

## Modeling Conversion in a Fluid Catalytic Cracking Regenerator in Petroleum Refining

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**Abstract:** This article discusses modeling and simulation of non ideal flow in a Fluid Catalytic Cracking (FCC) regenerator assuming mixed and plug flow regimes for various operating conditions using the tank-in-series model. An overall coke-on-catalyst conversion of 88.85% was obtained in the absence of dead volume in a perfectly mixed regenerator ( $n = 1$ ). The conversion reduced to 84.76% when a dead volume of 240.66 m<sup>3</sup> was introduced in the mixed regenerator for  $n = 2$ . Beyond  $n = 2$ , the conversion remained constant. A conversion of 99.99% was achieved with coke flow rate of 0.1 m<sup>3</sup>/h for  $n = 20$ . Generally, conversion increased with decreasing coke-on-catalyst flow rate but decreased with increasing dead volume in the mixed flow reactor. Conversion was found to be lower in the plug flow regenerator suggesting that if the regenerator had been designed using the usual plug flow model, its performance would be far less than expected.

**Key words:** Conversion, dead volume, regenerator, tank-in-series model

### INTRODUCTION

Fluid Catalytic Cracking (FCC) is an important process in oil refineries. It upgrades heavy hydrocarbons to lighter more valuable products by cracking, and is a major producer of gasoline in refineries. An FCC unit comprises three stages: a riser reactor, a catalyst stripper, and a regenerator (along with other accessories). In a typical FCC unit, the cracking reactions are carried out in a vertical reactor riser in which a liquid oil stream contacts hot powdered catalyst. The oil vaporizes and cracks to lighter products as it moves up the riser and carries the catalyst powder along with it. Simultaneously with the desired reactions, coke is deposited on the catalyst and renders it less catalytically active. The spent catalyst and the converted products are then separated. The catalyst passes to the regenerator where the coke is combusted to rejuvenate the catalyst. The rejuvenated catalyst then passes to the bottom of the reactor riser, where the cycle begins again (Helmer and Smith, 2004). Figure 1 is a schematic diagram of the FCC unit.

**Catalyst regeneration:** The main objectives of regeneration are to burn off the coke from the catalyst to restore its activity, and to maintain the heat balance in the unit (Roelofsen, 1991; Upson and Zwan, 1987). The catalyst in the regenerator is fluidized with the hot air entering through an air distributor at the bottom. The

oxygen present in the air reacts with the carbon deposited on the catalyst surface to give CO and CO<sub>2</sub>. The carbon monoxide further reacts with oxygen to give CO<sub>2</sub>. The regenerated hot catalyst flows to the riser.

Over the years, many models have been proposed for the FCCU. These models have been based on different sets of assumptions with respect to the kinetics of cracking reactions and hydrodynamics of the equipment involved, such as the riser and the regenerator. Some models concern themselves only with the regenerator (Krishna and Parkin, 1985; Lee *et al.*, 1989). Among the models proposed for the regenerator, most focus on the dense bed which is characterized by bubbles rising through an emulsion phase. The earliest models were single phase, simple contacting models with plug flow, mixed flow, dispersion and tanks-in-series.

This study aims at developing a mathematical model which simulates non-ideal flow in a mixed and plug flow regenerator. An appropriate mixing model in combination with the kinetics of the reactions occurring in the regenerator is developed to predict the reactant conversion at various operating conditions. To account for the non-ideality in the reactor, the tank-in-series model is assumed to estimate the exit age distribution (E) curve.

**Regenerator design and model:** The fluidized bed in the regenerator has been modeled as having two regions, a dense bed region and a dilute region. Since in the dilute

