

# On The Conversion Of Gas Oil In Fluid Catalytic Cracking Risers: Application Of Residence Time Distribution (Rtd) Concept

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**ABSTRACT:** Risers are considered vital parts on fluidized catalytic cracking (FCC) conversion units. It is inside the riser that the heavy hydrocarbon molecules are cracked into petroleum fractions such as gasoline and liquefied petroleum gas (LPG). A simplified kinetic flow model in combination with the Tank-In-Series model was used to predict the conversion response of an FCC riser to changes in feed temperature, feed flow rate as well as riser diameter and height. The various Residence Time Distribution (RTD) functions and flow-model parameters are used in the characterization of the mixing regime of the riser and the degree of any non-ideal flow behaviour. Conversion was observed to increase with increasing riser height and diameter with values of 95.16% and 94.0% at a riser height of 80 m and diameter of 1.0 respectively. Conversion also increased with increasing feed temperature. A feed flow rate of  $10 \text{ m}^3/\text{s}$  is converted at 95.95 % while a feed flow rate of  $40 \text{ m}^3/\text{s}$  is converted at 89.72%, indicating an inverse relationship between conversion and feed flow rate. The simulation also revealed that the riser reactor is equal to approximately 1–2 perfectly stirred tanks in series as conversion started to decrease after an N, the number of tanks in the Tank-In-Series model, of 1.5.

**Index Terms:** Conversion, gasoline, residence time distribution, risers, Tank-In-Series model

## 1. INTRODUCTION

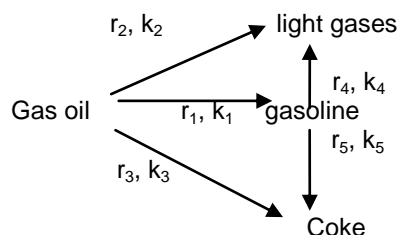
Fluid catalytic cracking (FCC) is one of the most important and complex processes in petroleum refining which is used to upgrade heavy petroleum gas oils into gasoline and other valuable products. The FCC process comprises mainly 2 parts: (1) a riser reactor where high molecular weight hydrocarbons come into contact with a catalyst and crack to lower molecular weight products with the simultaneous deposition of coke on the catalyst surface and (2) a regenerator where the coke on the catalyst is burnt with air and the catalyst is returned to the riser for the next run of cracking [1]. There have been several simulation studies focused on FCC due to its importance [2, 3, 4] with special attention on the riser reactor which is probably the most important equipment in an FCC plant. All cracking reactions and fuel formation occur in this reactor. Therefore, a mathematical model can be a valuable tool to design modifications or operational changes that give higher yields from the process. This explains why many of the models found in the literature describe the riser reactor [5, 6, 7, 8, 9]. However, most of these simulations assume idealized mixing conditions within the riser reactors.

This study, therefore, aims at developing a mathematical model which simulates non-ideal flow in a continuously stirred riser reactor (CSTR) and to demonstrate the relevance and application of the concept of residence time distribution (RTD). An appropriate mixing model in combination with the kinetics of the reactions occurring in the riser 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.

## 2. MATERIALS AND METHODS

### 2.1 Riser Design and kinetic model

The complexities of gas oil mixtures which are typical FCC feedstocks make it extremely difficult to characterize and describe the inherent kinetics at a molecular level. To allow for easy studies, similar components are grouped into few cuts or lumps [9]. The study of the reactions involved in the catalytic process has therefore followed the lumping methodology. The number of lumps of the proposed models for catalytic cracking reactions has been consecutively increasing to obtain a more detailed prediction of product distribution [10]. Since the simple models, with just a few slumps are usually more suitable for specific simulations and for reactor design purposes, the 4- lump kinetic reaction scheme will be adopted in the present study. The four-lump mechanism suggested by Juarez et al in [11] has been selected. It is shown in Fig. 1.



