

A MATHEMATICAL MODELING OF THE RISER REACTOR IN INDUSTRIAL FCC UNIT

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Abstract

In recent years, environmental regulations caused that the FCC units have found very important roles in oil refineries for improve the quality of oil products. Thus, availability of a modeling program for FCC is a major importance in unit optimization and scale-up or reducing the problems of a FCC unit. In this article a one-dimensional adiabatic model for riser reactor of FCC unit, was developed. The hydrodynamic model was described based on Patience et al. (1992) correlation. The chemical reactions were characterized by a four- lump kinetic model, (Han and Chung, 2001), (Juarez et al., 1997) and the optimization techniques applied to modify the kinetic parameters. Comparison of model prediction data with industrial ones shows that the model has been achieved adequately.

Simulation studies are performed to investigate the effect of changing process variables, such input catalyst temperature and catalyst to oil ratio (COR).

Key Words: FCC; Riser Reactor; Modeling; Hydrodynamic Model; Lump Kinetic Model

1. Introduction

Because the simple distillation of crude oil, production amounts and types of products that are not consistent with those required by the market place, subsequent refinery process change the product mix by altering the molecular structure of the hydrocarbons. One of the ways of accomplishing this change is through “ cracking” a process that breaks or cracks the heavier higher boiling- point petroleum fractions into more valuable products such gasoline, fuel oil and gas oils. The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking.

Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products. Use of a catalyst in the cracking reaction increases the yield of improved – quality products under much less severe operating conditions than in thermal cracking. Typical temperatures are from 480°C – 540°C at much lower pressure of 1-3 atm.

The three types of catalytic cracking process are moving – bed catalytic cracking, thermoform catalytic cracking (TCC) and fluid catalytic cracking (FCC).

The fluid catalytic cracking (FCC) unit consists of a reaction section and a fractionating section that operate together as an integrated processing unit. The reaction section includes two reactors, the riser reactor, where almost all the endothermic cracking reactions and coke deposition on the catalyst occur, and the regenerator reactor, where air is used to burn off the accumulated coke. The regeneration process provides, in addition to reactivating the catalyst powders, the heat required by the endothermic cracking reactions.

In the FCC unit process, the catalyst enters the riser as a dense bed, it is accelerated by the dispersion steam and the gas oil feed fraction that vaporizes, and it is pneumatically conveyed upwards by the vaporizes gas oil feed. During conveying, the catalytic cracking of gas oil feed is completed through efficient catalyst and gas contact.

The riser reactor is probably the most important equipment in a FCC plant. All cracking reactions and fuel formation occur in this reactor so a mathematical model can be a valuable tool to design modifications or operational changes that give higher yields from the process.

With presence of the high efficiency feed injection system in modern FCC units cause all cracking in the riser occur during the short time (about 2-5 sec). Therefore based on this fact, it is explainable that many of the models found in the literature [1,3,4,10], describe the riser reactor, with one- dimensional mass, energy and chemical species balances, so in the present work, a one – dimensional, adiabatic model for the FCC unit riser has been developed that combines with predicative riser hydrodynamic model and with a four –lump kinetic model. The increase in the gas velocity due to cracking and its effect on the axial profiles of the suspension density and hence conversion and yield is accounted for. The model has been validated by comparison with industrial FCC unit riser conversion and yield data available from literature.

2. Mathematical Modeling

2.1 Reactor model

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

- One- dimensional transported plug flow reactor prevails in the riser without radial and axial dispersion,
- the riser wall is adiabatic,
- feed viscosity and heat capacities of all components are constant,
- dispersion and adsorption in side the catalyst particles are negligible,
- the pressure changes throughout the riser length is due to the static head of catalyst in the riser,
- the coke deposited on the catalyst does not affect the fluid flow,
- in each section of riser, the catalyst and gas have a same temperature,
- the coke has the same specific heat as the catalyst,
- the riser dynamic is fast enough to justify a quasi- steady state model,
- instantaneous vaporization occurred in entrance of riser.

