} and partial pressure of O_2 in the regenerator (P_{O2}). The CO combustion reactions (20) and (21) are proportional to P_{O2} and partial pressure of CO in the regenerator (P_{co}). The rate expressions for these reactions are (Dave et al. 2001):

Rate of reaction 1

$$r_1 = (1-\varepsilon)\rho_{cat} k_1 \frac{C_{rgc} f_{O_2}}{MW_{coke} f_{Tot}} P_{rgn} \tag{23}$$

Rate of reaction 2

$$r_2 = (1-\varepsilon)\rho_{cat} k_2 \frac{C_{rgc} f_{O2}}{MW_{coke} f_{Tot}} P_{rgn} \tag{24}$$

Rate of reactions 3

$$r_3 = (x_{Pt}(1-\varepsilon)\rho_{cat} k_{3c} + \varepsilon k_{3h}) \frac{f_{O2} f_{CO}}{f_{Tot}^2} P_{rgn}^2 \tag{25}$$

Where, x_{Pt} is a relative catalytic CO combustion rate.

The initial ratio of CO/CO$_2$ at the catalyst surface given by Weisz (1966) is

$$\left(\frac{CO}{CO_2}\right)_{surface} = \frac{k_1}{k_2} = \beta_c = \beta_{c0} \exp(\frac{-E_\beta}{RT}) \tag{26}$$

If k_c is overall coke combustion rate then

$$k_c = k_1 + k_2 = k_{c0} \exp(\frac{-E_c}{RT}) \tag{27}$$

Where,

$$k_1 = \frac{\beta_c k_c}{\beta_c + 1} = \frac{\beta_c k_{c0} \exp(\frac{-E_c}{RT})}{\beta_c + 1} \tag{28}$$

$$k_2 = \frac{k_c}{\beta_c + 1} = \frac{k_{c0} \exp(-\frac{E_c}{RT})}{\beta_c + 1} \tag{29}$$

From the above equations, the overall rate of the reaction of O$_2$, CO, and CO$_2$ in jth compartment can be written as

$$r_{O2} = (1-\varepsilon)\rho_{cat} \left(\frac{k_1}{2} + k_2\right) \frac{C_{rgc} f_{O2,j-1}}{MW_{coke} f_{Tot}} P_{rgn} V_j + \frac{k_3 f_{O2} f_{CO}}{2 f_{Tot} f_{Tot}} p_{rgn}^2 V_j \tag{30}$$

$$r_{CO} = (1-\varepsilon)\rho_{cat} k_1 \frac{C_{rgc} f_{O2,j-1}}{MW_{coke} f_{Tot}} P_{rgn} V_j - k_3 \frac{f_{O2} f_{CO}}{f_{Tot} f_{Tot}} P_{rgn}^2 V_j \tag{31}$$

$$r_{CO2} = (1-\varepsilon)\rho_{cat} k_2 \frac{C_{rgc} f_{O2,j-1}}{MW_{coke} f_{Tot}} P_{rgn} V_j + k_3 \frac{f_{O2} f_{CO}}{f_{Tot} f_{Tot}} P_{rgn}^2 V_j \tag{32}$$

10 Dense Bed Modeling

The spent catalyst from the reactor enters the regenerator dense bed in which coke is burn-off in the presence of air to CO, CO$_2$ and H$_2$O. The oxidation of hydrogen is assumed to be instantaneous and complete and hence the amount of oxygen available for the carbon burning reactions at the dense bed inlet is that remaining after the hydrogen combustion reaction.

