Simulation of Light Olefins Yield from Direct Cracking of Heavy Fractions in Fluid Catalytic Cracking Unit

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The fluid catalytic cracking unit (FCCU) has for many years been described as the most important unit of the petroleum refinery because it can convert Vacuum Gas Oil (VGO) and other heavy refinery bottoms into useful fuels and light olefins. These conversions take place in the riser, which acts as a reactor in the FCC unit. In addition to steam cracking, FCCU is the second chief producer of propylene through direct catalytic cracking of these heavy fractions to produce basic petrochemicals, such as light olefins. In this study, the FCC unit was optimized to yield light olefin gases from direct crude oil (Arab super light oil) cracking. A four-lumped kinetic model was adopted and applied using the dynamic model in gPROMS software 7.0.7 for the modelling and simulation of the FCC unit. In this work, gPROMS modelling of crude oil cracking was validated with experimental data obtained from the literature to validate the simulation results. Simulation data and experimental data are highly correlated with an R2 0.9908 coefficient of determination. Based on the estimated catalyst deactivation function parameter with gPROMS, the proposed four-lump kinetic model simulated light olefin gas yields.

1. Introduction

The direct cracking of crude oil with fluid catalytic cracking (FCC) is being proposed to meet ever-growing demands for petrochemical feedstock, particularly light olefins (Al-Absi & Al-Khattaf, 2018; Corma et al., 2017). Conventionally, light olefins are by-products of petroleum refining processes such as FCC, which produce insufficient amounts to meet the world's ever-increasing demand.

Hydrocarbon feed vacuum gas oil (VGO) is pumped into the riser accompanied by a small quantity of steam, which improves atomization and lowers coke formation. The riser is where the cracking reaction of the hydrocarbon feeds takes place, and the regenerator is where the deactivated catalyst by the deposition of coke is regenerated (Han & Chung, 2001a). The feed is vaporized by the regenerator's heated catalyst and the hydrocarbon vapors in the riser undergo endothermic catalytic cracking. Catalyst and hydrocarbon vapours remain in the riser for 2–5 seconds.

Most researches have successfully cracked gas oil having a specific boiling point range in the FCC unit (Ahari, J. S. et al., 2008; Ali et al., 1997; Han & Chung, 2001a, 2001b; John et al., 2017). Al-Khattaf & Ali, (2018) and Usman et al., (2017) recent studies demonstrated cracking across a larger boiling point range (direct crude) utilizing an FCC catalyst. They have demonstrated various light olefin yields (even comparing different catalysts for light olefin yields). The current contribution of this research is an extension of previous two articles, in which olefin yield in an FCC riser was explored using modelling and simulation.

Moreso, cracking crude oil directly in an FCC unit could be an ideal process to expanding olefin gases production, which is the central aim of this study. In addition, direct cracking of crude oil into light olefins would be cost-effective as it will bypass some of the costly refining processes and also produce more light olefins as petrochemical feedstock as a result of the decline in transportation fuel demand. Thus, this study uses the gPROMS software to perform a simulation of the FCC unit to determine the various process factors that affect the production of light olefins from crude oil. Validation with experimental data obtained from the literature to validate the simulation results was achieved. Simulation and experimental data are highly correlated with an R^2

0.9908 coefficient of determination. Based on the estimated catalyst deactivation function parameter with gPROMS, the proposed four-lump kinetic model simulated light olefin gas yields.

