

# 1 Parameter Estimation of a Six-Lump Kinetic Model of an 2 Industrial Fluid Catalytic Cracking Unit

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9

## 10 Abstract

11 In this work a simulation of detailed steady state model of an industrial fluid catalytic  
12 cracking (FCC) unit with a newly proposed six-lumped kinetic model which cracks gas oil  
13 into diesel, gasoline, liquefied petroleum gas (LPG), dry gas and coke. Frequency factors,  
14 activation energies and heats of reaction for the catalytic cracking kinetics and a number of  
15 model parameters were estimated using a model based parameter estimation technique along  
16 with data from an industrial FCC unit in Sudan. The estimated parameters were used to  
17 predict the major riser fractions; diesel as 0.1842 kg-lump/kg-feed with a 0.81% error while  
18 gasoline as 0.4863 kg-lump/kg-feed with a 2.71% error compared with the plant data. Thus,  
19 with good confidence, the developed kinetic model is able to simulate any type of FCC riser  
20 with six-lump model as catalyst-to-oil (C/O) ratios were varied and the results predicted the  
21 typical riser profiles.

22 Keyword: FCC riser; modelling and simulation; six-lumped model; parameter estimation.

23

## 24 1. Introduction

25 As demand for heavy crude has decreased over the last decade, the demand for lighter end  
26 fractions, such as diesel, gasoline and olefins, have consequently increased. The FCC unit  
27 converts gas oil, with high boiling point petroleum fractions, into the much essential  
28 transportation fuels such as gasoline, diesel and jet fuel (Sadeghbeigi, 2000). This is to  
29 increase the refinery output of consumable/sellable products and meet demand, which would  
30 in turn maximise the profits of the refinery.

31 The conventional FCC unit is made up of the riser for cracking reaction and the regenerator  
32 for catalyst regeneration (John et al., 2017b, John et al., 2017a, Sadeghbeigi, 2000, Han and  
33 Chung, 2001a). When the gas oil is atomized with dispersed steam on the surface of the  
34 catalyst at the vaporization section of the riser, it vaporizes instantaneously and the bulk fluid  
35 moves pneumatically upward into the riser where the hydrocarbon vapour breaks down into  
36 lighter products as it journeys upward with the hot catalyst. As a result, coke, a by-product of  
37 the reaction, is deposited on the surface and pores of the catalyst thus, deactivating it. The  
38 cracked products are separated into catalyst and vapour in the disengaging section with the  
39 use of cyclones. While the vapour goes to the fractionators for further separation, the  
40 deactivated catalyst flows into the regenerator through the stripping section, where the coke  
41 deposited on catalyst is burnt off rendering the catalyst sufficiently hot and activated or  
42 regenerated. The hot regenerated catalyst is returned continuously to the riser reactor for  
43 continuous cracking reactions, which supplies the heat responsible for endothermic cracking  
44 reactions. This continuous catalyst circulation is possible because of both heat generation and  
45 consumption during chemical reactions along with the unit's hydrodynamic balance.

46 The heat balance of the FCC unit, a major influence of the hydrodynamics of the process,  
47 depends on the endothermic heats of the cracking reactions (Arbel et al., 1995) and needs to  
48 be adequately measured. During regeneration, heat produced compensates the heat necessary  
49 for the endothermic cracking reactions, resulting in the FCC unit operating under conditions  
50 of thermal balance (Arandes et al., 2000). These conditions of thermal balance are influenced  
51 by the heat from the feed, the vaporization steam, regenerated catalyst and the endothermic  
52 reactions in the riser. Most of the heat components are measureable with less difficulty  
53 compared with the heat produced or consumed during the endothermic reactions. To account  
54 for the endothermic heat of reactions, it is necessary to measure the enthalpy of reaction in  
55 the riser, which is important for the effective control, and stability of the FCC unit.

