



A Review on Lumped-Kinetic Modelling Methodologies for an industrial FCCU - riser reactor for catalytic cracking

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Abstract

A comprehensive review of scientific literature on various lumped kinetic models used in modelling Fluidised Catalytic Cracking Units (FCCU) used in the petrochemical industry has been done, along with a brief introduction to the working of FCCU. The most popular four lumped kinetic model has been discussed in detail along with the mathematical model and then solved using MATLAB. The modified form of the model that considers axial dispersion has also been discussed. The results of the simulation have been plotted and analysed. A brief overview of three, five, six, seven, nine, and twelve lumped kinetic models has also been discussed.

Keywords: Catalytic Cracking, Lumped Kinetics, Riser Reactor, Catalyst Regeneration, Fluidised Bed.

1. Fluidized Catalytic Cracking Unit - Introduction

The wide-ranging challenges in the petroleum refining industry are dynamic and are undergoing paradigm shifts. Energy sustainability is at a disastrous stake and detrimental to the energy security of humanity and future generations¹ along with the looming threat of climate change. Advancements in science and technology, human progress and the plethora of challenges the world has to deal with are the primordial issues of today's achievement in science². The exponential rise in energy demand and the need for energy security ushered in the improvement of refinery operations and led to transformative changes in its infrastructure and its dynamics³. The oil and gas markets and industries are expected to face stiff challenges and humongous pressure to accomplish the

market demand for high-quality fuels and keeping the supply chains resilient⁴.

The fluidized bed catalytic cracking (FCC) is a crucial conversion step across the world in the refinery operations⁵ and the Fluidized Catalytic Cracking Unit (FCCU) forms the primary conversion unit in the refineries. The FCC essentially is a secondary type of refining process⁶ used primarily for conversion of high molecular mass as well less volatile fractions with a higher boiling point to higher value-added products with higher volatility, lower molecular mass fractions such as petrol, liquefied petroleum gas (LPG), volatile alkanes in gaseous form, diesel, and some other products⁷, and is known to be one of the most extensive

heterogeneous catalytic operation in the wide diaspora of catalytic processes in the chemical industry⁸. FCCU is often called the “cash cow” of all refining operations⁹. What makes the FCC process unique is the robustness of the process which can that can catalytically convert feeds of different material origins and chemical compositions¹⁰ like vacuum oils, residual oils, crude oil, scrap tires, pyrolysis oil, LDPE waste, Biomass-based oils, natural terpenes in the form of oils into value-added automobile and transportation fuels and light olefins needed for the pharmaceutical and petrochemical industry¹¹ and thus form the basis of novel and innovative petrochemical technologies. It makes for one of the highest volumes of gasoline pool in the world and usually consists of 1/3 rd of the entire distillation capacity in chemical industry operations¹⁰. The estimates for a country like China for it accounts about 80% of gasoline production, and FCC is utilized in about 27% of petroleum processing¹². In the United States for example one-third of the gasoline pool comes from the FCC process⁷. About a quarter of FCC naphtha and about 45-50 % of reformer gasoline are the estimated figures for the EU countries like Germany, Italy and France as well as UK^{13 14}. As of 2006, in about 400 petroleum refineries worldwide FCC units are in operation for production of products like gasoline¹⁵. The production of the catalyst used in FCC account whopping ~2300 MT per day and is thus estimated to be around ~840 000 MT per year as per the data of 2015¹⁶. In 2018, the global demand for refining catalysts was 831 KiloTonnes per annum and is expected to register a growth of 1.1% through 2040. The global market is estimated to be at 2.9 billion USD, with a whopping largest market share (35%) being for FCC of zeolite-based catalysts¹⁷.

Although FCC is a mature and old process¹⁸ and has been in operation for over 60 years in commercial industrial use, it is dynamically evolving to cater to a wide range of new products, shift towards a propylene-oriented production from gasoline-based¹⁹, concerns on climate change and various issues associated with the catalyst. Light hydrocarbons²⁰ and olefins are one of the key products of FCCUs²¹. Around 34% of propylene production across the globe was from FCC unit as per the statistics of the year 2000^{22 23}. The FCCU accounts for approximately 20-30% of net CO₂ emissions from a refinery²⁴. The FCCU is unique in

refinery because of its unique features like catalyst replacement in a continuous fashion which can adjust, operate and regenerate without shutdowns, the robustness of the process, and wide range of applicability²⁵. Zeolite-based catalysts²⁶ in which zeolite component is dispersed in a silica-alumina support matrix²⁷ are popular in the fluidized catalytic cracking process¹⁶.

²⁸Generally, the FCC unit consists of a main Reactor unit and a Regenerator unit where the spent catalyst is regenerated. The FCC is available in two configurations namely Side by Side and Stacked. In the riser which is a long tube, intimate contact between the red-hot catalyst from the regenerator unit and the oil feed (generally Vacuum Gas Oil or VGO) occurs. The catalyst at a very high temperature is then allowed to rise through a lift media in the riser upwards which generally consists of steam or light olefinic gases. The riser part of the reactor is the battleground where all the endothermic catalytic cracking reactions and deactivation due to coke deposits on the catalyst occur²⁹, and the regenerator reactor, where heated air causes combustion of the accumulated deposits of coke on the catalyst³⁰. In this process, flue gases are released and the deactivated catalyst is regenerated. The tacit monitoring and subsequent control and regulation of flow rate of the catalyst in its spent or regenerated form maintains the enthalpy balance of the FCC unit³¹. This combustion reaction being exothermic heats up the catalyst and thus hot catalyst particles enter the riser. The regeneration process provides the necessary heat input required by the endothermic cracking react and thus reactivates the catalyst powders as the catalyst flows back into the reactor which operates in a fluidized bed configuration with a low residence time. The temperature of oil feed varies from 500 to 800°F (260 to 425°C). In a typical riser reactor average temperatures lie generally between 480 and 566°C, The temperature of catalyst at regenerator exit is about 650 to 815°C³².

