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Optimization of Fluidized Catalytic Cracking Unit Regenerator to Minimize CO_2 Emissions

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The Fluidized Catalytic Cracking (FCC) is known for its ability to convert products considered as wastes from various refinery units into useful fuels such as gasoline and diesel. It is considered as one of the most important units of the refinery. In spite of its importance, it is also considered as the major contributor of carbon dioxide. This pollutant, CO_2 comes mainly from the regeneration of spent catalyst in the regenerator. In this study, minimization of carbon dioxide exiting the dense bed of the regenerator is considered using model based techniques. The model for the regenerator dense bed was adopted from the literature for simulation. From the simulation, the exit mole fraction of carbon dioxide was found to be 16.21%. The minimized mole fraction was obtained as 15.36%. This is a 5.24% reduction on the yield of carbon dioxide which in turn will reduce the overall mass of carbon dioxide produced and released into the air or captured and stored. Any reduction achieved on carbon dioxide emission is progress made on solving the problems of global warming.

1. Introduction

The FCC unit converts heavy petroleum products such as vacuum gas oils and residues into more valuable, lower molecular-weight fuels such as gasoline and light products. The FCC unit has two major reactors: the riser where cracking reactions take place and the regenerator where the burning of coke is accomplished. During this process referred to as regeneration, large amount of flue gases; CO, CO_2, SO_2, SO_3, NO, N_2O and N_2 are generated (Wauquier, 1994). The flue gases are mostly considered as pollutants to the environment, hence, they are required to be found in little quantity in the air. The amount of CO_2 emitted from the FCC unit is about 30% of the total CO_2 emitted from the refinery and it is considered the highest in oil refineries (de Mello, Gobbo, Moure, & Miracca, 2013). Hence, the refinery is a major contributor to the Green House Gas (GHG), a culprit of global warming. To stop the use of fossil fuels may not be practicable because various projections make clear that fossil fuels will continue to be needed while renewable energy sources are not sufficient.

A recent report from the Nobel Prize-winning Intergovernmental Panel on Climate Change (IPCC) concluded that global CO_2 emissions must be cut by 50-80% by 2050 in order to elude the most destructive effects of climate change (CCP, 2016). To cut down on the CO_2 emission, Carbon Capture and Storage (CCS) is playing a vital role (de Mello et al., 2013; Metz, Davidson, Coninck, Loos, & Meyer, 2005), however, the approach has been proposed for more than 30 years, little is achieved with respect to commercial success of CCS projects. The principal concern is where to stockpile the immense volume of captured pure CO_2 every year (Peng & Zhuang, 2012). Therefore, an approach capable of mitigating the emission is required. To achieve this goal, the use of operational changes to bring about emissions reduction can be carried out in the FCC unit to reduce the extent of emission before it is being captured and stored (Moore, 2005).

This work will focus on minimizing the yield of CO_2 from FCC regenerator flue-gas as an important step in mitigating CO_2 emission of the refinery. Simulation and optimization of the regenerator can identify the scope for reducing the emission. The FCC regenerator is divided into dense bed and freeboard. The dense bed is modelled as a mixed-tank model for energy and coke balances but a plug flow reactor model for gas component balances. The freeboard is modelled as a plug flow reactor. In this work, only the dense bed is considered because most of the solids and gases are in the dense bed where almost all reactions take place

(Pinheiro et al., 2012), and the fact that the dense bed model can be used for the overall regenerator dynamics (Bollas et al., 2007).
To carry out the optimization studies, a single objective function was developed and implemented in gPROMS software which uses a successive reduced quadratic programing (SRQPD) optimization technique, a Sequential Quadratic Programming based solver to minimize the yield of CO_2. The optimization is done using the mathematical models (Han & Chung, 2001a, 2001b) of the regenerator and results obtained will be compared with CO_2 emissions from literature data.