Subject to these assumptions, the behavior of the system maybe described by the following set of equations:

$$\frac{d}{dZ} W_r = \frac{A_r (1-\varepsilon) \cdot \rho_{cat} \cdot r_i}{F_g} \quad \text{Eq.(1)}$$

$$F_g = F_{lg} + F_{ds} \quad \text{Eq.(2)}$$

@ Z= 0:

$$F_{cat} \cdot Cp_{cat} \cdot (T - T_{cat}) + F_{go} \cdot Cp'_{go} \cdot (T_{vap} - T_{go}) + F_{go} \cdot Cp^V_{go} \cdot (T - T_{vap}) + F_{go} \cdot \Delta H_{vap} + F_{ds} \cdot Cp_{ds} \cdot (T - T_{ds}) = 0 \quad \text{Eq.(3)}$$

@ Z= h:

$$(F_g \cdot Cp_g + F_{cat} \cdot Cp_{cat}) \cdot \frac{dT}{dZ} = \sum_{i=1}^n r_i \cdot (-\Delta H)_i (1-\varepsilon) \cdot \rho_{cat} \cdot A_r \quad \text{Eq.(4)}$$

$$-\frac{dP}{dZ} = \rho_{cat} \cdot g \cdot (1-\varepsilon) \quad \text{Eq.(5)}$$

2.2 Hydrodynamic and model of the riser reactor

The correlation of Patience et al. [15] for slip factor was used in this work. According of it, the numerical value of the slip factor, defined as the ratio of the gas interstitial velocity to the average particle velocity, will predict by following expression:

$$\psi = \frac{U_o}{\varepsilon \cdot V_p} = 1 + \frac{5.6}{Fr} + 0.47 Fr_t^{0.47} \quad \text{Eq.(6)}$$

The average particle velocity in the riser, V_p is defined by eq.7.

$$V_p = \frac{G_s}{\rho_s (1-\varepsilon)} \quad \text{Eq.(7)}$$

Combining eqs. 6 and 7 gives an expression (eq.8) for the average voidage in terms of solid mass flux, superficial gas velocity, riser diameter, and catalyst physical properties, all known quantities in industrial FCC operation.

$$\varepsilon = 1 - \frac{G_s \cdot \psi}{U_o \cdot \rho_s + \psi \cdot G_s} \quad \text{Eq.(8)}$$

2.3 FCC Reaction kinetics

The first problem for modeling of FCC units is the selection of the kinetic scheme. One approach to deal with multi-component mixtures, like typical gas oils that contains more than 10 000 different species [21]. An alternative approach to overcome the complexity of considering reacting multi-component mixtures is the formulation of lumped kinetic schemes. The literature suggests any where from 3 to 13 different lumps. In three-lump model, gas oil lump is converted into light gases plus coke lump and a gasoline lump. A subsequent study by Farag [8], considered the need to describe coke and light gases by separate lumps, creating a four- lump model (fig. 1) where gas oil is converted to gasoline lump, light gases lump and coke lump.

With more lumps, the mathematic be comes more complicated [5, 12,16], also Weekman [19] showed that for reactor design purposes, a three-lump model is sufficient, so in this paper a four - lump mechanism suggested by Juarez et al. [11], which used by Han and Chung [10] for modeling of FCC unit has been selected.

The four-lumped reaction schemes as follows:

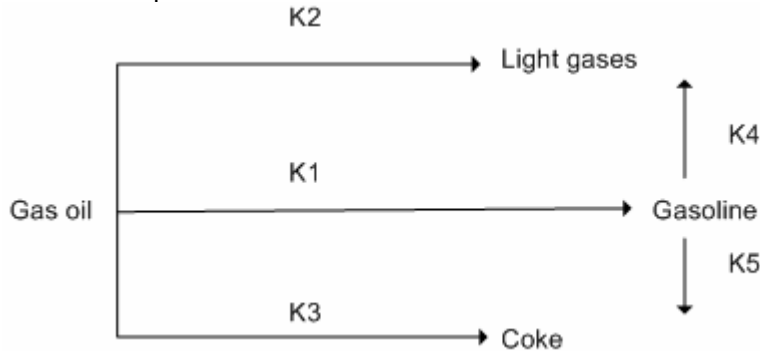


Figure 1: Schematic of four-lumped reactions

According of this scheme, a part of gasoline is also converted to light gases and coke. It is assumed that cracking of gas oil is a second- order reaction but that of gasoline is a first-order reaction, and that the reactions take place only in the gas phase.