A riser reactor typically is divided into 4 different zones, the prelift zone, the full reaction zone, the feed injection zone and the quenching zone³³. In the feed injection system of an FCC riser reactor, the liquid droplets in the oil feed enter the riser through multiple feed atomizing nozzles at a particular angle for an intimate catalyst oil contact²⁹. The hot catalyst and atomized feed oil then meet in the prelift zone and are

lifted by the action of riser media like steam. Then, the feed oil after getting contacted with the hot regenerated catalyst particles from the regenerator and get converted into vapours. The vapor formed cracks into lighter valuable like gasoline diesel and other light olefins³⁴ and traverses upward taking the catalyst particles along with it in the riser³³. This is called the full reaction zone. Because of vaporization and cracking, the vapor expands on heating which increases the volumetric flow rate, thus increasing the velocities of both vapor and catalyst along the riser. The higher catalyst speed due to this expansion leads to a decrease in the volume fraction of catalyst and hence lowers the catalyst-to oil (CTO) ratio locally. The hydrodynamics and phase contacting plays a crucial role in the yield and efficiency of the reactions.

The riser then is connected to the cyclone separation unit at the top in the ultimate zone called as the quenching zone. The cyclone units receive input as the catalyst in deactivated form the and products³⁵. The catalyst that enters the cyclone unit is fully deposited with the coke and is thus in deactivated state and needs to be sent to a regenerator for reactivation it so that it can be reused. The cyclone separation operation separates the hydrocarbon vapours and catalyst as a solid-fluid operation due to density difference and centrifugal action. The deactivated catalyst is separated from the hydrocarbon stream and thus exists through cyclones at the riser exit. After the coke burning³¹ in a regenerator operating at high temperatures, the catalyst is fed back to the riser to complete the loop of the circuit³⁶. The temperature control of the regenerator and coke burn-off temperature are controlled by intricate variation of the hot air flow rate. The enthalpy of combustion increases the temperature of the catalyst particles to 1150 to 1550°F (620 to 845°C), and a large fraction of this enthalpy of combustion is taken up by the oil feed in the feed riser to supply the cracking reactions which are endothermic in nature. 0.01 to 0.4 wt.% residual coke content is present in the regenerated catalyst, which practically depends upon the type of combustion complete or incomplete (burning to CO or CO₂) in the regenerator³². The olefinic hydrocarbon containing vapor is then sent to a distillation column for fractionation into selected desired products such as LPG, petrol, diesel, kerosene and other useful fractions.

The catalyst falls into the vessel due to action of

gravitational forces that contains the riser and cyclone units. The catalyst present in the vessel undergoes stream stripping in which direct intimate contact with high pressure steam is allowed to strip off the hydrocarbons from the surface. This is the overall working and process flow of the FCCU. Below figure shows a schematic diagram of a typical ‘side by side’ configuration FCCU.

There have been over the past years many attempts to address the new challenges in design and solve the major problems associated with the FCCU. The atomizing nozzle structure improvement attempts to develop alternate catalysts³⁷, improving the efficiency of riser and regenerator, preventing the erosion of cyclone separators, controlling the emissions (especially NO_x)⁷, reduction of quality of FCC feedstock, need of several hydrotreating technologies³⁸ to ensure good yield and efficiency etc.

To address these challenges, we require a combination of experimental and simulation-based analysis, and thus modelling of FCC is a very important step. The riser reactor is the most important piece of equipment and is the heart of the FCCU³⁹. The complexities associated with the endothermic catalytic cracking reactions occurring in the riser, coupled with resistances to heat and mass transfer as well as the kinetics associated with the deactivation of catalyst make the modelling elaborate, complex and cumbersome⁴⁰.

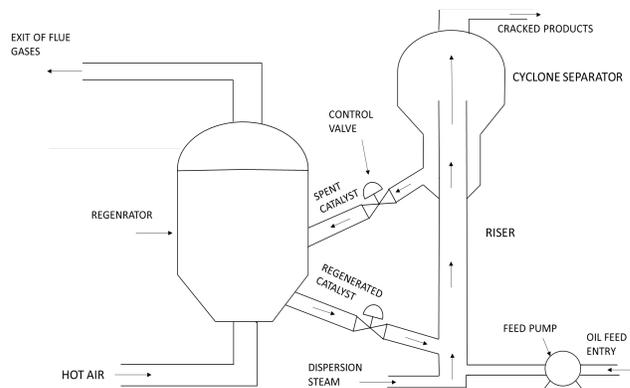


Fig 1. Fluidized Catalytic Cracking Unit Schematic

The main objective of the paper is to explore and review the various “lumped models” that are used to model these reactors and simplify the complex kinetic reactions involved in them. A brief flowchart of the chemistry of catalytic cracking is given below.

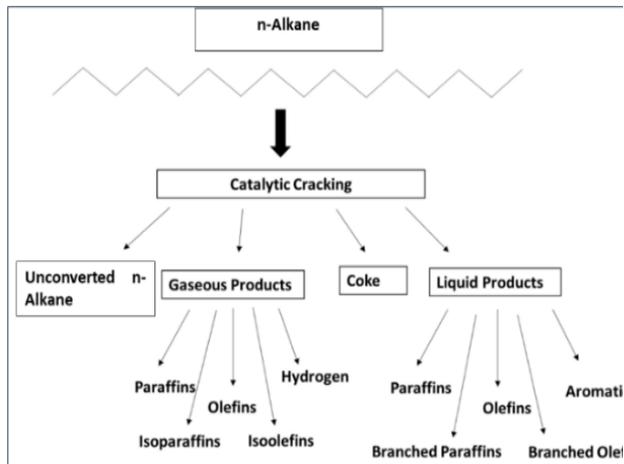


Fig 2. Chemistry of Cracking Reactions

2. Why do we need lumped kinetic models?

The most reliable method to determine the kinetic parameters is the experimental one, where the meticulous patience and the sangfroid determination of the researcher gives fruit when the data obtained starts to make sense. But doing experiments is not always that easy, when the participating species are highly reactive in nature and they need to be monitored as a function of time. For gas phase reactions theoretical methods do not always give accurate results⁴¹. Lumped models help us overcome these shortcomings. In a lumped model we divide the reactions into smaller schemes that involve only the molecular species. For an optimum lumped model we need to monitor all the species with respect to time.

In many cases the hydrocarbon mixture and the definition kinetic mechanism influences the complexity of the interacting systems. This is the case with pyrolysis⁴². Using the lumped models high dimensional models can be reduced into lower dimension smaller models. Lots of examples of such simplification can be found in a quintessential review⁴². With the advances in the computational power and as the knowledge in chemical engineering increases, models that are even more efficient than the lumped models would surely be seen in the literature to be published.