2. Regenerator

The FCC regenerator involves very strong exothermic coke burning reaction which takes place in fluidized bed reactor with composite hydrodynamics (Pinheiro et al., 2012). Different FCC units have different regenerator configurations. Some have single stage and others have two-stage regenerators like the Orthoflow F unit (Chiyoda, 1980), however, all regenerator have similar coke burning kinetics. Most FCC regenerators have two sections; dense bed and a freeboard. The dense bed is divided into two, that is, the emulsion containing much of catalyst where coke burning reactions takes place to produce regenerated catalyst, and the bubble phase with some entrained catalyst but having much of gaseous reactions converting CO to CO_2. The regenerator dynamics follow the well-known two-phase theory of fluidization (Kunii & Levenspiel, 1991). In the regenerator, several coke burning reactions take place; the homogenous and heterogeneous. The heterogeneous reactions happen in the phases where catalyst is present that is the emulsion phase and the freeboard, while the homogeneous reactions happen in gaseous phase. The regenerator bed in this work is modelled as a perfectly mixed reactor, hence no temperature gradient is considered in the bed (Cuadros, Melo, Filho, & Maciel, 2012).

The coke burning kinetics are as follows:

$$CH_q + (0.5 + 0.25q)O_2 \rightarrow CO_2 + 0.25qH_2O \quad (1)$$

$$r_{1i} = k_{1RG} C_{cki} C_{O_2 i}, \quad \text{i = emulsion, freeboard} \quad (2)$$

$$CH_q + (1 + 0.25q)O_2 \rightarrow CO_2 + 0.25qH_2O \quad (3)$$

$$r_{2i} = k_{2RG} C_{cki} C_{O_2 i}, \quad \text{i = emulsion, freeboard} \quad (4)$$

Equations 1 and 3 are coke burning reactions, while Equations 2 and 4 are their rates of reaction respectively (Weisz, 1966). The constants of reaction$k_{1RG} = \frac{k_{1*RG}}{1+\sigma}$, and $k_{2RG} = \frac{k_{2*RG}\sigma}{1+\sigma}$.

The gaseous reactions that take place in the regenerator is obtained from Han and Chung (2001a) and given in Equation (5):

$$2CO + O_2 \rightarrow 2CO_2 \quad (5)$$

When Equation (5) is homogeneous, it occurs in all the phases of the reactor, and its rate of reaction is given in Equation (6).

$$r_{3i} = k_{3*RG} C_{COi} C_{O_2 i}^{0.5} C_{H_2 Oi}^{0.5}, \quad \text{i=bubble, emulsion, freeboard} \quad (6)$$

When Equation (5) is heterogeneous, it occurs only in the emulsion and freeboard phases of the reactor, and its rate of reaction is given in Equation (7).

$$r_{4i} = k_{4*RG} C_{COi} C_{O_2 i}^{0.5}, \quad \text{i = emulsion, freeboard} \quad (7)$$

2.1 The regenerator mathematical model

The mathematical model of the regenerator was adopted from the work of Han and Chung (2001a) and the initial conditions and some process variables were taken from Han and Chung (2001b). The emulsion phase is modelled as a CSTR for energy and coke balances but a plug flow reactor model for gas component balances in the bubble phase. The component balance equations for the gaseous phases in emulsion and bubble are defined by the partial differential equations:

$$\frac{\partial C_{iE}}{\partial t} = -v_{gE}\frac{\partial C_{iE}}{\partial z} - \frac{C_{iE}S_{gE}}{\varepsilon_{gE}} + \frac{K_I}{\varepsilon_{gE}}(C_{iB} - C_{iE}) + R_{iE} \quad (8)$$

$$i = O_2, CO, CO_2, H_2O, N_2,$$

$$R_{O_2 E} = -\frac{\rho_c \varepsilon_{cD}}{\varepsilon_{gE}}\left[\frac{(0.5+0.25q)r_{1E}}{M_{wck}} + \frac{(1+0.25q)r_{2E}}{M_{wck}} + 0.5r_{4E}\right] - 0.5r_{3E} \quad (9)$$

$$R_{COE} = \frac{\rho_c \varepsilon_{cD}}{\varepsilon_{gE}}\left[\frac{r_{1E}}{M_{wck}} - r_{4E}\right] - r_{3E} \quad (10)$$

