CHEMICAL ENGINEERING TRANSACTIONS

VOL. 26, 2012

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

Guest Editors: Valerio Cozzani, Eddy De Rademaeker

ISBN 978-88-95608-17-4; **ISSN** 1974-9791

DOI: 10.3303/CET1226041

Fluid Catalytic Cracking Environmental Impact: Factorial Design Coupled with Genetic Algorithms to Minimize Carbon Monoxide Pollution

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Fluid Catalytic Cracking (FCC) process is a complex process in petroleum refining industry; it cracks long chain molecules from gas oil and residues to produce high value products like diesel and gasoline. FCC process is composed by two reactors: the riser where cracking reactions take place and the regenerator where combustion reactions eliminate coke deposition from catalyst surface; the last reactors are connected by two transport lines where catalyst circulates. Regenerator flue gas emissions are composed by carbon oxides (CO and CO_2), sulfur oxides (SO_2 and SO_3), nitrogen oxides (NO, N_2O, N_2), and particulates. This work focuses on the minimization of carbon monoxide (CO) in flue gases while maintaining high process conversion. A multi-objective optimization problem was established to maximize conversion and minimize emissions of CO. The problem was solved using genetic algorithms coupled with factorial design used to identify key process variables and to formulate objective optimization functions. Results showed a reduction in CO emissions in the order of 12.8 % with a conversion of 73 %, indicating genetic algorithms as an useful tool to comply environmental regulations and process demands with low computational burden and time.

1. Introduction

According to the Environmental Protection Agency (EPA), in 1999, 54 % of refineries in United States have committed persistent and serious violations of Clean Air Act (Cheng et al. 1998) due to huge volumes of air, water and solid waste. Currently, different technologies have been developed to reduce pollutant emission considering environmental legislation and process requirements. In this sense, the development of refining process simulators are key tools in petroleum industry to address process operation according to operational objectives and variables constraints subject to environmental regulations.

Refining processes are classified into separation and conversion processes, the first one splits a feed into light fractions and the second one generates new molecules having properties adapted to the products end use. Conversion processes are classified into thermal and catalytic processes. Fluid catalytic cracking is a key conversion refining process that operates at high pressures in the gas phase; it uses catalyst as a solid heat transfer medium. Products of conversion from catalytic cracking are largely olefinic for light fractions and strongly aromatic for heavy fractions. FCC by-products are: a) Refinery gases, b) Residue (slurry) or clarified oil (CO) used as refinery fuel, and c) Coke deposited on the catalyst which is burned in the regenerator producing the necessary heat for the reaction. Gases

Please cite this article as: Cuadros J., Melo D., Maciel Filho R. and Wolf Maciel M.R., 2012, Fluid catalytic cracking environmental impact: factorial design coupled with genetic algorithms to minimize carbon monoxide pollution, Chemical Engineering Transactions, 26, 243-248 DOI: 10.3303/CET1226041

produced also called flue gases are composed by CO, CO_2, SO_2, SO_3, NO, N_2O, N_2 and particulates that are cleansed when necessary (Wauquier, 1994).
Environmental regulations are affecting the design and operation of FCC process to reduce flue gases emissions. They are directed at criteria pollutants and air toxic compounds. Criteria pollutants include carbon monoxide, ozone, nitrogen oxides, sulphur oxides, and particulates. Carbon monoxide is the product of incomplete combustion of the coke-burning reactions in the FCC regenerator and is a criteria pollutant and a pollution problem. Air pollution authorities establish a limit of CO-emissions to the atmosphere of 500 ppm for new and existing sources (EPA, 2008). This work focuses on the operating analysis for the minimization of CO emissions from a Brazilian FCC unit, maintaining high levels of activity and selectivity from a regenerator reactor based on a Kellog Orthoflow F process deterministic model presented in Moro and Odloak (1995). A multi-objective optimization was applied in FCC process modeling based on genetic algorithm techniques obtaining a considerable reduction in CO emissions with high process conversion.

2. Fluid catalytic cracking process

FCC is a refining process that cracks heavy petroleum fractions like gas oil and residue from vacuum distillation tower into light fractions. It is composed by: riser, reactor vessel, regenerator and catalyst transport lines operating in a circulating fluid phase at high pressures, with endothermic cracking reactions taking place in riser device. Converter considered in this work is a stacked type reactor composed by two regeneration stages. They are hot, dense fluidized beds in which the coke on catalyst is burnt off producing flues gases and coke free regenerated catalyst. The required energy for cracking reactions is generated in regenerator device through combustion reactions. Catalyst from regenerator is sent to the riser and contacts the feed stream providing the heat required for the endothermic cracking reactions. FCC process emissions are mainly associated with regenerator exhaust. In Figure 1 a representation of FCC process considered is shown.