3. Preliminary discussion on Lumped-Kinetics:

The premise of lumped kinetic models is to group chemical compounds of similar properties as called ‘lumps’⁴³. The use of any kinetic model is one of the four major operations of any CFD simulation. The

other three are mass, energy, and momentum balance. This can be visualized by the flow chart given below.

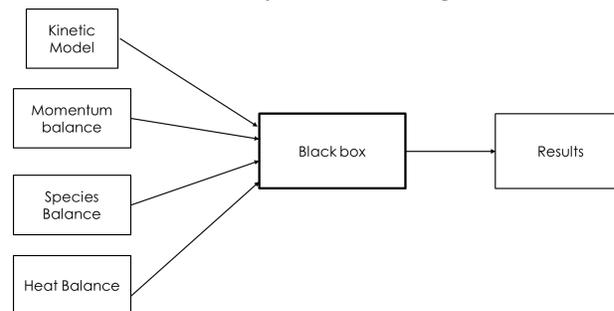


Fig 3. Scheme for CFD-based problems

The lumps are then considered as distinct entities and a kinetic model is applied. The specific process of developing lumped kinetic models is given by⁴³ in three distinct steps.

1. Description of the feedstock by choosing a set of lumps;
2. Description of the relationships between the lumps by building a kinetic network of lumped reactions;
3. Determination of the rate equations and their associated parameters by optimizing the model on experimental data.

Choosing lumps is generally a tough bargain between the needs of the end-user in terms of the accuracy and precision of the prediction, and the capabilities of the analytical techniques used to describe them. There have been reviews published earlier to assimilate the lumped kinetic models developed so far. The review of lumped kinetic models in the context of hydrocracking of heavy oils is done by⁴⁴. The development of lumped kinetic models started way back in the 1960s. The first model developed was a three-lumped model by Weekman⁴⁵ in the year 1968. Fast forward to the 1990s the complexity of the models increased rapidly as can be seen by 19 lumped models⁴⁶ in 1994. In 2010 Lopez-Garcia provided fundamental modelling of gas oil hydrotreating where a whopping 597 lumps were used in the model⁴⁷. Currently lumped kinetic models are extensively used to model various FCC units. A simple review of lumped models was done by Popa Christina⁴⁰ where along with a summary, four lumped and three lumped models were compared. Some exhaustive reviews are done by³⁴ and⁴³. The present article aims to summarize a few of the many important lumped-kinetic models. Approaches to estimate the parameters of lumped models are also discussed to a small extent.

3.1 Three-lumped kinetic model

The three-lumped kinetic model is one of the oldest and robust models that have been used for modelling catalytic cracking. Although its accuracy is less, it allows for a simplified kinetic approach that can be used to model the riser reactor. Here A represents the feed, B represents gases and C represents coke. The scheme of reactions is shown below. In 1968, Weekman studied the deactivation catalysis and the decay of catalysts for moving bed, fixed bed, and fluidized bed systems and put forward his 3 lumped kinetic model⁴⁵.

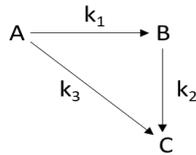


Fig 4. Weekman's Three-Lumped Kinetic Model

1. A pseudo-second-order reaction can be used to express the rate law for conversion of oil and gas during catalytic cracking may be represented by which is coupled with a first-order decay kinetics of the catalyst activity (deactivation kinetics).
2. A plug flow in the gas phase and for vapor was assumed in the riser.
3. The residence time of the reactants in the plug flow riser reactor is very small as compared to the decay time of catalyst, it is under these conditions the solution of the defining partial differential equation will give conversion with isothermal modelling in fixed, moving bed and fluidised bed reactors.
4. A thorough comparative study of the various models and experimental cracking results show that they can successfully represent the experimental data and have good applicability over a wide range of operating conditions.
5. In order to determine and define these models two sets of dimensionless groups were adopted: an extent of reaction group and an extent of catalyst decay group. Comparison of fixed, moving, and fluidized reactor simply gives a comparison of the appropriate dimensionless groups⁴⁰.

The kinetic rate laws have been tabulated below

Reaction	Reaction rate
A \longrightarrow B	$-r_1 = k_1 Y_A^2$
B \longrightarrow C	$-r_2 = k_2 Y_B$
A \longrightarrow C	$-r_3 = k_3 Y_A^2$

Applying material balance on A, B, and C, we get a set of three governing differential equations. The temperature profile equation is obtained by heat balance. The rate constants at various temperatures are obtained using Arrhenius theory⁴⁸. Following assumptions were made while obtaining the governing differential equations-

1. The plug flow conditions were assumed in a tubular reactor operating in adiabatic conditions for modelling the riser. A differential material balance can be applied along the riser cross-section for the calculation of the concentration profile for each lump throughout the riser height
2. Riser system is considered to be without inertia
3. The heat contributions of the pseudo components represented by olefinic gases, gasoline and coke, due to localized small flows and their resultant heat capacities are assumed to be negligible;
4. The transformation as well as the reduced conversion of the gasoline into olefinic gases and coke, and their corresponding enthalpy values of these reactions are considered negligible.

The following are the set of governing differential equations

$$\frac{dY_A}{dz} = -\frac{1}{U_v} (k_1 + k_3) \cdot Y_A^2$$

$$\frac{dY_B}{dz} = \frac{1}{U_v} (k_1 Y_A^2 - k_2 Y_B)$$

$$\frac{dY_C}{dz} = \frac{1}{U_v} (k_2 Y_B + k_3 Y_A^2)$$

The temperature profile equation thus obtained by applying heat balance is

$$\frac{dT_r}{dz} = \left(\frac{-dY_A}{dz} \right) \cdot \frac{(-\Delta H_{ri})}{(Y_{A,c} + Q_{abur} + \alpha \cdot c_{p,cat})}$$

The boundary conditions for the above governing differential equations are represented by-

$$Y_A(0) = 1, Y_B(0) = 0, Y_C(0) = 0, T(0) = T_{nod}$$

Arrhenius equation gives the empirical relationship between rate constants at various temperatures.

$$k_j = k_j' \cdot e^{\frac{E_j (\frac{1}{T_0} - \frac{1}{T})}{R}}$$

The conversion of the oil feed and gasoline is found to be practically better and closer to the experimental observations in the case of the 4-lump kinetic model

than in the case of the 3-lump kinetic model. The obtained results indicate fairly conclusively that the 4-lump kinetic model is more appropriate as well as accurate for the lumped kinetic modelling of the FCCU. The comparison values for both kinetic models are shown in the table⁴⁰.