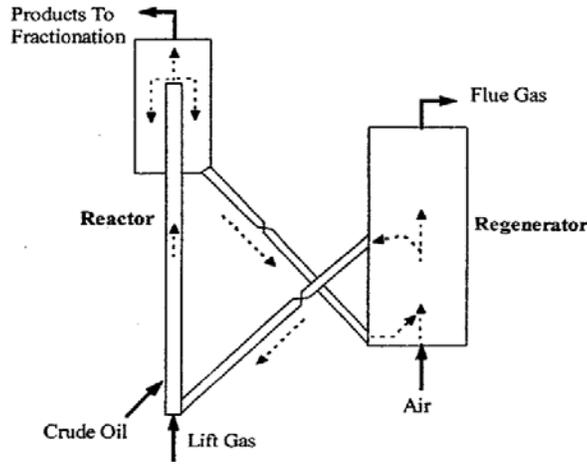


Fig.1: Schematic diagram of an FCC unit

region the catalyst inventory is very low, it is assumed that the dilute region has no effect on the regenerator performance (Ali *et al.*, 1997). Most of the combustion reactions occur in the dense bed region and will be the region of focus. This region is characterized by a bed of solid catalyst particles and the air which flows through the bed for catalyst regeneration. The dense bed is further divided into two sections namely the emulsion phase and the bubble phase. In this model however, the entire dense bed is considered as a single CSTR and a single PRF for the sake of simplicity. The assumption is also made that the regenerator is a constant density system. For a constant density fluid flowing in a system of volume  $V$  at a flow rate  $Q$ , the mean residence time ( $\tau$ ) of fluid is theoretically defined as  $\tau = V/Q$  (IAEA, 2008). It is also assumed that the coke consists of only carbon (Ali *et al.*, 1997).

The ideal steady-state mixed flow reactor is one in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor. For this type of reactor, mixing is complete, so that the temperature and the composition of the reaction mixture are uniform in all parts of the vessel and are the same as those in the exit stream (Levenspiel, 1999)

For a given reactor, the general material balance equation is given by:

$$\text{Input} = \text{output} + \text{disappearance} + \text{accumulation} \quad (1)$$

From Fig. 2, and at steady state, if  $F_{A0} = v_0 C_{A0}$  is the molar feed rate of component A to the reactor, then:

$$\text{Input of A, moles/time} = F_{A0}(1 - X_{A0}) = F_{A0} \quad (2)$$

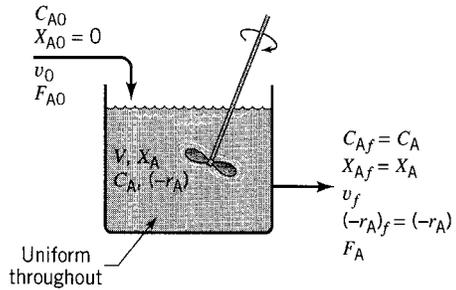


Fig. 2: Notation of a mixed reactor

$$\text{Output of A, moles/time} = F_{A0}(1 - X_A) = F_A \quad (3)$$

Disappearance of A by reaction, moles/time:

$$= (-r_A)V = \left( \frac{\text{moles of A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{Volume of reactor}) \quad (4)$$

Introducing (2), (3) and (4) into Eq. (1), we obtain:

$$F_{A0}X_A = (-r_A)V \quad (5)$$

This on rearrangement becomes:

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} \text{ or } \frac{V}{V_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A} \quad (6)$$

where  $X_A$  and  $r_A$  are measured at exit stream conditions. For the special case of constant density systems,  $X_A = 1 - C_A/C_{A0}$ , in which case Eq. (6) can be written in terms of conversion as:

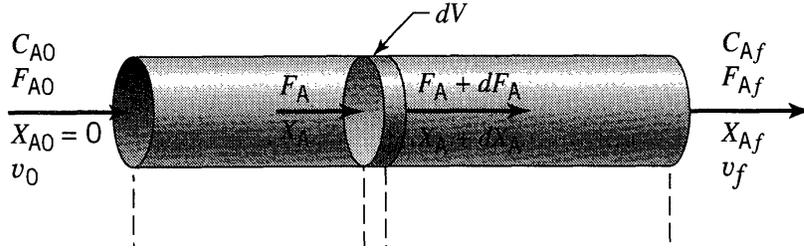


Fig. 3: Plug flow notation

$$\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A} \quad (7) \quad = (-r_A)V = \left( \frac{\text{moles of A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{Volume of reactor})$$

Equation (7) represents the performance equation for mixed reactors.