$$R_{CO_2E} = \frac{\rho_c \varepsilon_{cD}}{\varepsilon_{gE}}\left[\frac{r_{2E}}{M_{wck}} + r_{4E}\right] + r_{3E} \quad (11)$$

$$R_{H_2OE} = \frac{\rho_c \varepsilon_{cD} q}{\varepsilon_{gE} M_{wck}}[0.5r_{1E} + 0.5r_{2E}] \quad (12)$$

$$R_{N_2E} = 0 \quad (13)$$

$$S_{gE} = \frac{\partial \varepsilon_{gE}}{\partial t} + \frac{\partial (v_{gE}\varepsilon_{gE})}{\partial z} \quad (14)$$

I.C $\quad C_{iE}^{(0,z)} = C_{iE}^{(z)} \qquad i = O_2, CO, CO_2, H_2O, N_2, \quad (15)$

B.C $\quad C_{iE}^{(t,0)} = \frac{f_{iE}^{(0)} \rho_{gRG}}{M_{wgRG}^{(0)}} \quad i = O_2, CO, CO_2, H_2O, N_2, \quad (16)$

$$\frac{\partial C_{iB}}{\partial t} = -v_{gB}\frac{\partial C_{iB}}{\partial z} - \frac{C_{iB} S_{gB}}{\varepsilon_{gB}} + \frac{K_l}{\varepsilon_{gB}}(C_{iE} - C_{iB}) + R_{iB} \quad (17)$$

$i = O_2, CO, CO_2, H_2O, N_2,$

$$R_{O_2B} = -0.5r_{3E} \quad (18)$$

Figure 1 shows the schematic diagram of the regenerator as modelled in this work.

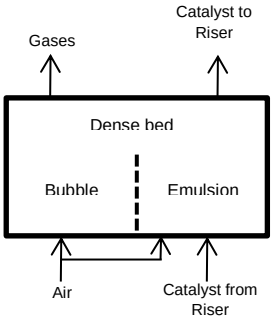

Figure 1: Schematic diagram of the regenerator dense bed model

Table 1 shows the regenerator parameters and initial conditions used in this work.

Table 1: Regenerator parameters and initial conditions

Parameter	Value
Mass flowrate of Air (kg/s)	66.09
Density of catalyst (kg/m^3)	1410
Holdup of catalyst (kg)	182000
Temperature of dense bed (K)	991
O_2 in emulsion and bubble at t = 0 (kg mol/m^3)	0.0005
CO in emulsion and bubble at t = 0 (kg mol/m^3)	0.0003
CO_2 in emulsion and bubble at t = 0 (kg mol/m^3)	0.004
H_2O in emulsion and bubble at t = 0 (kg mol/m^3)	0.003
N_2 in emulsion and bubble at t = 0 (kg mol/m^3)	0.02

3. Optimization problem formulation

Different modelling and optimization platform/software such as Matlab and Hysys were used for FCC regenerator simulations/optimization but not gPROMS, in spite of its robustness. gPROMS uses the successive reduced quadratic programing (SRQPD), it is a nonlinear programming optimization technique capable of handling the nonlinearity of the partial differential and algebraic equations that described the regenerator. In this work gPROMS is used for the regenerator dense bed optimization to minimize the yield of CO_2 from the dense bed of the FCC unit regenerator.

The optimization problem can be described as:

Given	the fixed volume of the dense bed regenerator
Optimize	the mass flowrate of air
So as to minimize	the yield of CO_2
Subject to	constraints on the yield of CO

Mathematically, the optimization problem can be written as;

$$\min_{T(x) or\ F_J(x)} Z \quad (26)$$

$$s.t.$$

$$f(x, z'(x), z(x), u(x), v) = 0 \text{ (model equations)} \quad (27)$$

$$x_f = x_f^* \quad (28)$$

$$F_L \leq F_{air} \leq F_U \quad (29)$$

$$Y_{CO} < Y_{CO}{}^* \quad (30)$$

Where Z is the yield of carbon-dioxide, F_{air} the mass flow rate of air into the regenerator, x_f the height of the regenerator, Y_{CO} the yield of carbon monoxide, F_L and F_U the lower and upper bounds of the mass flowrate of air ($60 \leq F_{air} \leq 80 \frac{kg}{s}$), x_f^* the fixed height of the regenerator and $Y_{CD}{}^*$ the maximum allowable limit for carbon monoxide $Y_{CO} < 0.0002$.