Reaction	Constants of reaction rate	Activation energy (kJ/mol)
A \longrightarrow B	0.769	10000
B \longrightarrow C	0.648	18000
A \longrightarrow C	0.055	10000

3.2 Mathematical modelling of riser reactor integrated in a fluidized bed catalytic cracker (based on 4-lumped model):

3.2.1 Material and Energy Balances:

Here we start with a simple material balance for a species applied across the riser used in the fluidized catalytic cracking unit is a tubular reactor that can be modelled as a plug flow reactor^{40,49-51}.

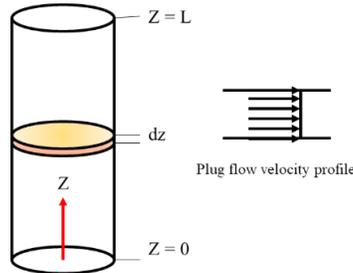


Fig 5. Schematic of a typical plug flow reactor showing the differential element over which the balances are written

1.	$(\rho_v U A x _z - \rho_v U A x _{z+\Delta z}) + r_x \rho_v A \Delta z = \frac{\partial(\rho_v A \Delta z)}{\partial t}$
2.	$(\rho_v U A x _z - \rho_v U A x _{z+\Delta z}) + r_x \rho_v A \Delta z = \frac{\partial(\rho_v A \Delta z)}{\partial t}$
3.	$\frac{(\rho_v U x _z - \rho_v U x _{z+\Delta z})}{\Delta z} + r_x \rho_v = \frac{\partial(\rho_v x)}{\partial t}$
4.	$-\rho_v U \cdot \frac{\partial x}{\partial z} + r_x \rho_v = \frac{\partial(\rho_v x)}{\partial t}$
5.	$-U \cdot \frac{\partial x}{\partial z} + r_x = \frac{1}{\rho_v} \cdot \frac{\partial(\rho_v x)}{\partial t}$

The riser bed acts as a transport bed, with a high

combined flow rate and a short residence time of seconds^{52,53}. Therefore, we can assume that the dynamic terms due to vapor phase, coke formation, and riser temperature are negligible compared to the corresponding terms for coke combustion and dense phase temperature in the regenerator. Therefore, the mass and energy balance equations are considered to be in a quasi-stationary state^{40,50,54,55}. With the assumption of quasi-steady state, the time-varying term cancels out giving:

6.	$-U \cdot \frac{\partial x}{\partial z} + r_x = 0$
7.	$\frac{\partial x}{\partial z} = \frac{m_g}{\rho_v \cdot A \cdot \epsilon} \cdot r_x$

To comprehend the model thus developed, the assumptions implicit while writing the balances are:

- One dimensional Plug-flow* for both the gas phase and catalyst-coke system as well as an adiabatic system⁵⁴.
*(This assumption is relaxed in the latter part of this paper wherein, a dispersion model is considered.)⁹
- The feed vaporizes immediately as and how it comes in contact with the catalyst regenerated at high temperature. The cracking reactions are fast enough to justify the steady-state calculations^{52,55}.
- Diffusion mass transfer resistances are not negligible, but adsorption is absent within the particle of the catalyst^{40,45}.
- No heat loss from the riser. The temperature decrease is only due to the endothermic nature of the reactions^{50,52,55}.
- Only the hydrostatic head due to the catalyst load is considered for pressure drop along the riser reactor.^{50,55}.
- Variable gas superficial velocity is assumed since the catalytic process is expanding the species' mole population along the riser reactor⁵⁶
- Cluster model used for catalyst particles to account for the use of slip factor; no effect on fluid flow due to particle deposition during catalyst deactivation⁵⁷.
- Both the catalyst-coke system and gas have the same temperature to keep the calculations simplified^{52,55}.

The general balance is thus shown, can be used for each of the individual species which, as shown in upcoming parts, are approximated as chemical lumps⁴⁰. Similarly, for heat transfer, we can write an energy balance, for a

component with no unsteady term.

8.	$m_g c_p \rho_v \cdot T _z + m_g c_p \rho_v \cdot T _{z+\Delta z} + m_{cat} c'_p \cdot T _z + m_{cat} c'_p \cdot T _{z+\Delta z}$
9.	$m_g c_p \cdot \frac{dT}{dz} + m_{cat} c'_p \cdot \frac{dT}{dz} = \Sigma(\Delta H_i r_i) \cdot A_{true} \rho$
10.	$\frac{dT}{dz} = \frac{A \cdot \epsilon \cdot \rho_v}{m_g c_p + m_{cat} c'_p} \cdot \Sigma(\Delta H_i r_i)$

The assumptions in writing down the equations are that the heat contributions due to individual lumps are negligible and are collectively represented by a constant heat capacity term to simplify the calculations^{3,40}.

3.2.2 Hydrodynamics of the fluidised bed reactor:

Here the average void fraction used in the balanced equation is defined as⁵⁴:

$$\epsilon = \frac{m_g \rho_{cat}}{m_g \rho_{cat} + m_{cat} \rho_v \cdot \psi}$$

It is implicit that the basis is the Particle model applied to packed beds, where, the slip factor is

$$\psi = \frac{V_o}{\epsilon \cdot V_p} = 1 + \frac{5.6}{Fr} + 0.47 \cdot Fr_t^{0.47}$$

This is a correlation given by Patience et al.^{49,50,56,58} for numerical calculation of slip factor ψ is explained as the ratio of interstitial gas velocity to the average particle velocity. The respective Froude numbers used are defined as follows:

$$Fr_t = \frac{V_t}{\sqrt{gD}}, V_t \text{ is particle terminal velocity.}$$

$$Fr = \frac{V_o}{\sqrt{gD}}, V_o \text{ is superficial gas velocity.}$$

The particle terminal velocity is estimated based on the intermediate regime ($1 < Re_p < 1000$). The vapor velocity is expressed as:

$$U = \frac{m_g}{\rho_v \cdot A_{true}} = \frac{m_g}{\rho_v \cdot A \cdot \epsilon}$$

Here the point of importance is that ρ_v is a function of temperature and hence varying along the riser length. For this, we assume simple ideal gas law to describe the vapor phase density.⁵⁵

Now as said previously,

$$\rho_v = \frac{P \cdot (m_{w_{gas}})}{101325 \cdot R \cdot T}$$

For P in Pascals, and $R = 0.082 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot m_{w_{gas}}$

is the average molecular weight for the vapor-phase.