56 Many riser models of FCC unit found in the literature do not use equations that account for  
57 the endothermic heat of reaction in the riser. At best, the temperature profile of the gas phase  
58 is presented. A real industrial plant located in Sudan is simulated in this work. It has five  
59 products and a feed, making it a six lumped kinetic model; they are gas oil, diesel, gasoline,  
60 liquefied natural gas (LPG), dry gas and coke. To simulate this industrial FCC unit, a six  
61 lumped kinetic model that adequately represents its product distribution is required.  
62 However, this six lumped kinetic model is unique and not readily used in the literature.  
63 Where this six lumped kinetic model was used (Du et al., 2014, Xiong et al., 2015, Zhang et

64 al., 2017), the riser model did not account for the heat of reaction, which is the endothermic  
65 heat required for the cracking of the feed. This heat of reaction is important and a  
66 requirement for the riser model used in this work (Han and Chung, 2001a, Han and Chung,  
67 2001b). This six-lumped kinetic model (Du et al., 2014, Xiong et al., 2015, Zhang et al.,  
68 2017) have their frequency factors and activation energies presented in the literature.  
69 However, they did not provide their enthalpies; hence, the data they used cannot be used to  
70 account for the endothermic heat of reaction. In this work, the endothermic heat of reaction  
71 will be calculated using a similar but new six lump kinetic reaction scheme which  
72 incorporates the new enthalpies of reaction, frequency factors and activation energies  
73 obtained through parameter estimation technique in gPROMS. These new estimated  
74 parameters will make it possible for the simulation of the FCC unit in Sudan using the robust  
75 riser model of Han et al., (2011a, b) and account for the endothermic heat of reaction.

76 Hence, in this work, the FCC unit simulation model of Han et al., (2011a, b) is used on  
77 gPROMS software for parameter estimation to estimate activation energies, frequency factors  
78 and enthalpies of a new riser cracking reactions scheme of an industrial FCC plant located in  
79 Sudan. This new and comprehensive kinetic model and parameters of the reaction scheme of  
80 the industrial plant in Sudan can be used to simulate other FCC units with similar product  
81 distribution.

### 82 **1.1. Kinetic modelling and model parameters**

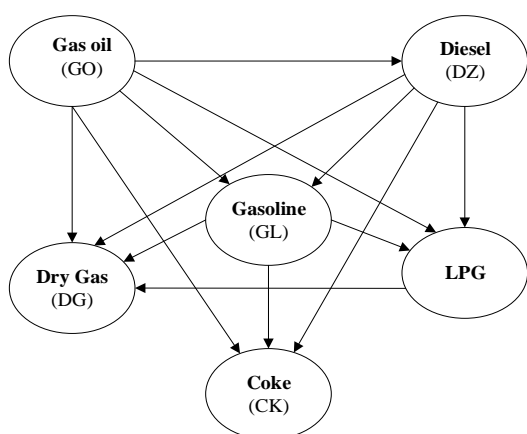
83 The FCC is a significant unit that has drawn the attention of many researchers. However,  
84 little achievements have been made when it comes to the accurate understanding of the riser  
85 unit behaviour. This could be due to the complexity of the riser's feed which is a complex  
86 mixture of extremely large number of unknown compounds. Also, there is the complex  
87 hydrodynamics of the riser owing to the three phases (solid, liquid and gas) nature along with  
88 gas phase volume expansion due to vaporization and cracking reaction (Kumar and Reddy,  
89 2011). The challenge with the cracking reaction is its characterization. Most research efforts  
90 to model cracking kinetics consider components with similar characteristics as a single lump  
91 and each lump is considered unique. There are three kinds of such lumping strategy. The first  
92 is the parametric strategy that considers a lump, being the feed, which cracks into some  
93 lumps such as gasoline, gas and coke as products of cracking reactions (Theologos and  
94 Markatos, 1993, Jacob et al., 1976). The second type of lumping strategy is pseudo-cracking  
95 where the feedstock and products are considered to be a mixture of some hypothetical or  
96 pseudo components (Bollas et al., 2004, Gupta et al., 2007) giving rise to many lumps. The