**Figure 1:** A Schematic diagram of the four-lump scheme

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According to this scheme, gasoil is converted into gasoline, light gases and coke. A part of the gasoline is also converted to light gases and coke. It is assumed that cracking of gas oil is a second-order reaction while that of gasoline is a first-order reaction, and that the reactions take place only in the gas phase. Based on the riser flow characteristics and dynamics which involves turbulence and mixing, the riser is considered as a CSTR. The assumption is also made that the riser 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  $\tau = V/Q$  [12]. It is also assumed the catalyst and gas have a same temperature along the riser, instantaneous vaporization occurred in entrance of riser and that there is no radial and axial dispersion in the riser. 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 [13]. According to Levenspiel, Equation (1) represents the performance equation for mixed reactors.

$$\frac{V}{v} = \tau = \frac{C_{A0}}{-r_A} = \frac{C_{A0} - C_A}{-r_A} \quad (1)$$

Therefore, for the second order reaction for the cracking of gasoil in an ideal mixed flow reactor, the performance equation is given by:

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

Where

$k$  = rate constant in the rate equation

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

$C_{A0}$  = inlet/initial concentration of A (gas oil) into reactor

$C_A$  = final or concentration of A at reactor outlet

However, real equipment always deviates from these ideals. Deviation from 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 [14]. Therefore, the  $E$  curve is the distribution needed to account for the non-ideal flow [13]. 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  $E(t)$  [15, 16]. The RTD curve can be used as a diagnostic tool for ascertaining features of flow patterns in reactors. These include the possibilities of bypassing and/or regions of stagnant fluid (i.e., dead space). Since these maldistributions can cause unpredictable conversions in reactors, they are usually detrimental to reactor operation. According to Levenspiel in [13], 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:

$$\bar{C}_A = \int_0^\infty C_A(t) E(t) dt \quad (3)$$

According to the tank in series model, the RTD is given by

$$E(t) = \frac{1}{\bar{t}} \left(\frac{t}{\bar{t}}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} \quad (4)$$

Where

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

$t$  = time

$N$  = number of tanks

Therefore, combining equations (3) and (4) results in:

$$\bar{C}_A = \int_0^\infty \frac{-1 + \sqrt{4k_\tau C_{A0}}}{2k_\tau C_{A0}} \frac{1}{\bar{t}} \left(\frac{t}{\bar{t}}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/\bar{t}} dt \quad (5)$$

Equation (5) is the performance equation for a non ideal mixed flow riser with A representing gas oil.

The following are the reactions occurring in the riser:



Where

$r_1$  = the rate of reaction of gas oil to form gasoline at rate constant  $k_1$

$r_2$  = the rate of reaction of gas oil to form light gases at rate constant  $k_2$

$r_3$  = the rate of reaction of gas oil to form coke at rate constant  $k_3$

$r_4$  = the rate of reaction of gasoline to form light gases at rate constant  $k_4$

$r_5$  = the rate of reaction of gas oil to form coke at rate constant  $k_5$

$C_{go}$  = concentration of gas oil

$C_{gl}$  = concentration of gasoline

$\phi$  = decay of catalyst activity due to coke

If  $k_{go}$  is the overall gas oil reaction rate constant, then:

$$k_{go} = k_1 + k_2 + k_3 \quad (7)$$

For the purposes of this study, only reaction rates 1, 2 and 3 were considered. The reaction rate constants were calculated by using Arrhenius type semi-empirical equation given by:

$$k_i = k_{i0} e^{-E/RT} \quad (8)$$

Where

$k_i$  = rate constant for reaction  $i$

$k_{i0}$  = pre-exponential constant/factor for rate constant  $k_i$

$E$  = activation energy

$R$  = Gas constant and

$T$  = temperature

Kinetic parameters for the FCC riser reaction and used for the simulation are provided in Table 1. Other useful riser parameters are given in the Table 2 below.

### 3. RESULTS AND DISCUSSION

#### 3.1 Riser simulation

The riser flow is simulated using the plant data given in Table 1 reported by Ali *et al.* in [8]. 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 Tables 1 and 2 and also used for the simulation. Using Eq. (5), an Excel Spreadsheet was developed for the gasoline conversion. Riser flow was simulated for various riser operating conditions such as feed rate, riser diameter and height, feed temperature and number of tanks in the one parameter Tank-In-Series model.