The material balance equation for the mass flow rate of the vapor phase through the riser can be expressed as:

$$m_g = m_f(y_1 + y_2 + y_3) + m_{ds} + m_{ls} \text{ ADDIN ZOTERO_ITEM CSL_CIT 52,55}$$

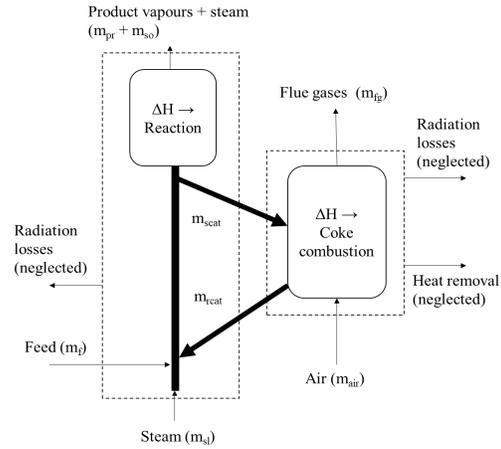


Fig 6. The control-volume approach applied to an FCC unit

Quantities	Equations
V_o	$\frac{m_g}{A_r \rho_g}$
V_p	$\frac{m_{cat}}{\rho_{cat} A_r \epsilon}$
Archimedes number - Ar	$Ar = \frac{d_p^3 \rho_v (\rho_s - \rho_v) g}{\mu_v^2}$
Particle Reynolds number - Rep	$Re_p = \frac{Ar}{18 + (2.3348 - 1.7439 \cdot \phi_{sph}) \cdot Ar^{0.5}}$
Particle Terminal Velocity V_t	$\frac{Re_t \cdot \mu_g}{\rho_g \cdot d_p}$

Also to keep the calculations simplified, a representative constant value for the viscosity of the reaction mixture is assumed^{9,40}. The Pressure drop is estimated by the fluid static equation, that is here we consider only the pressure drop due to the hydrostatic head loss^{50,55}:

$$\frac{dP}{dz} = \rho_{cat} \cdot g \cdot (1 - \epsilon)$$

3.2.3 Kinetics of the catalytic cracking inside the riser reactor of the FCC unit:

With this being defined, we now discuss the lump models used in the reaction modelling. The four lumps employed in the kinetics are **Vaporized gas oil (Feedstock), Light gases, gasoline, and coke**.⁴⁵ The model is referred to as the Gianetto Kinetic 4-lumped Model⁴⁰. The following diagram as well as the tables explain the rate laws assumed.

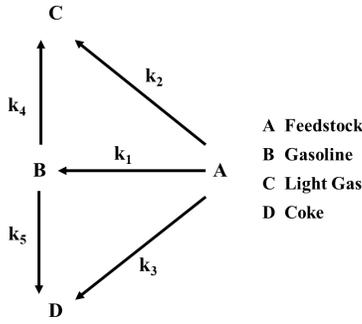


Fig 7. Gianetto Kinetic 4-lumped model

The specific reaction rates are based on Arrhenius' law⁵⁹ and are dependent on the temperature profile as described by the heat balance equation as well as their respective activation energies.

The four-lumped model is a popular scheme and hence all the parameter values are well-documented. However, if a new mechanism is to be proposed, the required parameters need to be estimated by a robust optimization program^{3,6,60,61}. For example, for four lump model, we need to estimate the pre-exponential factors, respective activation energies, and the heat given out in proposed reactions in the scheme making it 15 parameters in all. Higher lump models become a subject of computational complexity vs the numerical accuracy required. The four-lumped model fits within $\pm 3\%$ of the real-time industrial data and has been successfully tested for implementing process control strategies in industries^{40,55}.

Reaction	Rate Law
$A \rightarrow B$	$r_1 = -k_1 \phi x_1^2$
$A \rightarrow C$	$r_2 = -k_2 \phi x_1^2$
$A \rightarrow D$	$r_3 = -k_3 \phi x_1^2$
$B \rightarrow C$	$r_4 = -k_4 \phi x_2^2$
$B \rightarrow D$	$r_5 = -k_5 \phi x_2^2$

Where a rate constant is: $k_i = k_i^0 e^{-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$. The

reaction rates as solicited from the literature are shown⁵³. Also, the reaction rates are mass-based rate laws (unlike volumetric reaction rates)⁴³.

Reaction	Pre-exponential factor	Activation energy (J/mol)	Heat of reaction (ΔH_{rxn}) (kJ/mol)
$A \rightarrow B$	12600	57359	393
$A \rightarrow C$	2070	52754	795
$A \rightarrow D$	25.1	31820	1200
$B \rightarrow C$	2735	65733	1150
$B \rightarrow D$	0.006	66570	151

3.2.4 The Catalyst deactivation model:

Where ϕ denotes the catalytic activity which is a catalyst deactivation function. Catalytic activity denotes the ratio of reaction rate on a catalyst at any given time to the reaction rate on a fresh catalyst⁵¹. Though a lot of catalyst deactivation models for predicting product selectivity have been in the literature^{62,63} we will be using a simple model wherein the deactivation function for coke formation has been considered⁶⁴:

$$\phi = 1 - 45 \cdot \frac{(y_4 \cdot m_f) + m_{cok}}{m_{cat}}$$

Where y_4 represents the mass fraction of coke.