97 third is the structure oriented lumping, which offers a basis for molecular based modelling of  
98 all refinery processes. It creates reaction networks of varying sizes and difficulties and treats  
99 hydrocarbon molecules as structures that builds continually (Quann and Jaffe, 1992).  
100 Although each strategy has its advantage and disadvantage, the lumping strategy has gained  
101 acceptability in the characterization of reactants and products from the cracking reactions in  
102 the FCC unit, with different number of lumps used by different researchers.  
103 The 3-lump kinetic model (Weekman, 1968) was the first to be presented, where gas oil was  
104 cracked into two other lumps; gasoline and gases plus coke. Coke is useful when burnt in the  
105 regenerator to provide the heat required for the cracking reactions in the riser, hence, the 3-  
106 lump model was further broken to form the 4-lump model (Lee et al., 1989). The 4-lump  
107 model includes gas oil, gasoline, gases and coke. Further increment of lumps were added to  
108 acquire more detail and to achieve a higher level of accuracy in the lumping strategy. This led  
109 to the development of several lumps and although the number of lumps may be the same, the  
110 nature of lumps may be different. For instance, the six-lump model of Souza et al., (2011) is  
111 different from the six-lump model of Mu et al. (2005). The increase in number of lumps  
112 continued to the 5-lump model (Dupain et al., 2003, Jorge Ancheyta Juarez, 1999); the 6-  
113 Lump model (Takatsuka et al., 1987, Du et al., 2014, Xiong et al., 2015, Zhang et al., 2017);  
114 7-lump model (Heydari et al., 2010, Xu et al., 2006); 8-lump model (Gao et al., 2014,  
115 Hagelberg et al., 2002); 9-lump model (You, 2013, You et al., 2006); 10-lump model (Jacob  
116 et al., 1976); 11 lump model (Mao et al., 1985, Sa et al., 1985, Zhu et al., 1985) and so on. In  
117 this work, new kinetic parameters are developed for a new six-lump model.

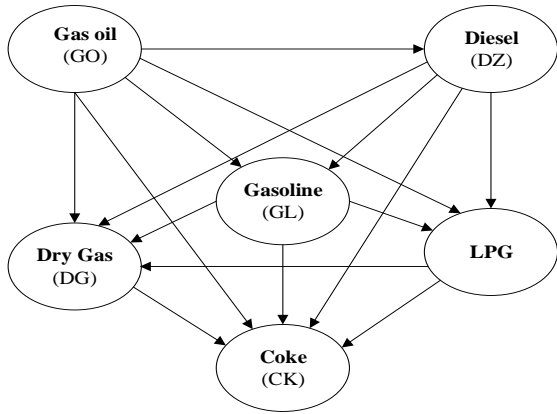
## 118 **1.2. Six-lump model**

119 Although several six-lump models have been used in the modelling of the FCC unit kinetic  
120 reactions, all have their unique characteristics. A six lump kinetic model (Baldessar and  
121 Negrão, 2005, Souza et al., 2011) was used that cracks gasoil into gasoline, LPG, fuel gas,  
122 light cycle oil (LCO) and coke lumps. Mu et al. (2005) presented a different six-lump model;  
123 it cracks residual fuel oil (RFO) into heavy fuel oil (HFO), light fuel oil (LFO), gasoline, gas  
124 and coke. Besides the fact that their product distributions are different, their respective  
125 frequency factors and activation energies are different and were presented (Mu et al., 2005)  
126 without the heat of reaction for each cracking reaction. Hence, these kinetic models may not  
127 be suitable for use with the comprehensive model (Han and Chung, 2001a, Han and Chung,  
128 2001b) of FCC unit used in this study. Another six-lump model, which is similar and  
129 presented the same lumps as the one developed in this work was presented in the literature