2. Process modelling

Several parameters have been used to determine the characteristics of different types of gas oil. These parameters can be used to determine the same properties of crude oil. It is important to note or assume that the heat generated by the crude oil (heavy fraction) would follow the same pathway as that generated by the gas oil, that is second order reaction. The main reason for this is that the heavy ends in crude oil dominate the composition of gas oil. In this study, for heavy fraction cracking in FCCU, a four-lump kinetic model consisting of heavy cycle oil (HCO) + light cycle oil (LCO) as heavy fraction (HF), naphtha (NP), coke (CK) and C_1-C_4 gases (GS), will be used to describe the catalytic cracking of crude oil directly. However, the crude oil in liquid form can be approximately distilled into three fractions: light (70 – 200ºC), middle (200 – 350ºC), and heavy (> 350ºC) (Selalame et al., 2022). Figure 1. Shows the four-lump model for catalytic cracking of direct heavy fraction in FCCU. The burning off of the coke in the regenerator supplies the heat that drives the catalytic cracking of crude oil in the riser reactor.
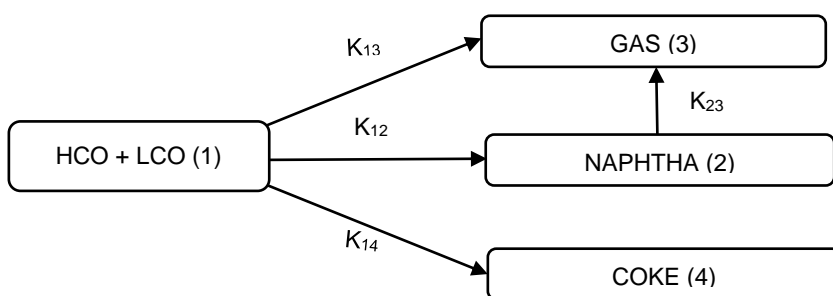

Figure 1: The four-lump model for catalytic cracking of direct crude oil in FCC unit (Usman et al., 2017)

2.1 The riser model

The industrial riser in this work is 35.0 meters in height and 1.2 meters in diameter.
Based on the following assumptions, the riser simulation model combines mass, energy, and momentum balance equations for the catalytic and gaseous phases:
   a) Catalytic cracking reactions take place instantaneously in the riser and the catalyst surface, accounting for the steady state operation of the reaction (John et al., 2019b).
   b) Vaporisation of the crude oil occurs as it meets the recycled hot catalyst, causing it to move vertically upward in thermal equilibrium, hence no heat loss is recorded (Ali & Rohani, 1997).
   c) Cracking occurs primarily on the surface of the catalyst. Therefore, dispersion and adsorption rates within the catalyst are very low and negligible (John et al., 2019b).
   d) The temperatures in which the reactor runs are described as isothermal. The measured temperature change was hardly noticeable throughout the duration of the reactions.

Endothermic heat generated by the regenerator is used during catalytic cracking and the rate of heat removal via reaction was set at zero for Qreact (Rate of heat generation or heat removal by reaction). The system's process model should include parameters that may be fine-tuned to ensure that model projections are sufficiently matched with real-world data

2.2 Kinetic modelling

A four-lumped kinetic model is used to study the catalytic cracking of direct crude oil in FCC. Cracking of crude oil occurs in the riser reactor once it comes into contact with the recycled hot catalyst. The catalyst acid sites promote the cracking reaction resulting in coke formation and deposition, which causes deactivation over time. Since the heavy fraction is a complex mixture of hydrocarbons with differing reactions rates, the cracking process can be assumed to follow second-order kinetics (John et al., 2019b).
The governing equations for heavy fraction cracking based on the four-lump model scheme used in this simulation were derived from the literature (Han and Chung 2001a, 2001b; John et al. 2019; Sulaiman S Al-Khattaf and Ali 2018; Usman et al. 2017). Rate equations, Riser equations, Arrhenius equation and all other equations were solved together using gPROMS (7.0.7).

3. Model Development of the FCCU Riser

Based on the energy balance over the riser compartment, Equations (1) and (2) are derived, which show the catalyst and gas phases temperature, respectively. Both model equations can be used to predict the temperature profiles of the two phases along the riser unit height.