Differential Balances:
Material and energy balance across a differential element of height dz of the dense bed are as follows (Dave et al. 2001):

Material Balance:

$$\frac{df_{O2}}{dz} = -A_{rgn}(\frac{r_1}{2} + r_2 + \frac{r_3}{2}) \tag{33}$$

$$\frac{df_{CO}}{dz} = -A_{rgn}(r_3 - r_1) \tag{34}$$

$$\frac{df_{CO2}}{dz} = -A_{rgn}(r_2 + r_3) \tag{35}$$

Energy Balance:

$$\frac{dT}{dz} = 0 \tag{36}$$

Initial Conditions:

$$f_{H_2O} = F_{rgc}(C_{sc} - C_{rgc}) \frac{C_H}{MW_H} \tag{37}$$

$$f_{O_2}(0) = 0.21 F_{air} - \frac{1}{2} f_{H_2O} \tag{38}$$

$$f_{CO}(0) = f_{CO_2}(0) = 0 \tag{39}$$

$$f_{N_2} = 0.79 F_{air} \tag{40}$$

Total gas flow rate at any cross section is given by:

$$f_{Tot} = f_{H_2O} + f_{O_2} + f_{CO} + f_{CO_2} + f_{N_2} \tag{41}$$

Bed Characteristics:
Gas molar density (kmol/m^3)

$$\rho_g = \frac{P_{rgn}}{RT_{rgn}} \tag{42}$$

Superficial linear gas velocity (m/s)

$$u = \frac{F_{air}}{\rho_g A_{rgn}} \tag{43}$$

Void fraction was calculated using the correlations reported by Ewell and Gadmer (1978):

$$\varepsilon = \frac{0.305u_1 + 1}{0.305u_1 + 2} \tag{44}$$

Where, u_1 = superficial linear velocity in ft/s.

Dense bed height is also calculated using the correlation reported by Ewell and Gadmer (1978):

$$Z_{bed} = 0.3048(TDH) \tag{45}$$

$$TDH = TDH_{20} + 0.1(D - 20) \tag{46}$$

$$Log_{10}(TDH_{20}) = \log_{10}(20.5) + 0.07(u_1 - 3) \tag{47}$$

Where, D is the regenerator diameter in ft, TDH means transport disengaging height.

The volume of a compartment jth in the regenerator dense bed is given by:

$$V_j = A_{rgn}\Delta z_j \tag{48}$$

Where, $\Delta z_j = \frac{H_{densebed}}{N_c}$.

Overall Balances:

Carbon balance for the regenerator in the dense bed:

$$C_{rgc} = \frac{F_{sc}C_{sc}(1 - C_H) - (f_{CO(Zbed)} + f_{CO_2(Zbed)})MW_c}{F_{rgc}(1 - C_H)} \tag{49}$$

Heat Balance:

Applying heat balance across the regenerator dense bed gives the expression for the dense bed temperature:

$$T_{rgn} = T_{base} + \left\{ \frac{\begin{array}{l} f_{CO(Zbed)}H_{CO} + f_{CO_2(Zbed)}H_{CO_2} + \\ f_{H_2O}H_{H_2O} + F_{air}C_{P_{air}}(T_{air} - T_{base}) + \\ F_{sc}C_{P_c}(T_{sc} - T_{base}) - Q_{loss,rgn} \end{array}}{\begin{array}{l} F_{rgc}C_{P_c} + f_{CO_2(Zbed)}C_{P_{CO_2}} + \\ f_{CO(Zbed)}C_{P_{co}} + f_{O_2}C_{PO_2} + \\ f_{H_2O}C_{P_{H_2O}} + f_{N_2}C_{P_{N_2}} \end{array}} \right\} \tag{50}$$

11 Dilute Phase Modeling

Plug flow kinetics is assumed in the dilute phase. The main reaction taking place in the dilute phase is the oxidation of CO to CO$_2$. As a result both carbon concentration and temperature varies as a function of height in the dilute phase. Material and energy balance in the dilute phase results in the following equation (Dave et al. 2001).