Therefore, for the second order reaction for the combustion of coke in an ideal mixed flow reactor with equimolar feed of coke and air, the performance equation is given by:

$$k\tau = \frac{C_{A0} - C_A}{C_A^2} \text{ or } C_A = \int_0^\infty \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} \quad (8)$$

where;

- k = rate constant in the rate equation
- τ = mean residence time
- C<sub>A0</sub> = inlet/initial concentration of A into reactor
- C<sub>A</sub> = final or concentration of A at reactor outlet

In the plug flow reactor, as shown in Fig. 3, the feed enters at one end of a cylindrical tube and the product stream leaves at the other end. The long tube and the lack of provision for stirring prevent complete mixing of the fluid in the tube. The absence of longitudinal mixing is the special characteristic of this type of reactor. In a plug flow reactor, the composition of the fluid varies from point to point along a flow path (Levenspiel, 1999). Consequently, the material balance for a reaction component must be made for a differential element of volume dV. Thus for reactant A, Eq. (1) at steady state, becomes

$$\text{Input} = \text{output} + \text{disappearance by reaction} + \text{accumulation}$$

From Fig. 3, we see for volume dV that  
 Input of A, moles/time = F<sub>A</sub>  
 Output of A, moles/time = F<sub>A</sub> + dF<sub>A</sub>  
 Disappearance of A by reaction, moles/time:  
 Introducing these into (1), we obtain:

$$F_A = (F_A + dF_A) + (-r_A)dV$$

Noting that:

$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

On replacement we obtain:

$$(-r_A)dV = F_{A0}dX_A \quad (9)$$

This then is the equation which accounts for A in the differential section of reactor of volume dV. For the reactor as a whole, the expression must be integrated. Now F<sub>A0</sub>, the feed rate is constant but r<sub>A</sub>, is certainly dependent on the concentration or conversion of materials. Grouping the terms accordingly, we obtain:

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

Thus:

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} \text{ or } \tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_0^{X_{Af}} \frac{dV}{-r_A} \quad (10)$$

For second order irreversible reaction with equimolar feed for any ε:

$$C_{A0}k\tau = 2\varepsilon_A(1 + \varepsilon_A)\ln(1 - X_A)\varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \frac{X_A}{1 - X_A} \quad (11)$$

For constant density systems, the expansion factor,  $\varepsilon = 0$ , Eq. (11) becomes:

$$C_{A0}k\tau = \frac{X_A}{1 - X_A} \text{ or } X_A = \frac{C_{A0}k\tau}{1 + C_{A0}k\tau} \quad (12)$$

where  $X_A$  = Conversion of A

This is the performance equation for a second order reaction in an ideal plug flow reactor. However, real equipment always deviates from these ideals. Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel. This is because elements of fluid taking different routes through the reactor may take different lengths of time to pass through the vessel. The time an atom spends in a reactor is called the residence time. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution E, or the Residence Time Distribution (RTD) of fluid (Richardson and Peakok, 1994). Therefore, the E curve is the distribution needed to account for the non-ideal flow (Levenspiel, 1999).

The RTD is determined experimentally by injecting an inert chemical molecule or atom called tracer, into the reactor at some time  $t = 0$  and then measuring the tracer concentration C, in the effluent stream as a function of time. The tracer usually possesses physical properties similar to those of the reacting mixture, so that its behavior will reflect that of the material flowing through the reactor. The tracer must not disturb the flow pattern of the system. The analysis of the output concentration with time, gives the desired information about the system and helps to determine the residence time distribution function E(t) (Meyers, 1992; Smith *et al.*, 1996; Fogler, 1997). However, in this work, the tank-in-series model is used to generate the RTD curve for the simulation.

The application of the RTD to the prediction of reactor behavior is based on the assumption that each fluid (assume constant density) behaves as a batch reactor and that the total reactor conversion is then the average of the fluid elements, that is:

$$\left[ \begin{array}{l} \text{Mean concentration} \\ \text{of reactant in reactor} \\ \text{outlet} \end{array} \right] = \sum \left[ \begin{array}{l} \text{concentration of reactant} \\ \text{remaining in fluid element} \\ \text{of age between } t \text{ and } t + dt \end{array} \right] \left[ \begin{array}{l} \text{fraction of exit stream that} \\ \text{consists of fluid elements of age} \\ \text{between } t \text{ and } t + dt \end{array} \right]$$

The RTD function given by the tank-in-series model is as follows:

$$E(t) = \frac{1}{\bar{t}} \left( \frac{t}{\bar{t}} \right)^{N-1} \frac{N^N}{(N-1)!} e^{-\frac{tN}{\bar{t}}} \quad (14)$$

where;

$\bar{t}$  = mean residence time =  $\tau$

t = time

N = number of tanks

Introducing (8), (12) and (14) into (13), we obtain:

$$\bar{C}_A = \int_0^\infty \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau C_{A0}} \frac{1}{\bar{t}} \left( \frac{t}{\bar{t}} \right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} dt \quad (15)$$

$$\bar{X}_A = \int_0^\infty \frac{C_{A0}k\tau}{1 + C_{A0}k\tau} \frac{1}{\bar{t}} \left( \frac{t}{\bar{t}} \right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} dt \quad (16)$$

Equations (15) and (16) therefore, are the performance equations for the non ideal mixed and plug flow regenerator respectively, with A equal to C, coke-on-catalyst.