3.1 Model Equations

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3.2 Riser equations from energy balance

The temperature of gas phase T_g and temperature of the catalyst T_c along the riser height are expressed in Equations (1) and (2). In Equations 3 and 4, the gas and catalyst temperature are subject to the boundary conditions. The riser length is within $0 \leq x \leq 35m$. (0 represent the conditions at the bottom of the riser and 35 m high). h_p is the heat transfer coefficient between the gas and catalyst phase, C_p is the specific heat capacity, F_g and F_c are flowrate of the gas and catalyst obtained in Equations (5) and (6), Ap is the interstitial area at the gas solid interphase and Q_{react} is the heat of reactions per unit mass of catalyst. h_p and A_p are given by (Han & Chung, 2001b; John et al., 2019b). where S_c is the sphericity of the particle and is assumed to be 0.72 for FCC catalysts. ε_c and ε_g are the local catalyst and gas volume fractions respectively, and V_c and V_g are the local velocities of the catalyst and gas phase respectively. These variables are determined by the solution of the momentum equations. μ_g is the viscosity of the gas. K_g is the thermal conductivity of the gaseous hydrocarbons mixture, given by Han and Chung (2001b). M_{wm} represents the mean molecular weight of the local gas mixture.

$$\frac{dT_g}{dx} = \frac{\Omega}{F_g C_{pg}}\left[h_p A_p \left(T_c - T_g\right) + \rho_c \varepsilon_c Q_{react}\right] \tag{1}$$

$$\frac{dT_c}{dx} = \frac{\Omega h_p A_p}{F_c C_{pc}}\left(T_g - T_c\right) \tag{2}$$

$$T_c^{(0)} = T_{cFS} \tag{3}$$

$$T_g^{(0)} = T_{gFS} \tag{4}$$

$$h_p = 0.03\frac{K_g}{d_c^{\frac{2}{3}}}\left[\frac{[(V_g - V_c)]\rho_g \varepsilon_g}{\mu_g}\right]^{\frac{1}{3}} \tag{5}$$

$$A_p = \frac{6\varepsilon_c}{d_c S_c} \tag{6}$$

$$K_g = 1 \times 10^6\left(1.9469 - 0.374M_{wm} + 1.4815 \times 10^{-3}M_{wm}^2 + 0.1028T_g\right) \tag{7}$$

3.3 Kinetic equations for four-lumped model

In the cracking of crude oil, the (HCO + LCO) and naphtha fractions are cracked on the same acidic sites of the catalyst and are consequently subjected to similar effects of catalyst deactivation due to the deposition of coke. The k_{ij} (K_{12}, k_{13}, k_{14}, and k_{23}) in the rate equations are temperature dependent rate constants, which can be determined using the Arrhenius equation. Since crude oil is a complex mixture of hydrocarbons with differing reactions rates, the cracking process can be assumed to follow second-order kinetics ((Al-Khattaf & Ali, 2018; Usman et al., 2017). In this study, four-lumps kinetic models which include ASL crude oil, naphtha, gas (including olefins), and coke will be applied. Based on the lump kinetic model scheme, the governing equations representing crude oil (co) cracking are shown in Equations (8–11) as follows:

Riser equations from material balance

HCO + LCO $\quad \frac{d_{y_{co}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{co}$ $\hfill (8)$

Naphtha $\quad \dfrac{d_{y_{np}}}{dx} = \dfrac{\rho_c \varepsilon_c \Omega}{F_g} R_{np}$ $\hspace{4cm}$ (9)

Gas $\quad \dfrac{d_{y_{dg}}}{dx} = \dfrac{\rho_c \varepsilon_c \Omega}{F_g} R_{gs}$ $\hspace{4cm}$ (10)

Coke $\quad \dfrac{d_{y_{ck}}}{dx} = \dfrac{\rho_c \varepsilon_c \Omega}{F_g} R_{ck}$ $\hspace{4cm}$ (11)

R is the rate of reaction for the gaseous lumps (co, np, gs, ck) per unit mass of catalyst and is analogous to Q_{react} in the energy equations. For each lump, R sums over the reactions that generate and/or remove the lump, for the present four-lump kinetic model the R terms are summarised in Equations (12 to 15):
Rate of reaction along riser:

HCO + LCO $\quad R_{co} = -(K_{12} + K_{13} + K_{14})y_{co}^2 \, \emptyset_c$ $\hspace{3cm}$ (12)

Naphtha $\quad R_{np} = \left((K_{12} y_{co}^2) - (K_{23}) \, y_{np} \right) \emptyset_c$ $\hspace{3cm}$ (13)