Material Balance:

$$\frac{df_{O_2}}{dz} = -A_{rgn}\left(\frac{r_1}{2} + r_2 + \frac{r_3}{2}\right) \tag{51}$$

$$\frac{df_{CO}}{dz} = -A_{rgn}(r_3 - r_1) \tag{52}$$

$$\frac{df_c}{dz} = -A_{rgn}(r_1 + r_2) \tag{53}$$

Energy Balance:

$$\frac{dT_{dil}}{dz} = \frac{1}{f_{Tot}C_{P,Tot}}\left(H_{co}\frac{df_{CO}}{dz} + H_{CO_2}\frac{df_{CO_2}}{dz}\right) \tag{54}$$

Where,

$$C_{P,Tot} = \left(\frac{\begin{array}{l} C_{P_{N_2}}f_{N_2} + C_{P_{O_2}}f_{O_2} + C_{P_{CO}}f_{CO} + \\ C_{P_{CO_2}}f_{CO_2} + C_{P_{H_2O}} + C_{P_c}F_{ent} \end{array}}{f_{Tot}} \right)$$

Entrainment is calculated by using the correlation of Ewell and Gadner (1978):

$$Y = \frac{W}{V\rho_f} \tag{55}$$

$$X = \frac{V^2}{gD_P\rho_P^2} \tag{56}$$

$$\log_{10} Y = \log_{10} 60 + 0.69\log_{10} X - 0.445(\log_{10} X)^2 \tag{57}$$

$$F'_{ent} = WA_{rgn} \tag{58}$$

$$F_{ent} = 0.4535(F'_{ent}) \tag{59}$$

Catalyst density and void fraction in the dilute phase:

$$\rho_{dil} = \frac{F_{ent}}{A_{rgn}u_{rgn}} \tag{60}$$

$$\varepsilon = 1 - \frac{\rho_{dil}}{\rho_c} \tag{61}$$

The initial flow rate of coke in the dilute phase is given by:

$$f_c(0) = F_{ent} C_{rgc} \frac{(1 - C_H)}{12} \tag{62}$$

The height of dilute phase is calculated from the following expression:

$$Z_{dil} = Z_{rgn} = Z_{bed} \tag{63}$$

12 Optimization

The optimal operations of the fluidized catalytic cracking unit, using five kinetic scheme are considered. This model is tuned using industrial data. The elitist non-dominated sorting genetics algorithm (NSGA-II) is used to solve the multiobjective (two) function optimization problem. The objective functions used are maximization of the gasoline yield, and minimization of the percent CO in the flue gas using a feed flow rate. It is well established that GA and its adaptations (like NSGA) are very robust and give global optima, and several studies are available that demonstrate that real life problems are better solved using GA than other techniques such as sequential quadratic programming (SQP). In fact SQP has to be used with the ε- constraint method and applied repeatedly for different values of ε to obtain the Pareto, whereas NSGA gives the Pareto in a single application of the algorithm (Kasat et al. 2003).

Initially, scientists considered DNA (Stryer 2000) as stable and invariable, and so the idea of jumping genes (JG) met with considerable cynicism. But in the late 1960s, scientists succeeded in the isolating JG from the bacterium, *Escherichia coli,* and named as transposons. In the 1970s, the role of transposons in transferring bacterial resistance to antibodies became understood, the led to increased interest in their study. Transposons are of several different kinds. They have attention only two kinds, namely those generated using processes known as insertion and inversion. Transposons, having a relatively small size of about 1-2 kb (kilo bases or kilo nucleotides), can get inserted (replace a sequence of the same length) in a (original) chromosome. These are referred to as insertion sequences. These consist of central coding sequences of bases that are flanked on both sides by short, inverted, repeat sequences. Transposons can also be of larger sizes of approximately 4-25 kb, and may carry a variety of resistances and other genes, with long repeat sequences at either end. Hence, a transposons can get attached to any of these sites randomly. Indeed, transposons can move (jump) from site to site on the same or on a different DNA molecules, a process referred to as transposition. This is used as probabilistic approach. A fraction P_{jump} of strings (selected randomly) in the population, are modified by the jumping gene operator.

In the case of replacement, a part of the binary string in the offspring population is replaced with a newly (randomly) generated binary string having the same length. The jumping string is generated using random numbers, using the same procedure as used for generating members of the initial population. In the case of reversion, the binaries between two sites selected using random numbers, in a chromosome in the offspring population, are reversed. The JG is introduced in mutation stage in NSGA-II. The reversion involves macro-mutation, while replacement involves macro-macro-mutation.