130 (Xiong et al., 2015, Du et al., 2014, Zhang et al., 2017), the difference being the secondary  
 131 cracking reactions of LPG and dry gas into coke. This difference is significant because many  
 132 authors assume that the cracking reactions of some lumps into others lumps can be neglected  
 133 to reduce the total number of kinetic parameters to be accounted for. However, with a  
 134 powerful tool that performs accurate parameter estimation, all parameters can be estimated,  
 135 and the data can then be subjected to the decision of whether to neglect some reactions or not.  
 136 Therefore, the new kinetic model accounts for kinetic data for the secondary cracking  
 137 reactions of LPG and dry gas into coke. Again, only kinetic data such as the frequency factors  
 138 and activation energies are presented (Du et al., 2014, Xiong et al., 2015, Zhang et al., 2017)  
 139 without the heat of reactions of the kinetic equations involved, which are required by the riser  
 140 model used in this study. The six-lump kinetic model developed in this work cracks gas oil  
 141 into diesel, gasoline, LPG, dry gas and coke. It estimates the heat of reactions involved in the  
 142 six-lump cracking reactions and presents kinetic data (frequency factors, activation energies  
 143 and heats of reaction) for the secondary reactions of the conversion of LPG and dry gas into  
 144 coke. Figure 1 shows a schematic diagram of the kinetic model presented by Du et al.,  
 145 (2014), Xiong et al (2015) and Zhang et al. (2017), even though Xiong et al (2015) did not  
 146 present the secondary cracking of LPG to dry gas, while Figure 2 shows the proposed kinetic  
 147 model to be used in this work. As stated earlier, the difference between Figures 1 and 2 is the  
 148 secondary cracking reactions of LPG and dry gas into coke.



149  
 150 Figure 1. Six-lump kinetic model (Du et al., 2014, Xiong et al., 2015, Zhang et al., 2017)

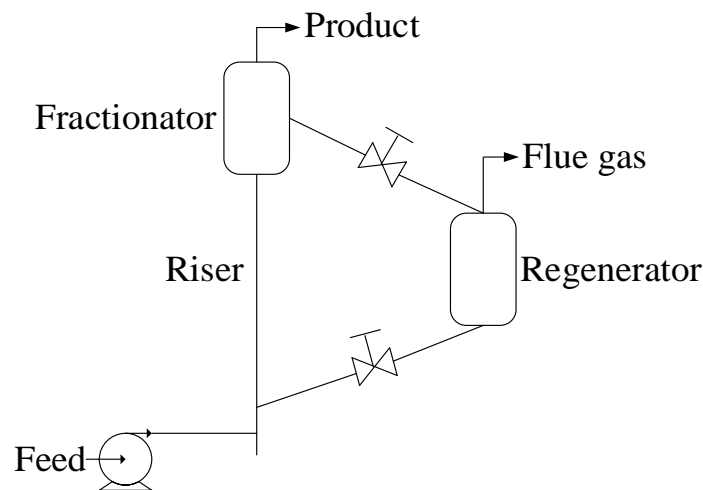


151  
152 Figure 2. Six-lump kinetic model as proposed in this work

153 **2. The Riser Model**

154 A typical configuration of a FCC process consist of two major units; the riser and regenerator  
155 as shown in Figure 3. The refinery in Sudan is a type of a residue FCC unit (RFCC)

156



157  
158 Figure 3. A schematic diagram of the RFCC unit

159

160 The FCC riser is modelled as a one-dimensional plug flow reactor without axial and radial  
161 dispersion. It was established that the one dimensional model is capable of predicting the  
162 overall performance of the riser (Theologos and Markatos, 1993), hence it can be adequate  
163 for the parameter estimation in this work. The regenerated catalyst meets gas oil and  
164 vaporizes almost immediately into the riser moving pneumatically upward. This leads to a  
165 cracking reaction on catalyst surface to form valuable fuels such as diesel, gasoline, LPG, dry  
166 gas and coke. The industrial riser considered in this work is 47.1 m in height and 1.36 m in  
167 diameter.

168 The riser simulation model combines mass, energy and momentum balance equations for the  
169 catalyst and the gaseous phases based on the following assumptions:

- 170 1. The hydrocarbon feed instantly vaporizes as it comes into contact with the hot catalyst  
171 from the regenerator, then moves upward in thermal equilibrium with the catalyst and  
172 there is no loss of heat from the riser (Ali et al., 1997).
- 173 2. The cracking reactions only take place in the riser and on the catalyst surface. The  
174 reactions are assumed fast enough to justify steady state operation.
- 175 3. The rates of dispersion and adsorption inside the catalyst particles are negligible.