$$\begin{aligned} r_1 &= K_1 \cdot \Phi \cdot W_{go}^2 \\ r_2 &= K_2 \cdot \Phi \cdot W_{go}^2 \\ r_3 &= K_3 \cdot \Phi \cdot W_{go}^2 \\ r_4 &= K_4 \cdot \Phi \cdot W_{gl} \\ r_5 &= K_5 \cdot \Phi \cdot W_{gl} \end{aligned} \quad \text{Eq.(9)}$$

Since the overall cracking rate is affected by the catalyst activity, its effect should be incorporated into the expressions. In the present paper, the deactivation kinetic model of the Weekman [19] is chosen, because of its simplicity and popularity in FCC modeling. In this scheme, the decay of the catalyst activity due to coke deposition is represented by a function Φ , which depends on the temperature and the catalyst residence time

$$\Phi = \exp(-\alpha \cdot t_c) \quad \text{Eq.(10)}$$

where α is the catalysts decay coefficient related to the riser temperature by an Arrhenius equation

$$\alpha = \alpha_0 \exp(-E/RT) \quad \text{Eq.(11)}$$

3. Details of calculations

3.1 Necessary data

The kinetic parameters for cracking reactions and catalyst deactivation from the literature [10,11,18] are given in tab1. The specifications of the commercial riser reactor [1] and fluid properties used in this work can be found in tabs.2, 3 and 4, respectively.

Table 1 Kinetic parameters reported from literature [10,11,18] for FCC cracking reactions

	K_o	E (kJ/mole)	ΔH (kJ/kg)
Gas oil to gasoline	1457,5	57,36	195
Gas oil to light gases	127,59	52,75	670
Gas oil to coke	1,98	31,82	745
Gasoline to light gases	256,81	65,73	530
Gasoline to coke	$6,29 \times 10^{-4}$	66,57	690
Catalyst deactivation	$8,38 \times 10^4$	117,72	-

Table 2 Riser dimensions [1]

	Length(m)	Diameter(m)
Riser Reactor	33	0.8

Table 3 Molecular weight and heat capacities used for simulation

Species	MW (kg/kmol)	C_p (kJ/kg.K)
Gas oil	333,0	2,67(Liquid), 3,3(Gas)
Gasoline	106,7	3,3
Light gases	40,0	3,3
Coke	14,4	1,087
Steam	18,0	1,9
Catalyst	N/A	1,087

Table 4 Thermodynamic properties of the feed

Gas oil vaporization temperature	698 K
Viscosity of gas	$1,4 \times 10^{-5}$ N.S/m ²
Gas oil enthalpy of vaporization	190 kJ /kg

3.2 Solution Algorithm

In this work, the first order differential equations (Eqs.1,4 and 5) must be solved by Runge-Kutta order 4, because the equations are not too stiff, so it has been developed a Matlab code for this purpose.

4. Results

4.1 Simulation results

The plant operating conditions data supplied by [1] can be found in table 5. In table 6 the this work model results with using of kinetic parameters reported from literature [10,11,19], are compared with the plant data, it is observed that the simulator cannot predict the plant data with a good accuracy. The major source of this discrepancy is attributed to kinetic parameters, because the weakness of lumping methodology for catalytic cracking reaction is that, the kinetic constants are a function of feed stock properties and the catalyst type [1,4,911].

Therefore in this article for nonlinear kinetic parameters optimization, a random search method has been applied with use of plant data for case 1, In this routine the goal function was built as the sum of squares of difference between measured and predicted weight percent yield of gasoline and coke, and also the outlet temperature of riser, These modified kinetic parameters are given in tab. 7

Table 5 Industrial riser operating conditions^[1] used in this study

	Case 1	Case 2	Case 3	Case 4
Feed rate (kg/s)	19,95	25,7	26,9	23,6
Feed Quality(API)	22,28	21,76	22,18	22,73
COR (kg/kg)	7,2	6,33	5,43	6,07
Inlet pressure (kPa)	294	294	294	294
Feed temperature (K)	494	494	494	494
Catalyst inlet temperature (K)	960	1033	1004	1006
Steam (wt%)	7	5,5	5	5,75
Steam temperature (K)	773	773	773	773