13 Formulation (Kasat et al. 2002)

Several objective functions can be considered in any optimization study of FCC unit to maximize its profitability and satisfy real-life constraint. In FCC unit, the gasoline, LPG, or diesel always leads to maximization of these yields should taken as the objective function. In contrast, an increase in the yield of gasoline has an adverse effect on (increase in) the coke formation. This coke decreases the activity of the catalyst and needs to be burnt off in the regenerator, requiring higher amounts of feed air.

The considered of all two objective functions simultaneously at the start of any multiobjective study is difficult to attempt and understand.

Max $F_1(T_{feed}, T_{air}, F_{cat}, F_{air})$ = gasoline yield
Min F_2 $(T_{feed}, T_{air}, F_{cat}, F_{air}) = F_{air}$

CO in flue gas $\leq 8\%$

The two objective functions are the maximization of the yield of gasoline (economic reasons) and the minimization of the air required to combust coke on catalyst during the cracking of heavy compounds (to minimize catalyst decay and so to reduce the production of CO). The decision variables used are the feed preheat temperature (T_{feed}), the air preheat temperature (T_{air}), the catalyst flow rate (F_{cat}), and the air flow rate (Fair). A constraint is put on the temperature of the regenerated catalyst (T_{rgn}).

Table 5: GA parameters and bounds used in optimization

Parameter	Value
N_P	100
P_{cross}	0.95
P_{mut}	0.05
P_{jump}	0.5
$N_{gen,max}$	50
l_{chr}	40
N_{seed}	0.88876
N	4
Bounds	$575\leq T_{feed} \leq 670$ K
	$450\leq T_{air} \leq 525$ K
	$115\leq F_{cat} \leq 290$ kg/s
	$11\leq F_{air} \leq 46$ kg/s

14 Result & Discussion

14.1 Solution of Modeling Equation

Most of the model involves the gaseous products as a lump and in some cases the gases are also lumped together with the coke yield. The prediction of coke yield separately from other lumps becomes very important to perform heat integration studies and to design and simulate air blowers and the FCC reactor and regenerator. In the present work, the 5-lump kinetic model for catalytic cracking which splits the light gas oil into dry gas and LPG. This separation is very important because the key FCC products can be predicted separately.

In the FCC unit, there are the riser reactor, stripper and regenerator modeling equations. These ordinary differential equations can be solved by the Runga Kutta method with the help of MATLAB. MATLAB is a high performance language for technical computing. It integrates computation, visualization, and programming in an easy to use environment where problems and solutions are expressed in familiar mathematical notation.

Table.6. shows a comparison of model predicted yields with the measured values for two data sets. The first seven rows of the table are required by the simulator as inputs. The match between the model predicted yields and the measured data is reasonably good. The performance of the model can be expected to remain the same as long as the feed composition remains the same.

Fig. 3. shows the progress of cracking along the riser /reactor length while fig. 4. shows the same against the residence time in the riser/reactor. Initially the conversion and hence, the product yields, increase sharply along the riser height but this rate temperature tapers off as we move up along the reactor length. Fig. 5. shows that the temperature profile along the riser length while Fig. 6. shows the same against the residence time in the riser. Since the reactions taking place in the riser are endothermic, a drop in the temperature is expected as one move up. The magnitude of the temperature drop obtained is consistent with the industrially observed data as seen from table 6.

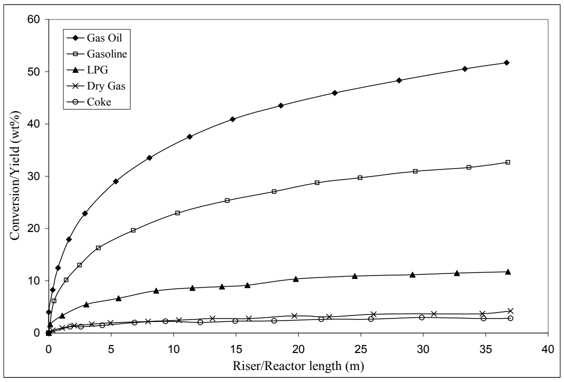

Figure 3: Product profile along the riser/reactor height

Fig. 7. shows that the flow rates of O_2, CO and CO_2 along the regenerated height. As ex-