3.2.5 The Axial - dispersion model:

There have been attempts to integrate axial dispersion in the 1D four-lumped model on the basis that it becomes important in heterogeneous catalysis⁹, prominently for porous catalysts such as the FCC zeolite catalyst¹⁴. Thus, the mass balance equation is modified to accommodate the dispersion term as follows:

11. $-\rho_v U \cdot \frac{\partial x}{\partial z} + D_u \rho_v \cdot \frac{\partial^2 x}{\partial z^2} + r_x \rho_v = \frac{\partial(\rho_v x)}{\partial t}$
12. $-U \cdot \frac{\partial x}{\partial z} + D_u \cdot \frac{\partial^2 x}{\partial z^2} + r_x = 0$
13. $\frac{\partial x}{\partial z} + \frac{D_u}{U} \cdot \frac{\partial^2 x}{\partial z^2} + \frac{m_g}{\rho_v \cdot A \cdot \epsilon} \cdot r_x = 0$
14. $\frac{\partial x}{\partial z} - \frac{D_u}{U} \cdot \frac{\partial^2 x}{\partial z^2} = \frac{m_g}{\rho_v \cdot A \cdot \epsilon} \cdot r_x$

The vessel dispersion number used here is assumed rather than being fitted (optimized) to the real-time data.

3.2.6 The Mathematical Problem setup:

To solve the above-developed model equations, a code was written in MATLAB R2021a environment. It did

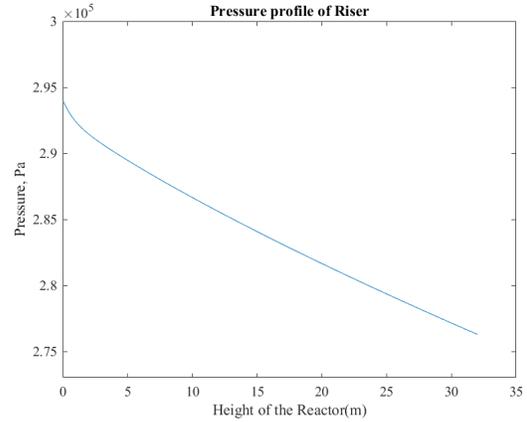
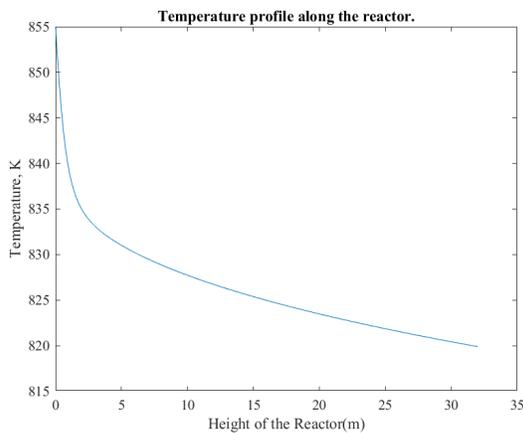
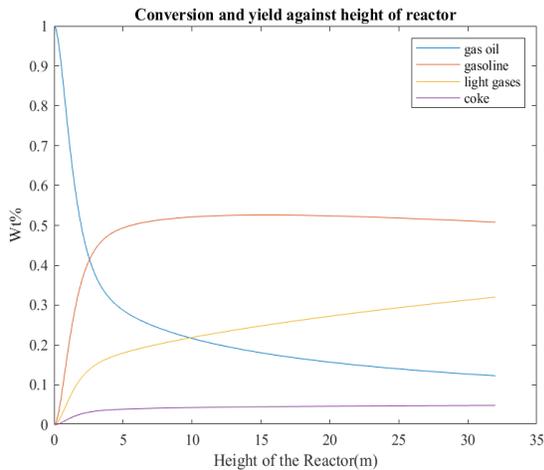
run at the start, for zero-dispersion and then gradually, the vessel dispersion number was varied till 0.06. The code helped to predict the yield of each lump along with temperature and pressure profiles. The following tables show the data assumed in the related calculations⁵³.

Operating Conditions	Data 1	Data 2	Data 3	Data 4
Feed rate (kg/s)	19.95	25.70	26.90	23.6
COR (kg/kg)	7.20	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	1000
Steam (wt.%)	7	5.50	5	5.75
Steam temperature (K)	773	773	773	773

2.2.7 Results of the simulations

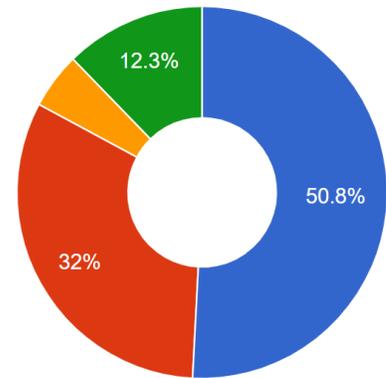
Following are the results obtained when the model thus developed is integrated with the axial-dispersion model

$$\left(\frac{D}{uL} = 0.06\right).$$

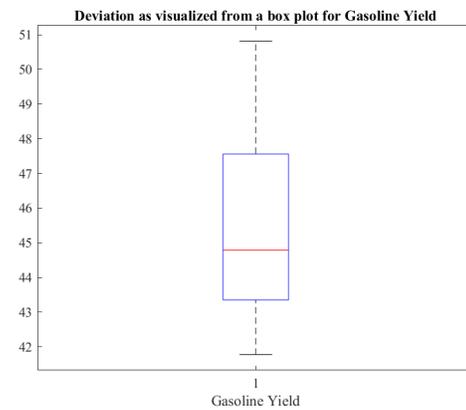


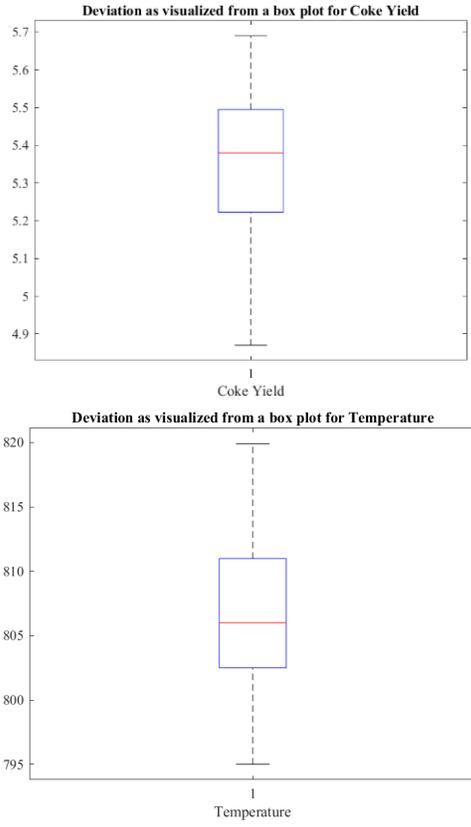
Component vs Composition (wt%)

- Gasoline
- Light-Gases
- Coke
- Gas-oil-conversion



The difference the real-time and calculated values in gasoline yield, coke yield, and temperature are visualized with the help of box plot:





3.3 Advanced Kinetic Lumped-Models

3.3.1 Five Lumped Kinetic Model

Bollas and co-authors⁶² used a five-lumped model to predict the product selectivity in the FCC process. The five lumps were gasoline, gas oil, coke, dry gas (C₁ --- C₂, H₂ and H₂S), and product gas (C₃ --- C₄). The model can be seen in the figure below. The reaction network consists of 9 reaction pathways.