Gas $\quad R_{dg} = \left(K_{13} y_{co}^2 + K_{23} y_{np} \right) \emptyset_c$ $\hspace{3cm}$ (14)

Coke $\quad R_{ck} = \left(K_{14} y_{co}^2 \right) \emptyset_c$ $\hspace{3cm}$ (15)

The Arrhenius formula can be used to represent the temperature dependent rate constant *Ki* in the equations. The K terms are the rate constants for each of the reactions in the four-lumped model, they are expressed in Arrhenius equation form as shown in Equations (16) to (19):

Overall rate constants:

Crude oil to naphtha overall rate constant $\quad K_{12} = k_{12} \exp\left(\dfrac{-E_{12}}{RT_g}\right)$ $\hspace{2cm}$ (16)

Crude oil to gas overall rate constant $\quad K_{13} = k_{13} \exp\left(\dfrac{-E_{13}}{RT_g}\right)$ $\hspace{2cm}$ (17)

Crude oil to coke overall rate constant $\quad K_{14} = k_{14} \exp\left(\dfrac{-E_{14}}{RT_g}\right)$ $\hspace{2cm}$ (18)

Naphtha to gas overall rate constant $\quad K_{23} = k_{23} \exp\left(\dfrac{-E_{23}}{RT_g}\right)$ $\hspace{2cm}$ (19)

The $\emptyset_c$ in Equations (12 - 15) represents the catalyst deactivation coefficient. It is commonly acknowledged that the deposition of coke on the catalyst is the principal cause of catalyst deactivation, and that the consequence of this is a function known as a catalyst deactivation function α. Equation (20) describes the deactivation of the catalyst. Catalyst deactivation model used is that of Usman et al. (2017), such that:

$$\emptyset_c = \exp\left(-\alpha_c X_{co}\right) \hspace{6cm} (20)$$

Where α_c is the deactivation coefficient and X_{co} is the conversion of $HCO + LCO$. Unfortunately, the paper by Usman et al. (2017) did not report the value for α_c, hence this will be fitted to experimental data in the present work as 3.930 through parameter estimation in gPROMS. As stated in the gas energy equation in Equation (1), Q_{react} links the four-lumped kinetic model to the hydrodynamics. It represents the rate of heat generation or heat removal by reaction in Equation (21):

$$Q_{react} = -\left(\Delta H_{12} K_{12} y_{co}^2 + \Delta H_{13} K_{13} y_{co}^2 + \Delta H_{14} K_{14} y_{co}^2 + \Delta H_{23} K_{23} y_{np}\right) \emptyset_c \hspace{1.5cm} (21)$$

3.3 Variables modelling estimating technique

From figure 1, the diagram shows how input and output variables data from the plant were used in simulation model to breed online data across the riser height which was used to represent experimental data in the gPROMS software for factor estimation. The riser length is assumed to be from 0 to 35 m, the riser diameter ranges from 0 to 1.2 m, the pressure of the riser is from 100 to 250 kPa, the catalyst flow rate from 200 to 400 kg/s and that of the gas is 5 to 62 kg/s, respectively (John et al., 2019b). Table 1 lists the process inputs and base case operating conditions used in the model.

Table 1: Riser initial operating conditions and parameters

Process variable	Variable model ranges
Riser length	0 - 35.0 (m)
Diameter (D)	0 - 1.2 (m)
Pressure of riser (P_{RS})	250 - 345 kPa
Catalyst flowrate (Fc)	200 - 400 (kg/s)
Gas flowrate (Fg)	5 - 62 (kg/s)