Table 6: Comparison of model results with industrial data when used the kinetic parameters from literatures (Table 5)

	Case1		
	Plant	Calc.	% dev.
Gasoline Yield (wt%)	43,88	26,79	-39
Coke Yield (wt%)	5,83	1,87	-68
Outlet Temperature (K)	795	805	+1,3

Table 7 Modified Kinetic Parameters

	K_0	E (kJ/mole)	$\Delta H(kJ/kg)$
Gas oil to gasoline	$1,15 \times 10^3$	59,66	393
Gas oil to light gases	$7,36 \times 10^1$	47,82	795
Gas oil to coke	1,79	30,95	1200
Gasoline to light gases	$4,26 \times 10^2$	68,83	1150
Gasoline to coke	$5,99 \times 10^4$	57,74	151
Catalyst deactivation	$5,91 \times 10^4$	67,21	-

Table 8 shows the predictions of model with of modified parameters (tab.7) are compared with all of exist plant data, According to this table a good agreement between the plant data and the model prediction is observed, and this show, that kinetic parameters modification has been achieved successfully.

Table 8 Comparison of this work predicted results with industrial plant data

	Case 1			Case 2		
	plant	Calc,	% dev,	plant	Calc,	% dev,
Gasoline yield, % wt,	43,88	43,86	-0,05	46,9	44,46	-5,20
Coke yield, % wt,	5,83	5,71	-0,34	5,34	4,98	-6,70
Outlet temperature, K	795	795,73	0,09	808	829,71	2,70
	Case 3			Case 4		
	plant	Calc,	% dev,	plant	Calc,	% dev,
Gasoline yield, % wt,	42,79	44,94	5,00	41,78	44,76	7,10
Coke yield, % wt,	5,43	5,35	-1,50	5,69	5,35	-6,00
Outlet temperature, K	805	798,9	-0,80	806	808,9	-0,40

This work, also investigated a typical simulation results for base case (case 3) operating condition, In figure 2 the temperature profile of reactions in the riser has been illustrated,

As it was expected, due to the nature of endothermic reaction, the temperature profile is descending, Figure 3 depicts the predicted axial profiles in the riser, The model predicts that much of

the gas oil conversion occurs in the first 5m of the riser, which is correspondence with other FCC unit riser simulation [1,2,4,5,13,14,16] and commercial data [6], There are a number of reasons for this, First, the bottom zone of the riser has a high catalysts concentration, In addition, this catalysts just have been reintroduced from the regenerator, has a higher temperature and activity than it does at higher axial location in the riser, Further more, the concentration of gas oil vapor is highest at the base of the riser in compared to that at higher axial locations, where reaction and molar expansion decrease the gas oil concentration, Thus, the reaction rate of gas oil to products is greatest at the bottom of the riser, contributing to rapid conversion,