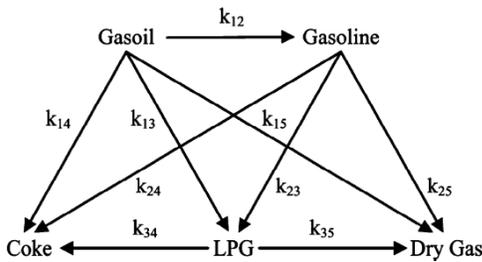


Fig 8. Five-lumped kinetic model (Bollas et. al.)

The relative errors of the predicted and experimental yields can be seen in the table below.

Table 1

Case examined	LPG	Gas oil	Coke	Petrol	Dry gas
Product oriented selective catalyst	3.86	1.56	4.78	2.10	4.63

deactivation					
Reactant oriented selective catalyst deactivation	4.34	1.57	5.31	2.15	8.96
Thermal cracking for dry gas production	4.43	1.65	5.30	2.07	10.73
Non-selective catalyst deactivation	4.38	1.73	5.51	2.17	9.45

The authors further examine the four scenarios in a way wherein the catalyst deactivation is dealt with in such mathematical representation for simulating the FCC operation at steady-state conditions. The usage of the four models clearly indicated that non-selective deactivation models performed satisfactorily, however, the usage of the product-oriented catalyst deactivation model showed a considerable improvement. This directly suggests that the products of the reactions play a dominant role in the catalyst deactivation effect in catalytic cracking.

Ancheyta-Juárez and Sotelo-Boyás³⁴ developed a sophisticated method to determine the rate constants in a five-lumped model. The model can be seen below where A, B, C, D, and E correspond to gas oil, gasoline, LPG, dry gas, coke respectively.

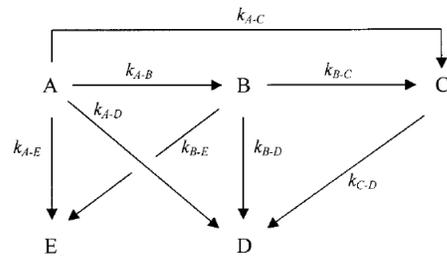


Fig 9. Parameter estimation for five-lumped model (Ancheyta-Juárez and Sotelo-Boyás)

The sequential methodology proposed to divide the original model into various with less lump to calculate few rate constants. The parameters can be correlated back to the original model after solving for them. Some divisions can be seen below.

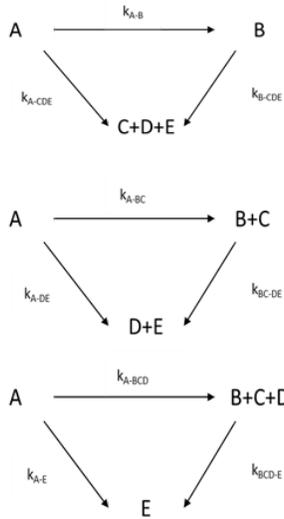


Fig 10. Sequential Methodology for determination of rate constants.

In the above figure as we can see the kinetic constants, for A going to B and A going to E might be calculated from the above lumped models. Also, k_{A-C} and k_{A-D} can be calculated as:

$$k_{A-C} = k_{A-CDE} - k_{A-DE}$$

$$k_{A-D} = k_{A-DE} - k_{A-E}$$

The existing model consisting of 5 lumps can be divided further into smaller three models each with 4 lumps to carry out akin exercise.

3.3.2 Six Lumped Kinetic Model

Asaee and co-authors⁶⁰ developed an algorithm to simplify a complex six-lumped model into a simpler one. The initial model can be seen in the figure below.

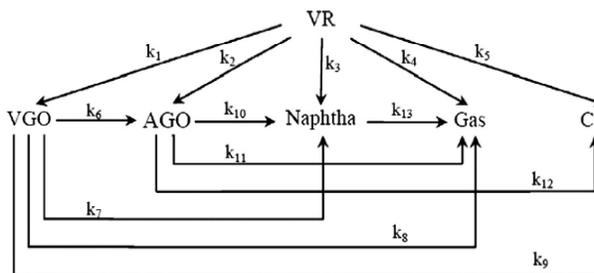


Fig 11. Six-lumped Kinetic Model (Asaee et. al.)

The simplified model after optimization can be seen below.

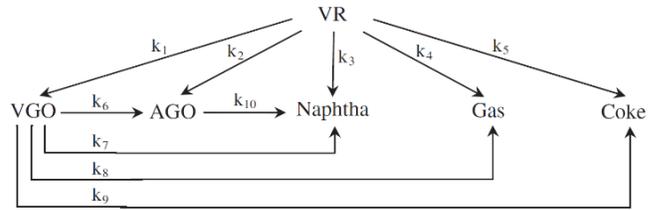


Fig 12. Simplified six-lumped model

3.3.3 Seven Lumped Kinetic Model

Modelling of an industrial RFCCU riser reactor is done by using 7 lumps⁵⁴. The lumped model they used can be seen in the picture below.

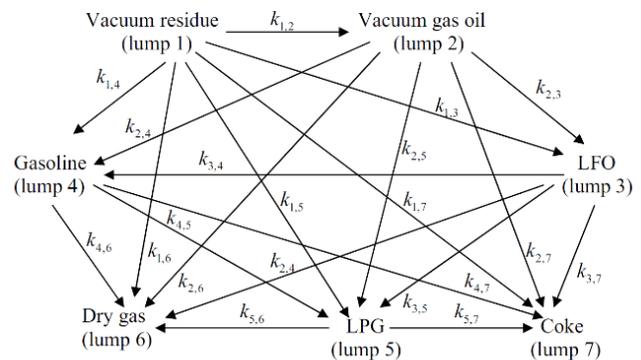


Fig 13. Seven-lumped Kinetic Model (Olafadehan et. al.)