4. Results and Discussions

Results from simulation are displayed in this section. A comparison was made between the results obtained from the cracking of crude oil using gPROMS simulation of FCC and those obtained from Al-Khattaf and Ali (2018) experiments at the same conditions (823K and 2s). The parity plot in Figure 2 illustrates the level of agreement between simulated and experimental data. In the chart, it can be seen that the simulation data and experimental data agree with a coefficient of determination (R^2) of 0.9908.
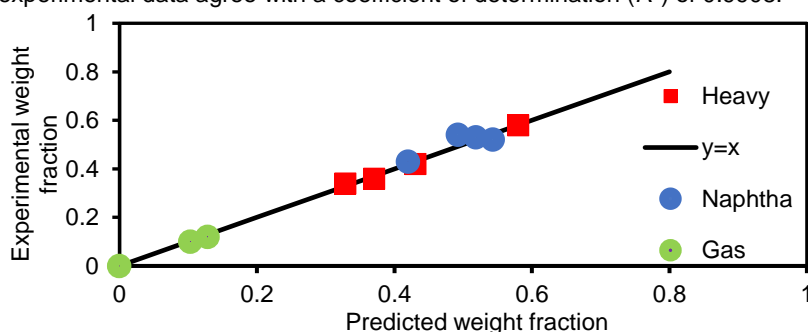

Figure 2: Parity plot comparing simulated and experimental data.

Figure 3 shows the gPROMS simulation result for crude oil conversion and yields of heavy fractions, naphtha, gas, and coke. As the riser reactor height increases, the crude oil conversion and gas yield appear to increase steadily. In terms of conversion, a maximum 44.2 % was achieved, while 12.6 % was produced as gas. A slight increase in the naphtha fraction yield was observed throughout the riser reactor, plateauing at 53.2 %.
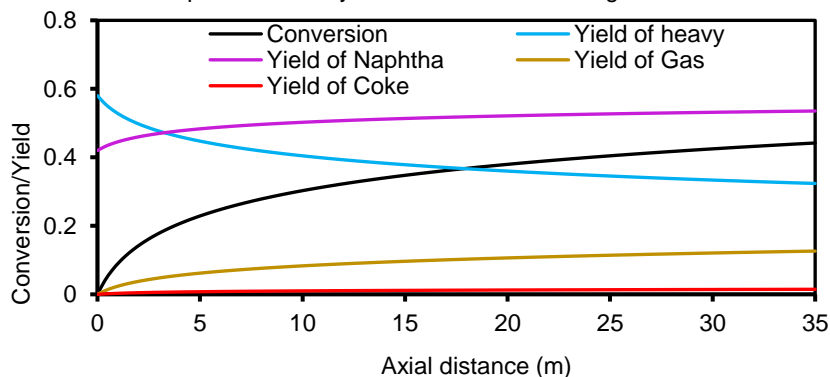

Figure 3: FCCU simulation result for crude oil conversion and yields of heavy fractions, naphtha, gas, and coke

On the other hand, the heavy fraction component decreases steadily as the riser reactor height increases, exiting it at 32.4 %. In the original crude oil, 58 % of the heavy fraction was in it and 42 % was in the naphtha fraction. Consequently, the amount of coke formed on the catalyst and deposition on it increase slowly as the riser reactor length increases. Approximately 0.13 % of coke is formed during the initial phase at the bottom of the riser reactor, while 1.5 % of coke is deposited on the catalyst upon exit of the reactor. The formation of coke is an indication of the occurrence of catalytic cracking promoted by its acid sites.

Furthermore, the deposition of coke on the catalyst because of crude cracking causes deactivation and a drop-in activity over time.

5. Conclusions

An analysis of direct crude oil cracking in FCCU was presented in this study, which led to the production of olefin gas used as a petrochemical feedstock. The simulation of olefin yield from direct cracking of crude oil was carried out in the FCC riser reactor using gPROMS. The kinetics of the cracking reaction was modelled with the aid of a four-lump kinetic model. Experimental data obtained from the literature validated the results obtained from the gPROMS simulation of the crude oil cracking in FCCU. A coefficient of determination of R^2 0.9908 indicates a high degree of agreement between the simulation data and experimental data.

In general, the amount of crude oil converted, and the amount of gas produced appears to increase steadily along the riser reactor length. Maximum conversion achieved was 44.2%, with gas production reaching 12.6% at 35 m riser reactor height. Heavy fractions, however, decrease steadily as reactor height increases. As a result of crude oil cracking catalytically, the amount of coke formed on the catalyst increases gradually as the riser reactor length increases, peaking at 1.5%.

Acknowledgments

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