Table 6: Comparison of the model predicted parameters with the plant value

Type	Set 1		Set 2	
	Measured (Dave et al. 2001)	**Predicted**	**Measured (Dave et al. 2001)**	**Predicted**
Feed flow rate (kg/s)	31.47	-	32.11	-
Feed preheat temperature (K)	617.4	-	620.7	-
Catalyst flow rate (kg/s)	208.33	-	205.00	-
Riser pressure (atm)	2.457	-	2.506	-
Air flow rate (kmol/s)	0.56	-	0.571	-
Air preheat temperature (K)	490.3	-	493.3	-
Regenerator pressure (atm)	2.588	-	2.638	-
Riser top temperature (K)	765.5	774.68	766.6	778.21
Regenerator temperature (K)	930.2	939.51	934.6	948.57
Gas oil (%)	48.1	51.858	44.1	52.815
Gasoline (%)	32.6	32.797	35.2	33.387
LPG (%)	12.1	11.912	12.6	12.093
Dry gas (%)	3.1	3.2749	3.8	3.3187
Coke (%)	4.1	3.772	4.3	3.783
Dense bed height (m)	-	6.514	-	6.5567
Coke on regenerated catalyst (%)	-	0.56726	-	0.54841
Entrained catalyst flow rate (kg/s)	-	32.609	-	32.609

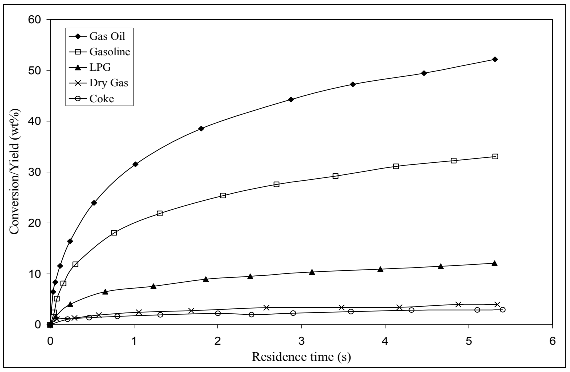

Figure 4: Product profile along residence time

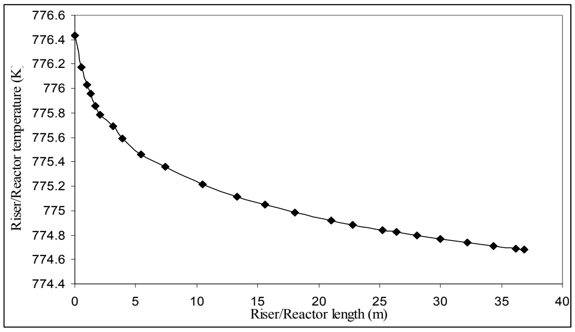

Figure 5: Temperature profile along riser length

pected oxygen concentrations decrease while due to combustion oxide of carbon are formed.

Fig. 8. and Fig. 9. both shows that the NSGA-II JG is better than the NSGA-II. The adaptation of concept of JG or transposons inspired in natural genetics, the multiobjective optimization of FCC units in almost one fifth of the CPU time (number of generations) as compared to as taken as NSGA-II. For the 7 & 10 gen the multiobjective optimization increase the diversity through the JG operator compensates for the decrease in diversity associated with elitism. The compare the performance is better for JG operators which are the associated with CPU time.