**Table 1:** Kinetic Parameters for cracking kinetics in riser

Reaction	$k_0$	$E$ (kJ/mol)
Gasoil to gasoline	1457.5	57.36
Gasoil to light gases	127.0	52.75
Gasoil to coke	1.98	31.82
Catalyst deactivation	$8.38 \times 10^4$	117.72

(Source: [17])

**Table 2:** Industrial Riser operating parameters

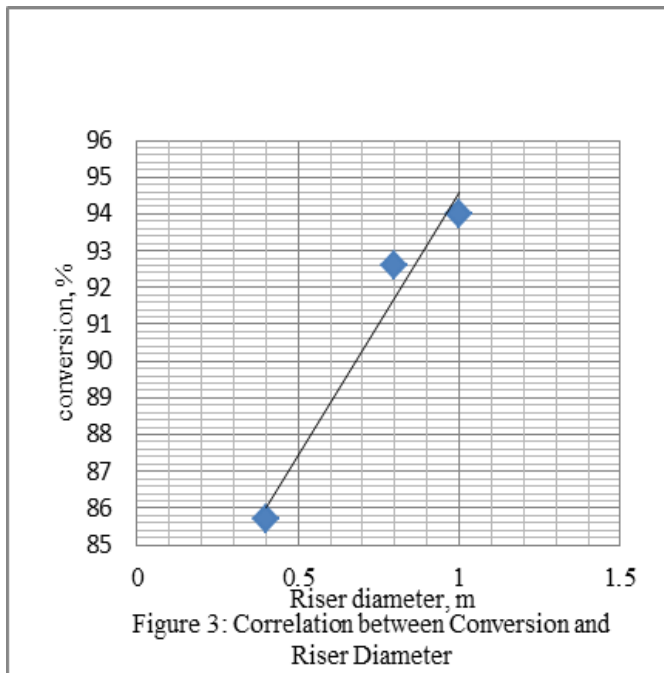
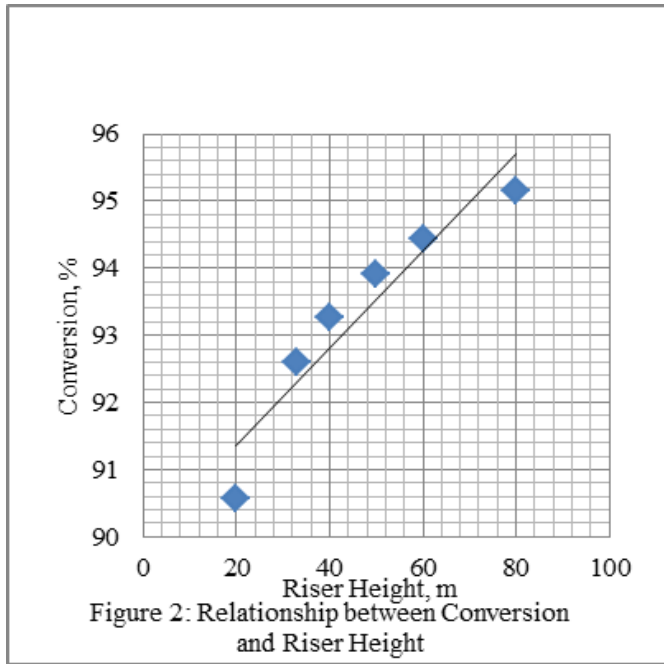
Parameter	Value
Riser diameter (m)	0.8
Riser height (m)	33
Gasoil molecular weight (kg/kmol)	333
Feed vaporization temperature (K)	698
Gas oil Feed rate (kg/s)	19.95
Gas oil density (kg/m <sup>3</sup> )	835
Gas constant (kJ/(kmol K))	8.314

(Source: [17])