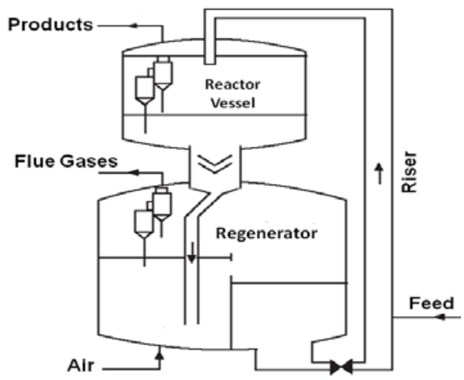

Figure 1. Fluid catalytic cracking converter. Modified from Patan and Korbicz (2007)

Regenerator reactor: According to the Kellog Orthoflow F converter deterministic model presented by Moro and Odloak (1995), regenerator equations represents a dense and diluted phase of two regeneration stages with partial CO burning considered as a system of lumped parameters. Regenerator bed is assumed to be perfectly mixed with homogeneous temperature and concentrations. Combustion reactions taking place in dense phase of regenerator first and second stage are:

$$C + O_2 \rightarrow CO_2$$
$$C + 1/2O_2 \rightarrow CO \quad (1)$$

In the diluted phase it is assumed that there is only CO combustion:

$$2CO + O_2 \rightarrow 2CO_2 \tag{2}$$

In this work, presence of nitrogen and sulfur in coke are neglected. This simplification may not be acceptable for the design of the regenerator, but for the purpose of the work cited, it is no relevant.

3. Process Optimization Methodology

Genetic algorithms (GA) are search algorithms based on the mechanism of natural selection and natural genetics of optimization evolutionary theory. They select the best fit among individuals of a population through generations using mutation and recombination operations for information interchange. Some features associated to GA optimization are related to improve performance towards some optimal point or points. The optimization problem can be focused on to maximize or to minimize a response variable for an objective function with the values of independent variables subject to various constraints. The multi-objective optimization problem to attains three conflicting goals is defined as follows in Equation (3):

$$\begin{aligned}
&\textit{Maximize} \quad SEVERI\\
&\textit{Minimize} \quad CO1\\
&\textit{Minimize} \quad CO2\\
&\textit{Subject to} \quad \textit{Deterministic Model Equations}\left(\textit{Moro et al.2005}\right)\\
&\qquad \textit{and Operational Restrictions}\\
&\qquad 0.42 \le CTCV \le 0.92\\
&\qquad 488.15 \le TFP \le 518.15\\
&\qquad 0.091 \le RTF \le 0.116
\end{aligned} \tag{3}$$

Where SEVERI represents process conversion objective function data published in Moro and Odloack (1995), CO1 represents dense phase first stage molar flow of carbon monoxide objective function and CO2 represents dense phase second stage molar flow objective function. CO1 and CO2 are simplified models obtained through factorial design methodology and problem constraints are represented by: opening porcentage of regenerate catalyst slide valve (CTCV), feed flow rate (RTF) and feed temperature (TFP). The classical approach to solve a multi-objective optimization problem is to assign a weight wi to each normalized objective function so that the problem is converted into a single objective problem with a scalar objective function represented by:

$$max \quad z = w_1 z_1'(x) + w_2 z_2'(x) + \ldots + w_i z_i'(x) \tag{4}$$

Where z'i(x) is the normalized objective function zi(x) and Σ wi =1. Penalty function approach was the constraint handling strategy to solve each single genetic algorithm optimization problem. Once the penalized function is formed, multi objective optimization method established in Equation (3) was used. Since all penalized functions are to be maximized, CO1 and CO2 were transformed using (1/(1+ f)) in a maximization problem. In the work of Deb (2000), the penalty function method is defined for applications of GA's to constrained optimization problems. In this method for handling inequality constraints in minimization problems the fitness function F(x) is defined as the sum of the objective function f(x) and a penalty term that depends on the constraint violation gj(x) as shown in Equation (5):

$$F(x) = f(x) + \sum_{j-1}^{J} R_j \left(g_j(x)\right)^n \tag{5}$$

Absolute value of the operand $g_j(x)$ have to be considered when exponent "n" is the unity, if the operand is negative and a zero value if not for minimization problems. Also, quadratic exponent of the operand could be considered when a strong effect of restriction violation on objective function is preferred .The parameter Rj is the penalty parameter of the jth inequality constraint. The purpose of the penalty parameter Rj is to make the constraint violation gi(x) of the same order of magnitude as the objective function value f(x). For the case of study z'_I is the normalized function value of F(x).