4. Results and discussions

This section shows both simulation and optimization results. The results are presented to show the capability of gPROMS in solving complex nonlinear PDAEs by validating the results against those predicted by the same model but using different solution software as DSim-FCC (Han & Chung, 2001b).

4.1 Simulation

When air comes in contact with coke on the surface of the catalyst, the coke gets burned and the catalyst is regenerated under high temperature which provides enough energy that is required for the endothermic cracking of gas oil in the riser. Figures 2 shows the yields of carbon dioxide from the regenerator during the coke burning reactions.

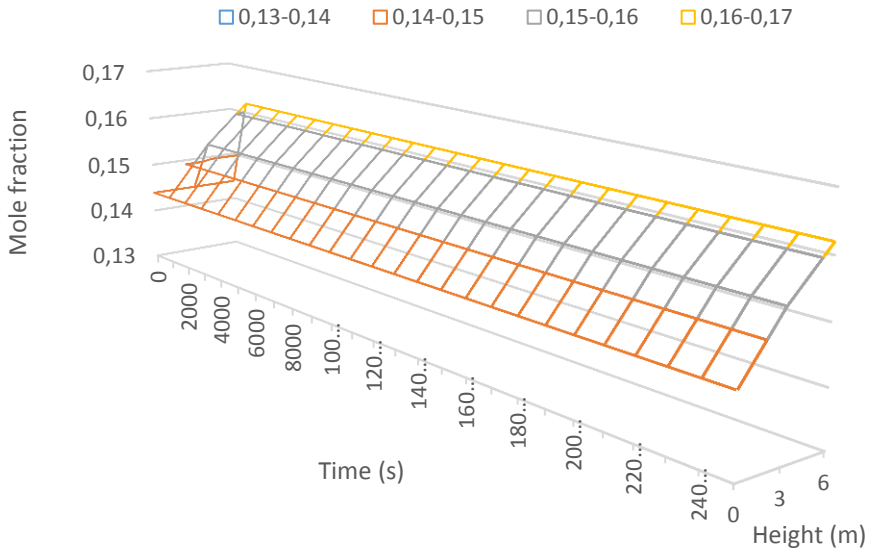

Figure 2: Concentration of carbon dioxide from dense bed - simulation

At 66.09 kg/s gas flowrate and constant temperature of 991 K, the mole fraction of carbon dioxide at the exit of the dense bed of the regenerator is 0.1621. This is 16.21 % carbon dioxide, 0.23 % carbon monoxide, 10.95 % water, 72.24 % nitrogen and 0.36 % oxygen. These results are very much closer to gases mole fractions obtained by Han and Chung (2001b) where the model of the regenerator in this work was taken. Han and Chung (2001b) obtained 14.80 % carbon dioxide, 0.60 % carbon monoxide, 9.20 % water and 0.20 % oxygen. The CO_2 yield from this simulation (16.21%) is higher than what was obtained by Han and Chung (2001b) (14.80%), this is because the mass flowrate of air used in this simulation is 66.09 kg/s while the mass flowrate of the simulation of Han and Chung (2001b) is 34 kg/s. Again, only the regenerator dense bed was considered in this work while Han and Chung (2001a, b) considered the entire FCC unit (riser, disengage, stripper and the regenerator – including the freeboard which was not considered in this work). This could account for the difference in the CO_2 yield for both simulations, however, the simulation results in this work agrees with other literature results with little margin of errors of less than 5% (Zheng, 1994).
Figure 3 shows the results of the minimization of carbon dioxide using the optimized process condition.