**Table 3:** Calculated parameters

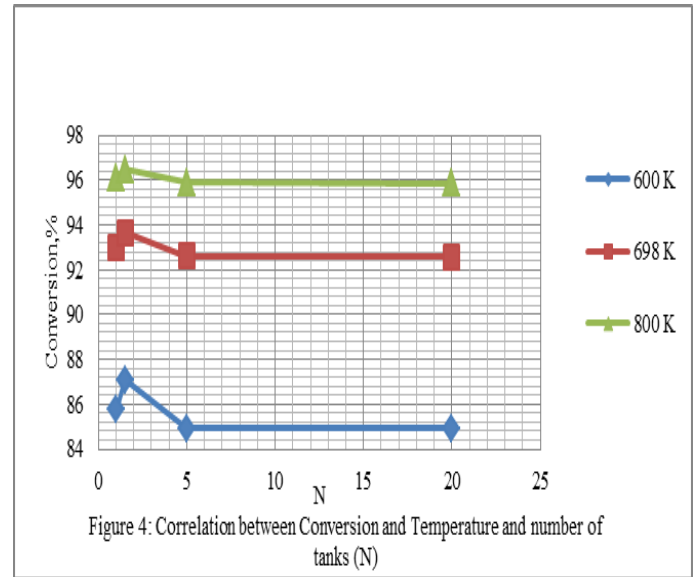
Rate constant for overall cracking of gasoil	0.0969
Gas oil volumetric flow rate, (m <sup>3</sup> /s)	0.024
Mean residence time (s)	691.24
Initial gas oil concentration, (kmol/m <sup>3</sup> )	2.508
Riser volume (m <sup>3</sup> )	16.59

In order to study the effect of changing one independent variable on the gas oil conversion, all others must be held constant. Therefore to study the effect of riser height on conversion, the flow rate was kept constant at 19.95 kg/s, as well as the feed temperature at 698 K and riser diameter at 0.8 m. Holding these parameters still constant with a riser height of 33 m, the effect of riser diameter on conversion was simulated. All other conditions being roughly equal, riser height correlates with residence time and for that matter gas oil conversion [18]. It can be observed from Figs. 2 and 3 that a positive correlation exists between conversion and riser height and with riser diameter. As riser height and diameter increase, residence time also increases and hence conversion. This suggests, therefore that the design of shorter and small diameter risers is not economical.



With a feed flow rate of 19.95 kg/s, riser diameter of 0.8 m, riser height of 33 m, the effect of feed temperature on conversion was simulated. It can be seen from Fig. 4 that gasoil conversion increased linearly with increasing feed temperature. This observation is supported by Dasila et al in [19]. Increased temperature means increased kinetic rate constant, thereby increasing rate of reaction and hence conversion because the cracking of gasoil to gasoline is endothermic. Increasing temperature can help bring gasoline conversions up as shown in Fig 4. However, the heat balance in whole FCC system and limits on operating temperature in the regenerator can limit the increase possible in operating temperature in the riser [18]. Though generally conversion is observed to decrease with increasing number of mixing tanks, there seem to be a

sharp increase in conversion from N=1 to N=1.5 after which the conversion declines.



Keeping constant the riser diameter of 0.8 m, height of 33 m and the feed temperature at 698 K, the effect of feed flow rate and number of mixing tanks (N) on conversion was investigated. It was observed that a negative correlation exists between flow rate (or the residence time) and conversion. Table 4 shows in general that a decrease in residence time will decrease conversion. This observation is corroborated by [18, 19, 20]. Generally, conversion was also found to decrease as the number of tanks increased in the model. It is interesting to note a deviation from the general trend as conversion increased sharply from N=1 to N=1.5 tanks and declines thereafter. The small value of N depicts that, the riser characteristics turns are those of a single CSTR or perhaps 2 CSTRs in series rather than a plug flow reactor [16]. As the value of N increases, plug flow is approached tanks have no mixing in the direction of flow and thus conversion is reduced [12].