3.1 Statistical design

The process of selecting relevant variables by screening and correlating them using statistical techniques to obtain linear or quadratic models is named statistical design. Factorial design is a technique based on statistical considerations that brings the most meaningful information about the influences of factors on a specific problem, including the effects of interactions among variables. It evaluates at the same time all process variables in order to determine which ones really exert significant influence on the final response, giving a better analysis of it. In order to obtain objective functions to CO1 and CO2 factorial design was applied in the deterministic model proposed by Moro and Odloak (1995) to obtain a reduced model to be used for optimization purposes. Initially, it was applied a factorial design 2k being k the number of factors to be analyzed. The influence of four factors: feed flow rate (RTF), feed temperature (TFP), regenerator air (RAI) and opening percentage of regenerate catalyst slide valve (CTCV) were evaluated on process variables dense phase first stage mass flow of carbon monoxide (CO1) and dense phase second stage mass flow of carbon monoxide (CO2). Equation (6) presents reduced statistical model for CO1 with a correlation coefficient (R^2) of 0.98752. It was considered up to two ways of interaction terms with a significance level of 95 %.

$$\begin{aligned} CO1 = 12.81 - 0.0501*RAI - 28.075*CTCV - 0.0007*RTF + 0.0732*TFP + \\ +0.1850*(RAI*CTCV) + 5.91\text{E-}6*(RAI*RTF) - 0.0002*(RAI*TFP) \\ -0.0015*(CTCV*RTF) + 0.0190*(CTCV*TFP) - 2.576\text{E-}6*(RTF*TFP) \end{aligned} \tag{6}$$

A central composite design was applied to obtain a reduced model for CO2 with a correlation coefficient (R^2) of 0.9398 as presented in Equation (7). It was considered up to two ways of interaction terms with a significance level of 95%.

$$\begin{aligned} CO2 = -52.2062 + 0.2708*RAI - 0.0008*RAI^2 - 1.1230*CTCV - 4.1550*CTCV^2 \\ +0.0033*RTF - 1.537\text{E-}07*RTF^2 + 0.0857*TFP - 0.0002*TFP^2 - 1.53*10^{-7}*RTF^2 \\ +0.0857*TFP - 0.0002*TFP^2 + 0.0535*RAI*CTCV + 2.310\text{E-}06*RAI*RTF \\ +2.777\text{E-}06*RAI*TFP - 0.0008*CTCV*RTF + 0.0272*CTCV*TFP - 1.856E-6*RTF*TFP \end{aligned} \tag{7}$$

It is important to note that because factor values are in real form, all factors and their interactions have to be taken into account. In Figures 2 and 3 a comparison between reduced statistical and deterministic model responses is presented showing the very good accuracy of model predictions represented by Equations (6) and (7).

Once the optimization problem was established, a genetic algorithm parametric study was performed to identify the parameter combination that gives as result high conversion with low rates of CO1 and CO2. GA initiates with a population of represented random solutions in some series of structures. After this first stage, a series of operators was applied repeatedly until convergence was achieved. The GA used was Genetic Algorithm Driver by David Carroll, Version 1.7. 0 (Carroll, 1999).

3.2 Optimization results

Genetic algorithm parameters used in this work to analyze their influence on reactor conversion are: population size, uniform and single point crossover, jump and creep mutation, generations and niche search. The initial estimates of genetic algorithm parameters used in the optimization are presented in Table 1 taken from Carroll (1999). Parameters to be optimized were codified in real form.

Table 1. Initial values of genetic algorithms parameters from (Carrol, 1999)

Genetic Parameters	Population size	Single point and uniform crossover	Jump mutation	Creep mutation	Generations
Values	20-100	50-70 %	1 %	2 %	26

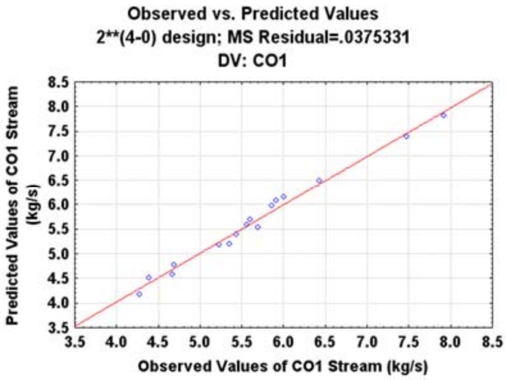

Figure 2. Prediction of CO1 for deterministic (observed values) and reduced statistical models.

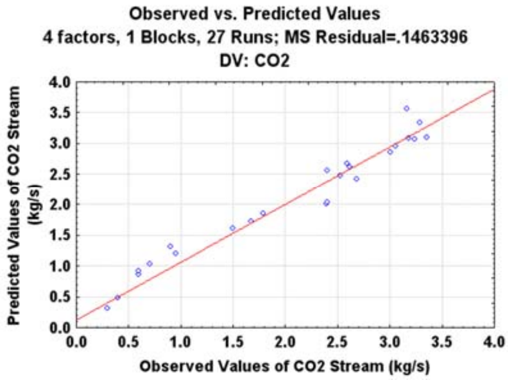

Figure 3. Prediction of CO2 for deterministic (observed values) and reduced statistical models.