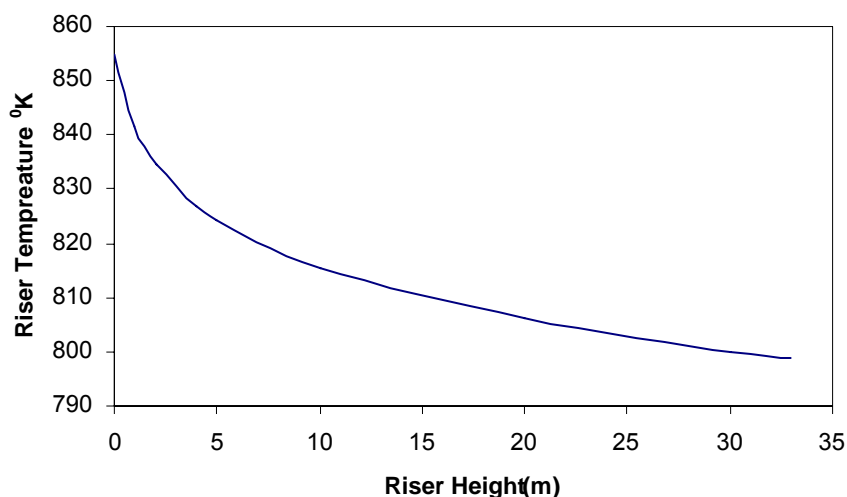


Figure 2: Temperature Profile of Riser for Base Case Operating Conditions

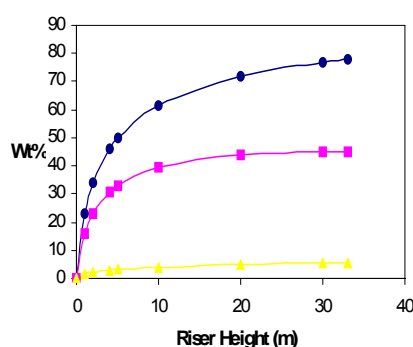


Figure 3: Conversion and Yield vs, Height of Riser for Base Case Operating Conditions

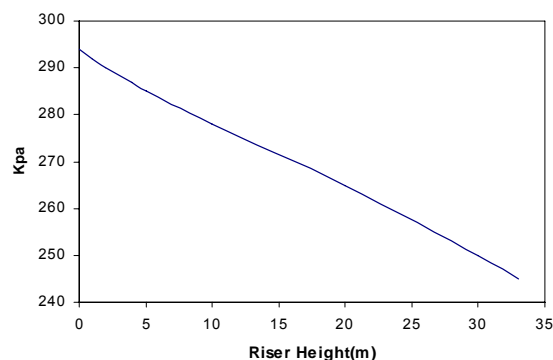


Figure 4: Pressure Profile of Riser for Base Case Operating Conditions

Figure 4 shows the axial pressure profiles, it shows an almost linear decrease of pressure along the riser with the total drop of about 50 KPa,

4. 2 Process variables

In order to investigate the effects of some process variables on FCC units, the this work model was performed, for the mentioned riser dimensions (tab. 2), at the following typical conditions:

Feed = 26,9 Kg/s API= 22,18 Feed temperature= 494°K
 P = 294 Kpa Steam = 5 wt% Steam temperature = 773°K

4. 2.1 Input catalyst temperature to riser

According of figure 5, for all catalyst to oil ratio (COR), outlet temperature increased with increasing of input catalyst temperature, so the rate of the cracking reactions will increase (Fig.6)

Figure 7 show that for all COR, the gasoline yield passed through a maximum with input catalyst temperature and with increasing of COR, the maximum shifted to lower temperature (1300 K for COR= 3, 1100 K for COR 6), The highest yield of 46% was obtained at 1300 K for COR = 3, It should

be noted that this maximum point is a function of the feed quality, catalyst type and reaction temperature [20],

With refer to fig. 8, for all COR, gas and catalyst velocities increased with increasing of input catalyst temperature, so the catalyst residence time will decrease (fig. 9), The short residence time minimizes gasoline cracking and coke yield [7] (fig. 10), resulting in better yield of the more valuable products [20], (fig. 7 & fig. 11) , This result also, can be concluded from the Voorhies [20] relationship

$$C = c t_c^n \tag{Eq.12}$$

According of above relationship, coke yield is a function of catalyst residence time, so the coke yield increased with increasing of catalyst residence time,

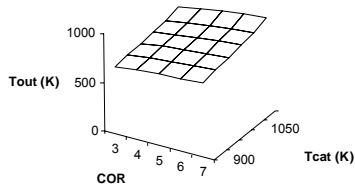


Figure 5: Dependence of Effluent Stream Temperature from Riser (T_{out}) on, Input Catalyst Temperature (T_{cat}) and Catalyst to Oil Ratio(COR)

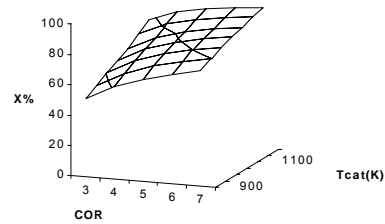


Figure 6: Dependence of Feed (gas Oil) Conversion on Input Catalyst Temperature (T_{cat}) and Catalyst to Oil Ratio (COR)

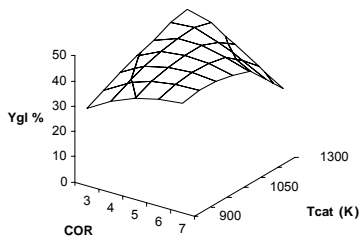


Figure 7: Dependence of Gasoline Yield on Input Catalyst Temperature (T_{cat}) and Catalyst to Oil Ratio (COR)