**Regenerator kinetics:** The reactions taking place in the regenerator are coke combustion reactions. This coke is the byproduct of the cracking reactions taking place in the riser and gets deposited on the catalyst surface in the course of cracking. The intrinsic carbon combustion on the surface of the catalyst corresponds to a couple of reactions producing CO and CO<sub>2</sub> with second order kinetics (Bollas *et al.*, 2005). The oxidation of CO takes place by two ways with different first order rate constants, one is homogeneous oxidation in the gas phase and the other is catalytic oxidation (Krishna and Parkin, 1985; Arbel *et al.*, 1995). The overall rate expression for the CO oxidation can be obtained by adding the rates of homogeneous and heterogeneous oxidation reactions.

The following combustion reactions are considered to be taking place in the regenerator where the summation is over all fluid elements in the reactor exit stream which can be written analytically as:

Table 1: Industrial data for the regenerator reported by Ali *et al.* (1997)

Regenerator diameter (m)	5.8
Regenerator height (m)	11
Catalyst flow rate (kg/s)	144
Coke on spent catalyst (kg coke/kg catalyst)	0.0081
Regenerator temperature (K)	960
Regenerator volume (m <sup>3</sup> )	290.66
Density of coke (kg/m <sup>3</sup> )	2267
Density of CO (g) (kg/m <sup>3</sup> )	4.355

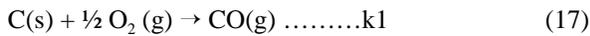
Table 3: Calculated parameters

Coke-on-catalyst (kg/h), (m <sup>3</sup> /h)	4197.6, 1.8516
Mean residence time, τ, (h)	156.98
Initial coke concentration, C <sub>AO</sub> , (kmol/m <sup>3</sup> )	1.203
Coke combustion rate constant, k <sub>c</sub> (1/atm.h)	1098
CO Combustion rate constant, k <sub>co</sub> (1/atm.h)	150.12

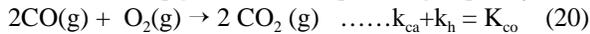
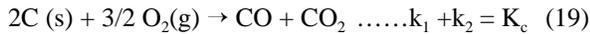
where  $k_1 = (\beta_c k_c / \beta_c + 1)$ ,  $k_2 = k_c / \beta_c + 1$   
 $K_c = k_{co} e^{-E_c/RT}$   $K_{ca} = k_{cao} e^{-E_{cao}/RT}$   $K_h = K_{ho} e^{-E_{ho}/RT}$

$$\overline{C_A} = \int_0^{\infty} C_A(t) E(t) dt \text{ or } \overline{X_A} = \int_0^{\infty} (X_A)_{element} \cdot E dt$$

in conversion terms (13)



Combining Eq. (1) and (2) gives:



The initial ratio of CO/CO<sub>2</sub> at the catalyst surface given by Weisz (1966) is:

$$\left( \frac{CO}{CO_2} \right)_{surface} = k_1 / k_2 = \beta c = \beta_{c0} e^{-E \beta / RT} \quad (21)$$

where

$k_1$  = Coke combustion rate constant to form CO [1/(atm s)]

$k_2$  = Coke combustion rate constant to form CO<sub>2</sub> [1/(atm s)]

$\beta_c$  = CO/CO<sub>2</sub> ratio at the catalyst surface in the regenerator

$\beta_{c0}$  = Pre-exponent constant in  $\beta_c$  expression

$E_\beta$  = Energy of activation

$R$  = Gas constant [kJ/(kmol K)]

$T$  = Temperature (K)

If  $K_c$  is the overall coke combustion rate, then:

$$K_c = k_1 + k_2$$

**Regenerator simulation:** The regenerator is simulated using the plant data given in Table 1 reported by Ali *et al.* (1997). The values of other parameters used in the simulation are listed in Table 2. Table 3 also presents parameters which were calculated with data from Table 1 and 2 and also used for the simulation.