The optimization results for conversion considering the population size and uniform crossover variations are presented in Figure 4. The highest conversion was obtained for a population size of 60 with 60 % of uniform crossover. Conversion results for variations on single-point crossover showed lower values. Results for carbon monoxide mass flow in first and second regenerator stage for variations in population size and uniform crossover are in the range of 4.3-4.7 kg/s for CO1 and 1.2-1.3 kg/s for CO2. In order to reduce carbon monoxide emissions, variations in weights of multi- objective optimization function of Equation (2) are presented in Table 2.

The values of weights considered in multi- objective function to be optimized with genetic algorithms were 0.1 for WSEVERI, 0.8 for WCO1 and 0.1 for WCO2 because of this combination represent low values of CO1 and CO2 with high values of SEVERI.

Table 2. Model responses for multi-objective function parameters combinations

WSEVERI	WCO1	WCO2	SEVERI (%)	CO1 Flow (kg/s)	CO2 Flow (kg/s)
0.33	0.33	0.33	78.3	4.67	1.31
0.1	0.1	0.8	54.4	5.13	0.51
0.1	0.8	0.1	73.0	4.06	1.17
0.8	0.1	0.1	81.2	5.09	1.40

Once the multi-objective function parameters have been defined, variations in mutation rates with ranges between 0.1-20 % and niche search operator applied in GA to maintain diversity among feasible solutions were studied. Values of uniform crossover and single point crossover were established in 50 and 60 % respectively with a Population size of 60. Creep mutation rate was established in 2 %. As can be seen in Figures 4 and 5 with a population size of 60, 60 % of uniform crossover rate, creep mutation of 10 % and jump mutation 20 % produce the highest conversion with low flows of carbon monoxide. Other analyses considering variations in creep mutation and niche search operator do not show better results.

4. Conclusions

In this work a reduction of 12.8 % of carbon monoxide represented by CO1 and CO2 with a process conversion of 73.3 % was achieved. In industrial FCC units process conversion range between 70 % to 85 % (Abadie, 2002), showing the good results obtained . A computational time of 10s on an Intel Core 2Quad, 2.66 GHz PC showed that genetic algorithms (GA) coupled with factorial design are powerful tools in multi-objective applications based on static penalty function approach with low computational burden and time, maintaining high levels of activity and selectivity while reducing carbon monoxide emissions from regenerator reactor. A genetic algorithm parameters combination of 60 for population size, a rate of 60 % for uniform crossover, 10 % for creep mutation, 20 % for jump mutation, 26 generations with niche search genetic algorithm operator and elitism produce the lowest CO emission with high conversions. Also it is important to highlight the good performance of heuristic optimization techniques as genetic algorithms for pollutant emissions reduction in the petroleum refining process.

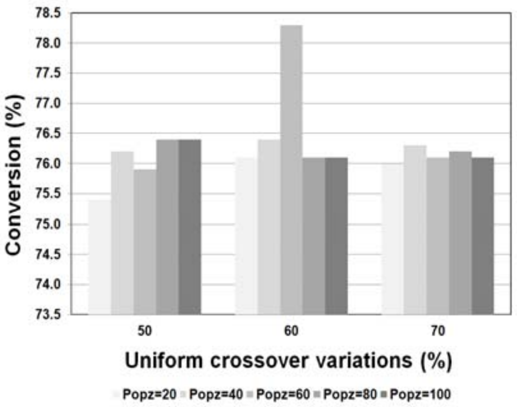

Figure 4. Effect of uniform crossover and population size variations on conversion process

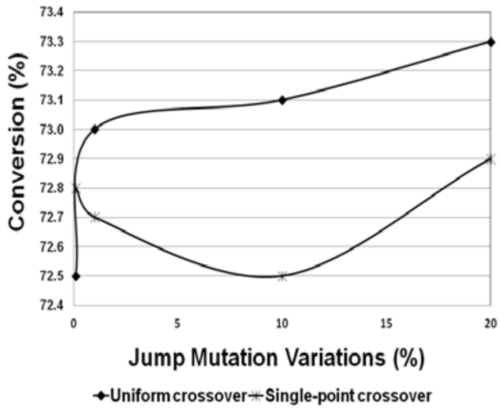

Figure 5. *Conversion profiles considering Uniform crossover , single point crossover and Jump mutation rates variations*

Acknowledgements

The authors would like to thank David L. Carroll for the FORTRAN GA code and the National Council for Scientific and Technological Development (CNPq) for the financial support

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