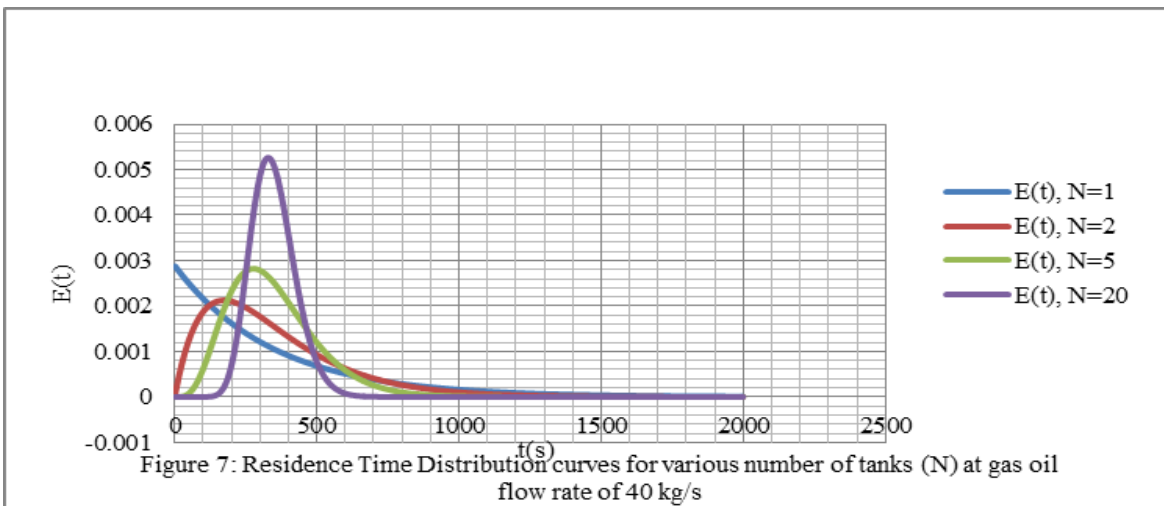
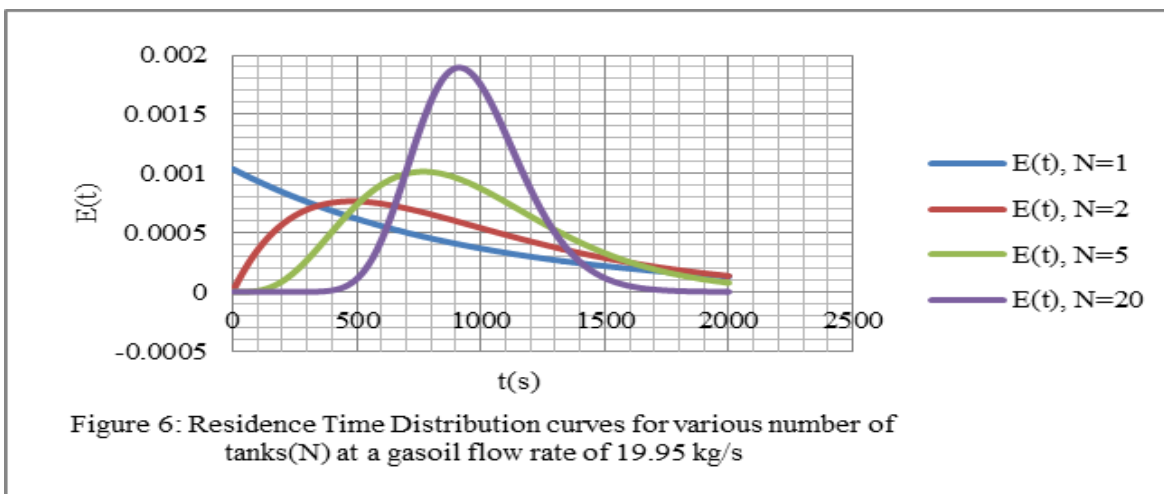
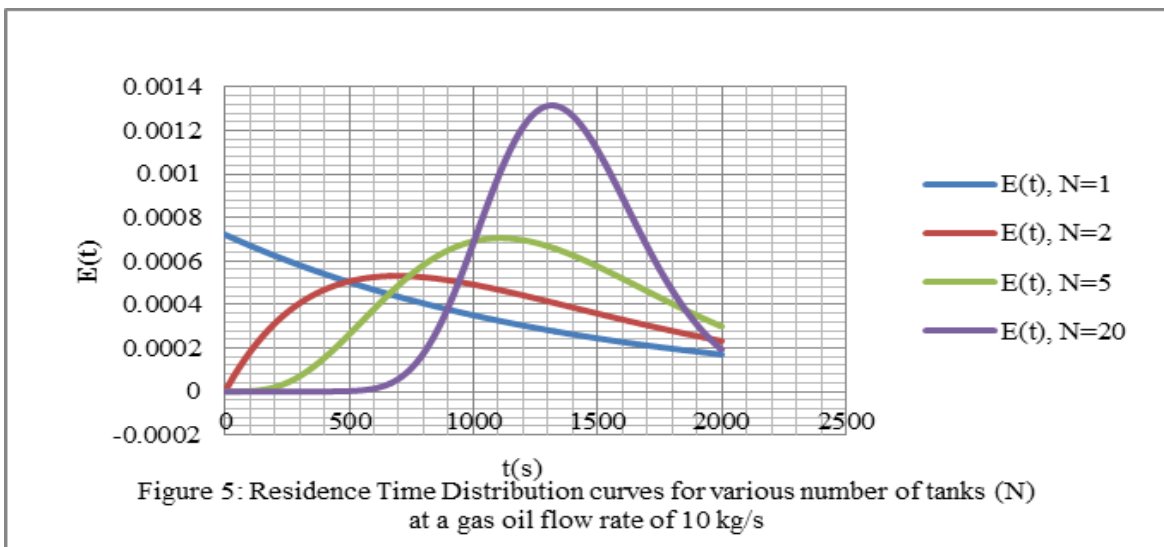
**Table 4:** Effect of feed flow rate and number of tanks (N) on conversion