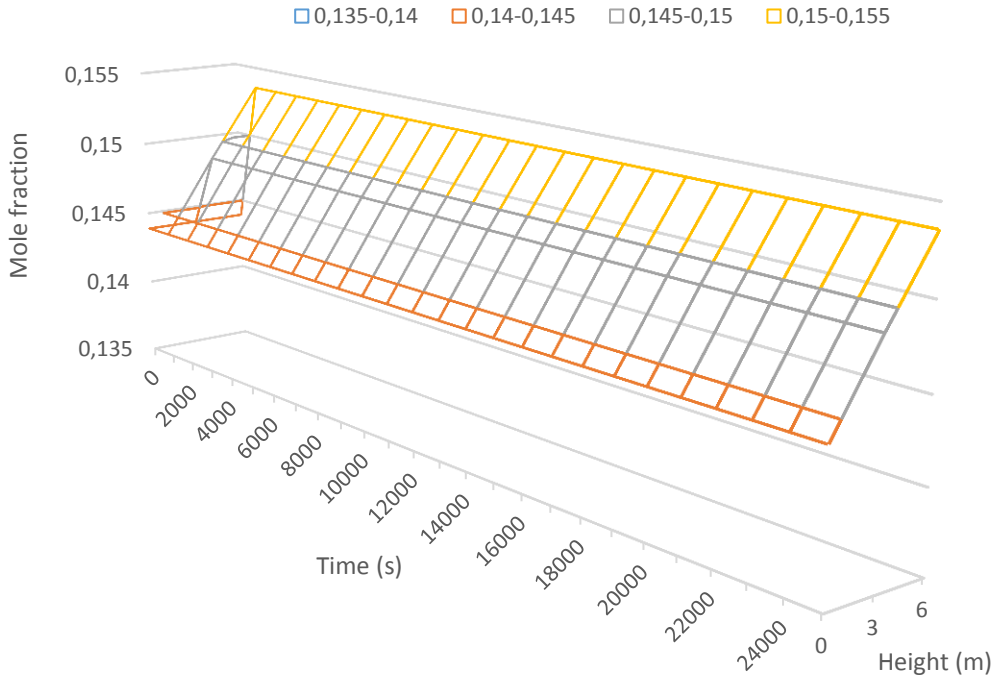

Figure 3: Concentration of carbon dioxide from dense bed – optimization

The mass flowrate of air for the simulation is 66.09 kg/s, while the optimized mass flowrate of air is 83.09 kg/s. This is a 20 kg/s increase in the mass flowrate of air to the regenerator bringing about a slight reduction on the mole fraction of carbon dioxide, which is 0.1536 at the exit of the dense bed. Compared with the mass fraction of 0.1621 of the simulation result, it shows a decrease of 5.24 % of carbon dioxide emitted at the exit of the reactor. Though, the optimization result in this work could not compare favourably with Han and Chung (2001b) simulation result, it shows the simulation result of this work was minimized by 5.24%. As stated earlier, the regenerator model used in this model was for the dense bed only, further work would be required to include the freeboard of the regenerator and all other units of the FCC as was done by Han and Chung (2001a, b). It is expected that with the increase in air mass flowrate, more carbon dioxide should be produced, due to availability of oxygen to burn more coke. However, it was observed that the catalyst holdup decreased slightly, and that could reduce the amount of coke available for the exothermic reaction. This observation is consistent with what was presented by Han and Chung (2001b).

5. Conclusions

The regenerator of FCC unit was simulated and optimized to minimize the carbon dioxide exit concentration so as to cut down on emission of the greenhouse gas. With an increase of 20 kg/s mass flowrate of air, 5.24

% of carbon dioxide was reduced. On carbon dioxide emission, 5.24 % reduction is good step in cutting down the effect of CO_2 emission from the FCC unit on global warming.

The regenerator model considered is not exhaustive, because it did not consider the freeboard and other section of the FCC unit like the riser, disengage and stripper, hence, further work is ongoing to include all the units as simulated concurrently by Han and Chung (2001a, b). This will capture the entire hydrodynamics of the regenerator which will provide detailed insight into the optimization of the unit. Nevertheless, with 5.24 % reduction on this simulation, it shows that using operational changes in process variables of the regenerator can bring about great reduction in CO_2 emission.

Acknowledgments

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