176

177 Some model equations along with some of their parameters used in this simulation study  
178 were adopted from literature (Han and Chung, 2001a, Han and Chung, 2001b, John et al.,  
179 2017a, John et al., 2017b). The feed conditions and other parameters were obtained from an  
180 industrial refinery from Sudan and presented in Appendix Table A.3. Material balance  
181 equations for the various lumps showing the six-lump; gas oil, diesel, gasoline, LPG, dry gas  
182 and coke are represented by Equations (15-20). The overall rates of reaction for the six  
183 lumps: gas oil  $R_{go}$ , diesel  $R_{gdz}$ , gasoline  $R_{gl}$ , LPG  $R_{lpg}$ , dry gas  $R_{dg}$ , and coke  $R_{ck}$ , were  
184 developed from the six-lump kinetic reaction scheme and are presented in Equations (21-26).  
185 These equations are new six lumped model equations since they include the secondary  
186 reactions of the cracking of LPG and dry gas to coke which were not in the literature. Each  
187 overall rate of reaction is a function of an overall rate constant that is described by the  
188 Arrhenius equation given in Equations (27-41), which include the new overall rate constants  
189 of the secondary reactions of the cracking of LPG and dry gas to coke. During the catalytic  
190 cracking, endothermic heat from the regenerator is utilized in the riser, and the rate of heat  
191 removal by reaction,  $Q_{react}$ , is estimated by Equation 42, a unique feature of the current riser  
192 model used in this study. Equations (43 and 44) are derived from the energy balance of the  
193 riser showing the temperature of catalyst and gas phases. The equations that govern the  
194 hydrodynamics of the riser are described in Equations (45-59), with Equations (55-56)  
195 describing the momentum balance equations, which gives the catalyst and gas velocity  
196 distributions across the riser. The gas volume fraction,  $\epsilon_g$ , and catalyst volume fraction,  $\epsilon_c$ ,  
197 are obtained from Equation 45. They give a hydrodynamic constraint such that, the  
198 summation of the volume fractions add up to unity. Equation (51), the riser pressure, is  
199 obtained from the simple ideal gas relationship but well accounted for with  $Z$  as the  
200 compressibility factor (Equation 70). Equations (1-14) are riser model equations for four

201 lumped kinetic model used in this work to demonstrate the capability of the parameter  
202 estimation technique to predict the right kinetic parameters.

203 The riser model equations are a set of nonlinear and algebraic equations and gPROMS is used  
204 for the solution. gPROMS is a general process modelling system for simulation, optimisation  
205 and control (both steady state and dynamic) of highly complex processes such as the FCC  
206 unit riser. It is an equation oriented software and all solvers have been designed specifically  
207 for large-scale systems such as the FCC unit with no restrictions regarding problem size other  
208 than those imposed by available machine memory (Mujtaba, 2012). In spite of the robustness  
209 of gPROMS, there are just a few known literature on the use of the software to solve the  
210 models of the FCC unit. These (John et al., 2017a, John et al., 2017b, John et al., 2017c,  
211 Jarullah et al., 2017) are the first attempts and gPROMS proves to be a reliable software. The  
212 riser model is constructed in the model section and the parameters are specified in the process  
213 section of the gPROMS software 4.2.0. The gPROMS software is capable of analysing the set  
214 of equations to determine the stiffness of the system and calls on the appropriate solvers, in  
215 this case, solvers capable of solving the nonlinear system of equations of the riser model and  
216 perform adequate parameter estimation.