N	Feed flow rate = 10kg/s (τ =1385.245s)	Feed flow rate = 19.95 kg/s (τ =691.24s)	Feed flow rate = 40 kg/s (τ = 346.311s)
1	95.95	92.99	89.72
1.5	96.37	93.64	90.86
1.6	96.06	93.57	90.78
1.9	95.93	93.04	90.07
2	95.84	92.73	89.68
5	95.51	92.59	89.68
20	94.88	92.58	89.68
100	94.70	92.58	89.68

The RTD curves for a gas oil flow rate of 40 kg/s as shown in Fig 7, exhibit long tails, an indication of the presence of dead volumes or stagnant volume with little exchange in the riser at those conditions. A short residence time of 346.3 s may mean that the reactants do not spend adequate time in

the riser for conversion to take place which also explains why the conversion is lower.

From the shapes of the curves, it can be seen that mixing is best in Fig. 5, better in Fig. 6 and poor in Fig. 7. This explains why the conversion also follows a similar pattern.



#### 4. CONCLUSION

The concept of residence time distribution curves has been used to simulate the flow in a riser reactor. Parametric studies were done on the effects of temperature, feed flow rate and FCC riser height and diameter (to vary residence time) on gasoil conversion. Results indicated that shortening the residence time and decreasing gas oil feed temperature may significantly reduce overall conversion.