The coupled differential equations generated in the model were solved using MATLAB built-in function of ode23t. The comparison of predicted yield and the actual plant data can be seen in the table below.

Lump s	Plant data	Instantaneous		One dimensional	
		Yield	% Error	Yield	% Error
CSO	0.0469	0.0473	-0.85	0.0392	16.42
LFO	0.2152	0.2203	-2.37	0.1891	12.13
GA	0.4433	0.4413	0.34	0.4160	6.16
LPG	0.1544	0.1494	3.24	0.1131	26.75
DG	0.0441	0.044	0.23	0.037	16.10
GK	0.0932	0.0935	-0.32	0.0789	15.34

Another example of a 7 lumped model to describe in the domain of catalytic cracking can be found in⁶⁵ wherein the model is to describe residual oil cracking. Apart from catalytic cracking the 7 lumped model is used in the methanol to olefin (MTO) process⁶⁶.

3.3.4 Nine Lumped Kinetic Model

You Hongjun and other co-authors⁵⁶ studied the aromatization reaction of FCC gasoline with the help of

nine lumped models.

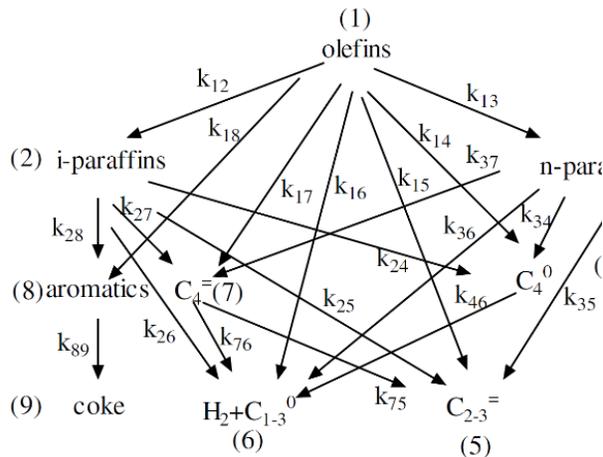


Fig 14. Nine-lumped Kinetic Model (You et. al.)

The catalyst used was LBO-A from Lanzhou Petrochemical Institute. The components and operating conditions for the aromatization of FCC gasoline can be seen in the table below.

Name	n-Paraffin	i-Paraffin	Olefins	Aromatics	Naphthalene
Shenghua	5.19	15.51	54.70	16.30	9.30
Fushun	5.91	32.52	39.20	13.06	9.30
Lanlian	4.78	27.45	36.99	23.66	7.12

Parameters	Value
Reaction temperature (degree Celsius)	390-470
Weight hour space velocity (h^{-1})	20-40
Water inflow (ml/min)	2
The mass ratio of catalyst to oil	3-12
LBO-A (g)	60
Reaction time (s)	8-33

To detect the volume percentage of aromatic compounds an HP6890 Gas Chromatograph with Chem Section software is used while to obtain mass fractions of paraffin, naphthalene, olefins, and aromatics TSY-1132 Liquid Petroleum Hydrocarbon Measuring Equipment was used. The average error concerning experimental data was 0.08%. The authors have demonstrated that this model is effective, economic, and convenient to use for refineries in China.

3.3.5 Twelve Lumped Kinetic Model

Chen and co-authors⁶⁷ provided a 12 lumped reaction network consisting of 54 reaction pathways. The division could be understood based on the feedstock, the products formed, gasoline, and the cracked gas. The oil is divided into three lumps aromatics (HA), saturations (HS), and resin plus asphaltene (HR). The products are lumped as follows: diesel is treated as a group because it is not further divided into most studies on FCC lumped models. Gasoline is divided into three lumps: saturated hydrocarbon (GS), olefin (GO), and aromatics (GA) with high octane numbers. The authors have considered propylene and butylene as high-value products in

the FCC processes. The cracked gas is classified into dry gas (DGAS), propylene (LO3), butene (LO4), and alkanes (LPGD) in liquefied gas. Coke, a final condensation product in the FCC reaction process and is lumped alone because of its important effect on the catalyst activity. The model can be seen in the figure below.

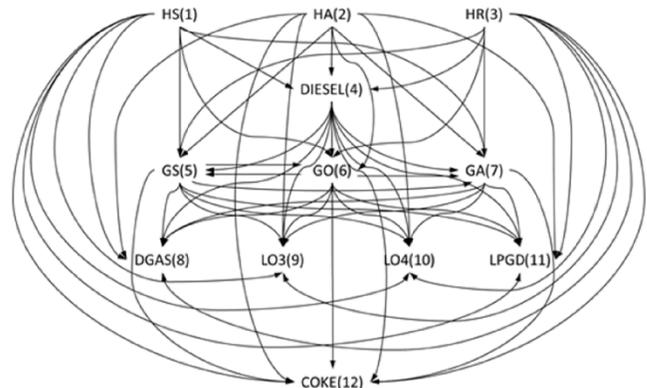


Fig 15. Twelve-lumped Kinetic Model (Chen et. al.)

The product formation was estimated at 12 different sets of catalyst to oil ratios. The relative error of prediction of product yields by the model is less than 5%.

4 Conclusion

In this paper, mathematical modelling techniques for various reactions occurring in the FCC unit of a refinery are discussed in detail. In addition to this, a theoretical background of advanced lumped models is also provided.

Even though lumped model become more complex with increase in number of lumps, the number of reactions remain finite. The reaction mechanism too, remains simple (pseudo-order reactions for example). Moreover,

the model parameters can be determined by simple optimization algorithm with limited computing power requirements which is a feature in itself.

However, lumping introduces two drawbacks. The first being, the inability to account for the transient nature of the lumps and the second being, its dependence on experimental data. This has in turn led to rise of mechanistic and molecular models with greater theoretical depth and accuracy.

5 Conflict of Interests

We have no conflict of interest to declare. We warrant that the article is the Authors' original work. We warrant that the article has not received prior publication and is not under consideration for publication elsewhere.

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