Using Eqs. (15) and (16), an Excel Spreadsheet was developed which gives the overall coke-on-catalyst conversion. The regenerator was modeled as a mixed reactor and as a plug flow reactor assuming various regenerators operating conditions, such as number of tanks, dead volume and flow rate.

In a mixed flow regenerator, the influence of the presence of dead volume (Vd) on the overall conversion was investigated keeping the volumetric flow rate of coke constant. The dead volumes assumed to exist in the regenerator are 40.66, 90.66 and 140.66 m<sup>3</sup> and their corresponding calculated mean residence times are 135.02 h, 108.01 h and 81.01 h. The effect of flow rate on conversion was also investigated. Coke-on-catalyst flow rates of 1.5, 0.5, and 0.1 m<sup>3</sup>/h and their corresponding mean residence times of 193.77, 581.32 and 2906.6 h were used for the simulation. The results of the simulation are shown in Fig. 4-8.

## RESULTS AND DISCUSSION

For the regenerator modeled as a mixed flow reactor, the maximum overall coke-on-catalyst conversion of 88.85% was obtained for  $n = 1$ , which represents perfect mixing condition of continuously stirred tank as shown by the E-curves (Fig. 5) generated by the simulation. This conversion is the same as what was obtained when the performance equation of a continuously mixed reactor (without the RTD function) was used. As the number

Table 2: Parameters used for the simulation of regenerator

MW coke, Molecular weight of coke (kg/kmol)	12.0 (Arbel <i>et al.</i> , 1995)
$\beta_{c0}$ , Pre-exponent constant in $\beta_c$ expression	$9.53 \times 10^{-4}$ (Arbel <i>et al.</i> , 1995)
$k_{c0}$ , Pre-exponent constant in $k_c$ , [1/(atm s)]	$1.069 \times 10^3$ (Arbel <i>et al.</i> , 1995)
$K_{cao}$ , Pre-exponent constant in $k_{ca}$ [kmol CO/(kg catalyst atm <sup>2</sup> s)]	116.68 (Arbel <i>et al.</i> , 1995)
$E_c$ , Activation energy for coke combustion [E/R, °K]	18889 (Arbel <i>et al.</i> , 1995)
$E_h$ , Activation energy for homogeneous CO combustion [E/R, °K]	35556 (Arbel <i>et al.</i> , 1995)
$E_{ca}$ , Activation energy for catalytic CO combustion [E/R, K]	13889 (Arbel <i>et al.</i> , 1995)
$K_{ho}$ , Pre-exponent constant in $k_{sh}$ [kmol CO, (m <sup>3</sup> atm <sup>2</sup> s)]	$5.064 \times 10^{14}$ (Arbel <i>et al.</i> , 1995)
Density of coke (kg/m <sup>3</sup> )	2267

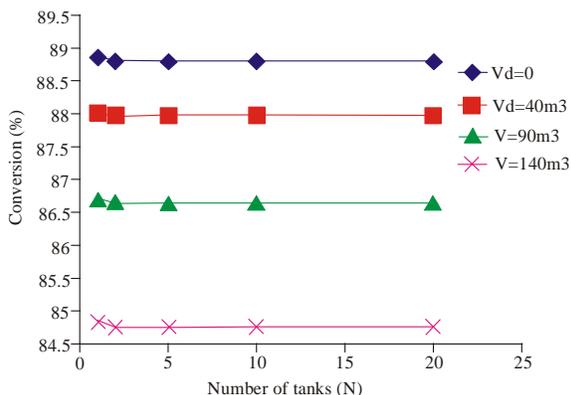


Fig. 4: Effect of dead volume (Vd) on coke-on-catalyst conversion in mixed flow regenerator

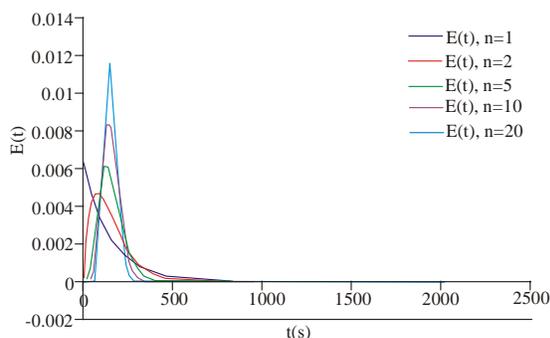


Fig. 5: E(t) functions for different degrees of non-ideality in a mixed fcc regenerator