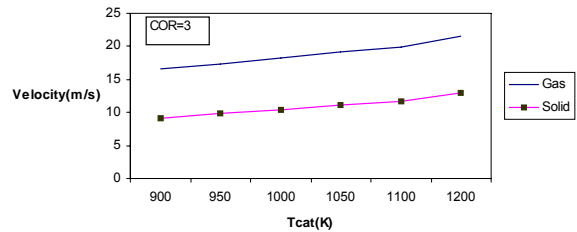


Figure 8: Riser Outlet Gas and Solid Velocities vs. Input Catalyst Temperature (T_{cat}) at constant Catalyst to Oil Ratio (COR)

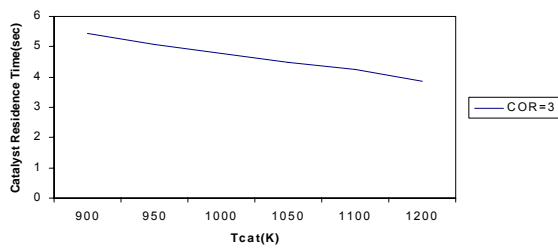


Figure 9: Catalyst Residence Time vs, Input Catalyst Temperature (T_{cat}) at constant Catalyst to Oil Ratio (COR)

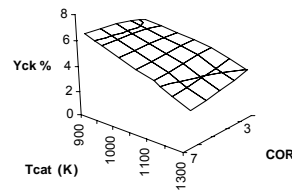


Figure 10: Dependence of Coke Yield on Input Catalyst Temperature (T_{cat}) and Catalyst to Oil Ratio (COR)

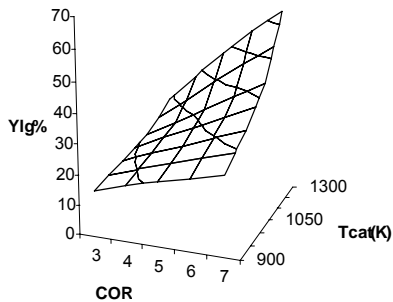


Figure 11: Dependence of Light Gas Yield on Input Catalyst Temperature (T_{cat}) and Catalyst to Oil Ratio (COR)

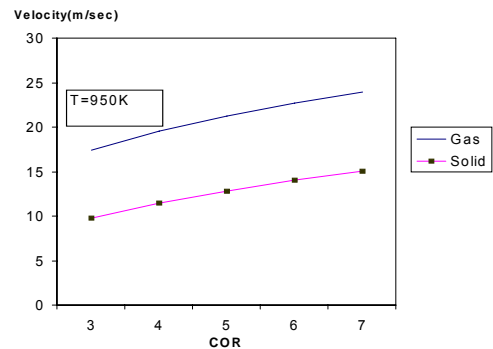


Figure 12: Riser Outlet Gas and Solid Velocities vs, Catalyst to Oil Ratio (COR) at constant Input Catalyst Temperature (T_{cat})

The motor and research octan number (MON & RON) were determined using a correlations developed from the literature ^[7] :

$$MON=72,5+0,05(T-900^0F)+0,17(X-0,55) \quad \text{Eq.(13)}$$

$$RON=1,2931MON+12,06897 \quad \text{Eq.(14)}$$

So, the RON & MON also, increased with in creasing of outlet temperature,

4.2.2 Catalyst to oil ratio (COR)

The COR is very important parameter in FCC process, hold up of catalyst ($1-\epsilon$) increased with increasing of COR, so for all investigated input catalyst temperature, the increasing of hold up can lead to higher feed conversion (fig. 6) and pressure drop, However, increasing of feed conversion caused the large molecules crack to smaller molecules, so it is reasonable to expect that the interstitial velocities of gas and catalyst will increased and catalyst residence time will decreased with increasing of COR (fig.12 & fig.13)

As a mentioned above, the decreasing of catalyst residence time, with increasing of COR, cause the coke yield to decreased (fig.10) so the yields of the more valuable products must be increased (fig.7 & fig.11)