Table 1: Equations and descriptions

Description of variable	Equations	Eq.No
<b>Kinetic model equations for the four-lumped model (Han and Chung, 2001a, Han and Chung, 2001b)</b>		
Gas oil fractional yield along the riser height	$\frac{dy_{go}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{go}$	(1)
Gasoline fractional yield along the riser height	$\frac{dy_{gl}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{gl}$	(2)
Light gas fractional yield along the riser height	$\frac{dy_{gs}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{gs}$	(3)
Coke fractional yield along the riser height	$\frac{dy_{ck}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{ck}$	(4)
Rates of reaction for gas oil $R_{Go}$	$R_{go} = -(k_1 + k_2 + k_3)y_{go}^2 \phi_c$	(5)
Rates of reaction for gasoline $R_{Gl}$	$R_{gl} = (k_1 y_{go}^2 - k_4 y_{gl} - k_5 y_{gl}) \phi_c$	(6)
Rates of reaction for light gas $R_{Gs}$	$R_{gs} = (k_2 y_{go}^2 - k_4 y_{gl}) \phi_c$	(7)
Rates of reaction for coke $R_{Ck}$	$R_{ck} = (k_3 y_{go}^2 - k_5 y_{gl}) \phi_c$	(8)
Overall rate constants for cracking gas oil to gasoline	$k_1 = k_{10} \exp\left(\frac{-E_1}{R_g T_g}\right)$	(9)
Overall rate constants for cracking gas oil to gases	$k_2 = k_{20} \exp\left(\frac{-E_2}{R_g T_g}\right)$	(10)
Overall rate constants for cracking gas oil to coke	$k_3 = k_{30} \exp\left(\frac{-E_3}{R_g T_g}\right)$	(11)

Overall rate constants for cracking gasoline to gases	$k_4 = k_{40} \exp\left(\frac{-E_4}{R_g T_g}\right)$	(12)
Overall rate constants for cracking gasoline to coke	$k_5 = K_{50} \exp\left(\frac{-E_5}{R_g T_g}\right)$	(13)
$Q_{\text{React}}$ is the rate of heat generation or heat removal by reaction	$Q_{\text{react}} = -(\Delta H_1 k_1 y_{go}^2 + \Delta H_2 k_2 y_{go}^2 + \Delta H_3 k_3 y_{go}^2 + \Delta H_4 k_4 y_{gl} + \Delta H_5 k_5 y_{gl}) \phi_c$	(14)
<b>Kinetic model equations for the six-lump model developed in this work</b>		
Gas oil fractional yield along the riser height	$\frac{d_{y_{go}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{go}$	(15)
Diesel fractional yield along the riser height	$\frac{d_{y_{dz}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{dz}$	(16)
Gasoline fractional yield along the riser height	$\frac{d_{y_{gl}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{gl}$	(17)
LPG fractional yield along the riser height	$\frac{d_{y_{lpg}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{lpg}$	(18)
Dry gas fractional yield along the riser height	$\frac{d_{y_{dg}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{dg}$	(19)
Coke fractional yield along the riser height	$\frac{d_{y_{ck}}}{dx} = \frac{\rho_c \varepsilon_c \Omega}{F_g} R_{ck}$	(20)
Overall rate of reaction for gas oil $R_{go}$	$R_{go} = -(k_{go-dz} + k_{go-g} + k_{go-ck} + k_{go-lpg} + k_{go-dg}) y_{go}^2 \phi_c$	(21)
Overall rate of reaction for gasoline $R_{dz}$	$R_{dz} = ((k_{go-dz} y_{go}^2) - (k_{dz-ck} + k_{dz-gl} + k_{dz-lpg} + k_{dz-dg}) y_{dz}) \phi_c$	(22)