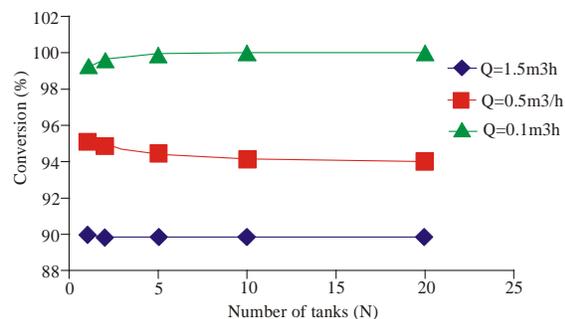


Fig. 6: Effect of coke-on-catalyst flow on conversion in mixed regenerator

of tanks (n) increased, conversion of coke-on-catalyst decreased as seen in Fig. 4. Increasing n implies more mixing zones indicating more non-ideality and malfunction resulting in poor conversion. It is also evident from the above figures that beyond n = 2, there was no change in the model prediction.

Simulation results also revealed that for a given n, conversion decreased with increasing dead volume. The dead volume normally is considered a blocked zone which

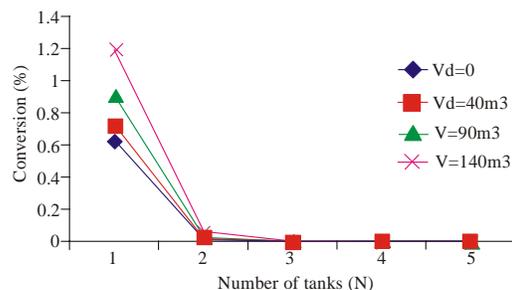


Fig. 7: Effect of dead volume (Vd) on coke-on-catalyst conversion in a plug flow regenerator

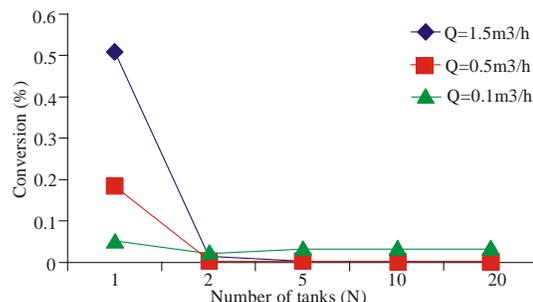


Fig. 8: Effect of coke-on-catalyst flow rate on coke conversion in plug flow regenerator

does not take part in the reaction. It could be caused by scaling, solidified material or other barrier or poor equipment design. The long tails of the E-curves depicts the slow exchange of flow between the active and the dead volume (IAEA, 2008). Thus the presence of dead volume reduces effective volume of reactants for reaction, thereby decreasing conversion.

Conversion decreased with increasing n for coke-on-catalyst flow rates 1.5 and 0.5 m<sup>3</sup>/h. For a flow rate of 1.5 m<sup>3</sup>/h, the model prediction of conversion did not change beyond n = 5. However, at a flow rate of 0.1 m<sup>3</sup>/h, it was observed that conversion increased with increasing n. Generally, however, conversion increased with decreasing coke flow rate as shown by Fig. 6. A conversion of 99.99% was obtained for a flow rate of 0.1 m<sup>3</sup>/h for n = 10 in the mixed flow regenerator. A small flow rate implies a large residence time. When the residence time is large, there is a higher chance for mixing to occur in the reactor since on average reactants are spending more time in the reactor, thus increasing the chance of conversion, holding all other parameters constant (Ingham *et al.*, 2000). For a plug flow regenerator, conversion was found to increase with increasing dead volume for a given n and decrease with increasing n for a given dead volume. Beyond n = 5, conversion did not change (Fig. 7). It was also observed that conversion decreased with decreasing flow rate for a given n and for

a given flow rate conversion decreases with increasing  $n$  (Fig. 8). Since the ideal plug flow reactor has no provision for mixing or dispersion, there is no easy interaction between the reactants and hence the generally poor conversion in the plug flow regenerator.

### CONCLUSION

The simulation of conversion of coke-on-catalyst in a mixed flow and plug flow regenerator suggests that it is less efficient as plug flow reactor. This may be due to several factors such as channeling or bypassing of the fluid in the reactor. If the reactor had been designed using the usual plug flow model, the actual performance in the plant would be far less than expected. For a higher conversion in the reactor, some modifications would be required to remedy the non-ideal flow.

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