15 Conclusion

From the present work, it is concluded that the five lump kinetic model predictions are more realistic and closer to the actual results. The advan-

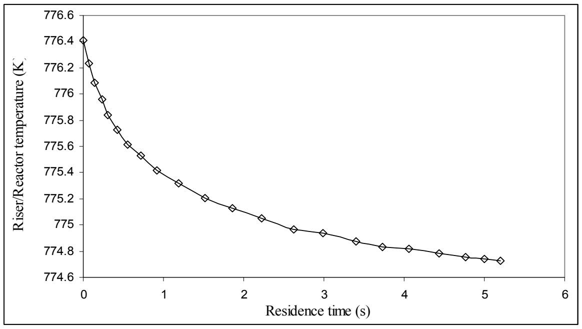

Figure 6: Temperature profile against residence time

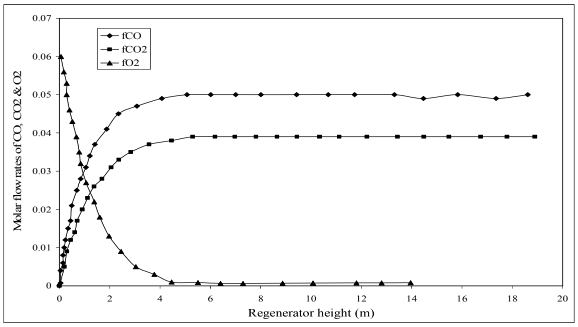

Figure 7: Flue gases profile along the regenerator height

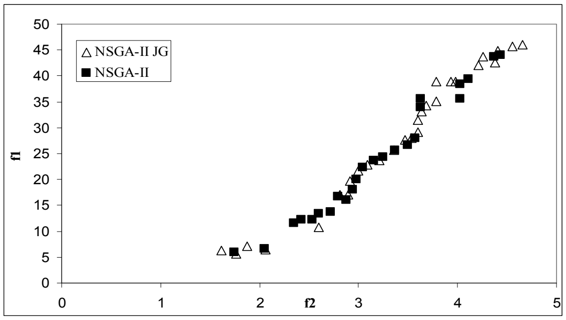

Figure 8: For 7 Gen optimization (NSGA-II-JG & NSGA-II)

tage of five lumps model that it can predict the coke formation, which supplies the heat required for the heating and vaporization of the feedstock and to perform the endothermic reactions; LPG, which contains important hydrocarbons used together with iso-butane as alkylation and MTBE feeds; and dry gas, which is used as a fuel gas in refinery. But one limitation is that the kinetic model does not consider products heavier than gas oil, such as light cycle oil and heavy cycle oil.

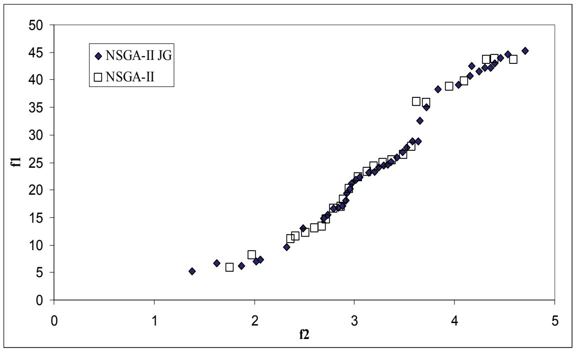

Figure 9: For 10 Gen optimization (NSGA-II-JG & NSGA-II)

The integrated reactor regenerator model developed in this study is quite simple and makes gross assumptions about hydrodynamics in both the reactor and the regenerator. But the general agreement between predicted and measured yields and other parameters establishes that the assumptions are justified. Such models can be used with advantage in optimizing the operating conditions of FCC units. The type of feed may increase or decrease the gasoline yield, depending upon the composition. A naphthenic feedstock gives maximum yield of gasoline, but at the same time LPG, coke and dry gases yield is also high. Paraffinic feedstock is next, to give the highest yield of gasoline and least yield of coke. Aromatic feedstock gives minimum yield of gasoline.

An empirical model is tuned using some data on an industrial FCC unit. The procedure is quite general and any other FCC unit can be similarly modeled and tuned using associated industrial data. A new method is implemented to optimize the multi-objective function in FCC unit. One can easily infer from the results of the above problem that the binary-coded NSGA-II with the jumping gene adaptation incorporated performs better than the elitist NSGA-II (at least for the problems studied here), for multiple objectives.

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