#### 5. ACKNOWLEDGEMENTS

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#### 6. REFERENCES

- [1]. Moharir, A.S., Sarae, S.K., Kinetic Modeling of Vacuum Gasoil Catalytic Cracking, Chem. Age of India, **35**; 433-440, (1984).
- [2]. Landeghem, F.V., Nevicato, D., Pitault, I., Forissier, M., Turlier, P., Derouin, C. and Bernard, J.R. Fluid Catalytic Cracking: Modeling of an Industrial Riser. Applied Catalysis A: General, vol. **138**, pp.381-405, (1996)
- [3]. Theologos, K.N., and Markatos, N.C Advanced modeling of fluid catalytic cracking riser-type reactors. AIChE J, **43**,486-493, (1993).
- [4]. Derouin, C., Nevicato, D., Forissier, M., Wild, G., & Bernard, J.R. Hydrodynamics of riser units and the impact on FCC operation. Industrial and Engineering Chemistry Research, **36**, 4504–4515, (1997)
- [5]. Arandes, J. M. and H. I. Lasa. Simulation and Multiplicity of steady states in fluidized FCCUs, Chem.Eng.Sci., **47**, 2535-2540,(1992)
- [6]. Arbel, A., Z. Huang, I.H. Rinard, R. Shinnar and A.V. Sapre. Dynamics and control of fluidized catalytic crackers. Modeling of the current generation FCC.s. Ind. Eng. Chem. Res., **34**: 1228-1243, (1995)
- [7]. Han, I. S. and Chung, C. B. Dynamic modeling and simulation of a fluidized catalytic cracking process Part I: Process modeling, Chem.Eng.Sci., **56**, 1951-1971, (2001)
- [8]. Ali, H., S. Rohani and J.P. Corriou. Modeling and control of a riser type Fluid Catalytic Cracking (FCC) unit. Chem. Eng. Res. Des., **75(A4)**: 401-412. (1997).
- [9]. Coxon, P.G., and Bischoff, K.B., Lumping Strategy. Introduction To Techniques and Application of Cluster Analysis, Ind. Eng. Chem. Res., **26**, 1239-1248, (1987).
- [10]. Bollas,G.M., Lappas, A.A., Iatridis, D.K. and Vasalos,I.A. Five-Lump Kinetic Model with Selective Catalyst Deactivation for the Prediction of the Cracking Process, Catalysis Today, Vol. **127**, No. 1 , pp. 31-43,(2007).
- [11]. Juarez, J. A., Isunza, F. L., Rodriguez, E. A. and Mayotga, J. C. M.; A strategy for Kinetics Parameter Estimation in the Fluid Catalytic Cracking Process, Ind.Eng.Chem. Res., **36**, 5170-5174, (1997)
- [12]. International Atomic Energy Agency (IAEA). Radiotracer Residence Time Distribution method for industrial and environmental applications, IAEA-TCS-31(2008), Vienna.
- [13]. Levenspiel, O., 1999. Chemical Reaction Engineering. 3rd Edn., John Wiley & Sons, Inc., 605 Third Avenue, New York.
- [14]. Richardson, J.F. and D.G. Peacock, Coulson and Richardson's Chemical Engineering, 3rd Edn., Pergamon, Great Britain, **3**: 71-80, 102-103. (1994).
- [15]. Smith, J.M., H.C. Van Ness and M. M. Abbott, (1996). Introduction to Chemical Engineering Thermodynamics, 5<sup>th</sup> Edn., pp: 64-5, 189-91, 604-8, 831-37, McGraw-Hill, Singapore.
- [16]. Fogler, H.S., Elements of Chemical Engineering Reaction. 2nd Edn., Prentice-Hall of India Private Ltd., New Delhi, pp: 708-723, 759-765, (1997).
- [17]. Ahari, J.S, Farshi, A. and Forsat, K. A. Mathematical Modeling of the Riser Reactor in Industrial FCC Unit. Petroleum & Coal, **50 (2)**, 15-24. (2008).
- [18]. Chang, S.L., Lottes, S.A., Zhou, C.Q. and Petrick. M A numerical study of short residence time FCCriser flows with a new flow/kinetics modeling, submitted to International Mechanical Engineering Congress and Exposition, Nov. 15-20, (1998), Anaheim, CA
- [19]. Dasila, P.K., Choudhury, I., Saraf, D., Chopra, S., Dalai., A Parametric Sensitivity Studies in a Commercial FCC Unit. Advances in Chemical Engineering and Science, **2**, 136-149, (2012).
- [20]. Dagde, K.K., and Puyate, Y. T. Six-lump kinetic modeling of adiabatic plug-flow riser-reactor in an industrial FCC unit. International Journal of Engineering Research and Applications. Vol. **2**, Issue 6 , pp.557-568, 557, 2012