It should be noted that, a limitation of risers is the choking limit for the COR, since there exists a maximum amount of catalysts that can be pushed upward by the gas against gravity, so for design of riser the maximum value of COR is found such that, the gas velocity in operating conditions must be higher than choke velocity,

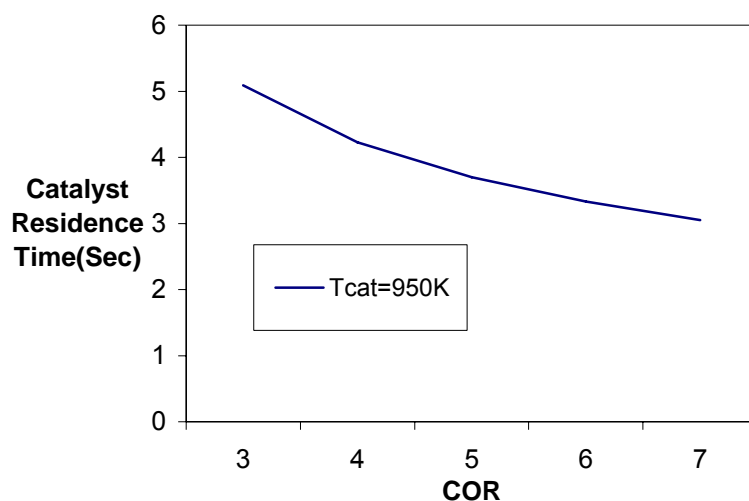


Figure 13: Catalyst Residence Time vs, Catalyst to Oil Ratio (COR) at constant Input Catalyst Temperature (T_{cat})

5. Conclusion

In this work a one- dimensional adiabatic model for FCC unit riser was developed, that combines with predictive riser hydrodynamic model and a four- lump kinetic model with modification of the kinetic parameters,

The developed model was applied to the industrial FCC unit and a good a agreement between the industrial data and simulation result are observed,

The effects of input catalyst temperature to riser and catalyst to oil ratio (COR) on products, is also studied,

The results shows that for all investigated COR, the gasoline yield passed through a maximum with input catalyst temperature; also it increased with increasing of COR, for all input catalyst temperature,

Nomenclature:

A_T : cross-sectional area of riser (m^2)
 C : coke deposited on catalyst (wt%)
 c : function of feed quality
 C_p : specific heat (kJ/kg.K)
 D : riser diameter (m)
 E : activation energy (kJ/mole)
 F : mass flow (kg/s)
 Fr : Froude number= $U_o/(gD)^{0.5}$
 Fr_t : Froude number based on terminal velocity
 g : gravitational constant; 9.8(m/s^2)
 G : solid mass flux ($kg/m^2.s$)
 ΔH : heat of reaction(kJ/Kg)
 ΔH_{vap} : gas oil enthalpy of vaporization(kJ/kg)
 K : Kinetic rate constant ($kg.s^{-1}.kgcat^{-1}$)
 K_o : pre exponential factor ($kg.s^{-1}.kgcat^{-1}.wt^{-2}$); 2nd order, ($kg.s^{-1}.kgcat^{-1}.wt^{-1}$), 1st order
 r : rate of reaction($kg.s^{-1}.kgcat^{-1}$)
 R : gas constant; 8,314e-3(kJ/mol.K)
 MW : molecular weight (kg/kmole)
 P : pressure (kPa)
 t_c : catalyst residence time (s)
 T : temperature ($^{\circ}K$)
 U_t : terminal velocity of the catalyst particle (m/s)
 U_o : riser superficial velocity (m/s)

V_p : average catalyst velocity (m/s)
 W_i : mass fraction of component I
 Z : axial position (m)
 X : gas oil mass conversion (wt%)
 Y : mass yield (wt%)

Greek symbols

α : coking constant
 ϵ : void fraction
 Ψ : slip factor
 ρ : density (kg/m^3)
 Φ : catalyst decay function (-)

Subscripts

cat: catalyst
 ck: coke
 ds: dispersion steam entering the feed injection system
 lg: light gases
 g: gas
 go: gas oil
 gl :gasoline
 s: solid

Superscripts

v: vapor
 l: liquid

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