Overall rate of reaction for gasoline $R_{Gl}$	$R_{gl} = (k_{go-g} y_{go}^2 - k_{dz-gl} y_{dz} - (k_{gl-lpg} + k_{gl-dg} + k_{gl-ck}) y_{gl}) \phi_c$	(23)
Overall rate of reaction for light gas $R_{lpg}$	$R_{lpg} = (k_{go-lpg} y_{go}^2 + k_{dz-lpg} y_{dz} + k_{gl-lpg} y_{gl} - (k_{lpg-dg} + k_{lpg-ck}) y_{lpg}) \phi_c$	(24)
Overall rate of reaction for light gas $R_{dg}$	$R_{dg} = (k_{go-dg} y_{go}^2 + k_{dz-dg} y_{dz} + k_{gl-dg} y_{gl} + k_{lpg-dg} y_{lpg} - k_{dg-ck} y_{dg}) \phi_c$	(25)
Overall rate of reaction for coke $R_{ck}$	$R_{ck} = (k_{go-ck} y_{go}^2 + k_{dz-ck} y_{dz} + k_{gl-ck} y_{gl} + k_{lpg-ck} y_{lpg} - k_{dg-ck} y_{dg}) \phi_c$	(26)
Overall rate constants for cracking gas oil to diesel	$k_{go-dz} = k_{0_{go-dz}} \exp\left(\frac{-E_{go-dz}}{R_g T_g}\right)$	(27)
Overall rate constants for cracking gas oil to gasoline	$k_{go-gl} = k_{0_{go-gl}} \exp\left(\frac{-E_{go-gl}}{R_g T_g}\right)$	(28)
Overall rate constants for cracking gas oil to LPG	$k_{go-lpg} = k_{0_{go-lpg}} \exp\left(\frac{-E_{go-lpg}}{R_g T_g}\right)$	(29)
Overall rate constants for cracking gas oil to dry gas	$k_{go-dg} = k_{0_{go-dg}} \exp\left(\frac{-E_{go-dg}}{R_g T_g}\right)$	(30)
Overall rate constants for cracking gas oil to coke	$k_{go-ck} = k_{0_{go-ck}} \exp\left(\frac{-E_{go-ck}}{R_g T_g}\right)$	(31)
Overall rate constants for cracking diesel to gasoline	$k_{dz-gl} = k_{0_{dz-gl}} \exp\left(\frac{-E_{dz-gl}}{R_g T_g}\right)$	(32)
Overall rate constants for cracking diesel to LPG	$k_{dz-lpg} = k_{0_{dz-lpg}} \exp\left(\frac{-E_{dz-lpg}}{R_g T_g}\right)$	(33)
Overall rate constants for cracking diesel to dry gas	$k_{dz-dg} = k_{0_{dz-dg}} \exp\left(\frac{-E_{dz-dg}}{R_g T_g}\right)$	(34)

Overall rate constants for cracking diesel to coke	$k_{dz-ck} = k_{0_{dz-ck}} \exp\left(\frac{-E_{dz-ck}}{R_g T_g}\right)$	(35)
Overall rate constants for cracking gasoline to LPG	$k_{gl-lpg} = k_{0_{gl-lpg}} \exp\left(\frac{-E_{gl-lpg}}{R_g T_g}\right)$	(36)
Overall rate constants for cracking gasoline to dry gas	$k_{gl-dg} = k_{0_{gl-dg}} \exp\left(\frac{-E_{gl-dg}}{R_g T_g}\right)$	(37)
Overall rate constants for cracking gasoline to coke	$k_{gl-ck} = k_{0_{gl-ck}} \exp\left(\frac{-E_{gl-ck}}{R_g T_g}\right)$	(38)
Overall rate constants for cracking LPG to dry gas	$k_{lpg-dg} = k_{0_{lpg-dg}} \exp\left(\frac{-E_{lpg-dg}}{R_g T_g}\right)$	(39)
Overall rate constants for cracking LPG to coke	$k_{lpg-ck} = k_{0_{lpg-ck}} \exp\left(\frac{-E_{lpg-ck}}{R_g T_g}\right)$	(40)
Overall rate constants for cracking dry to coke	$k_{dg-ck} = k_{0_{dg-ck}} \exp\left(\frac{-E_{dg-ck}}{R_g T_g}\right)$	(41)

<p><math>Q_{\text{React}}</math> is the rate of heat generation or heat removal by reaction</p>	$Q_{\text{react}} = -(\Delta H_{\text{go-dz}} k_{\text{go-dz}} y_{\text{go}}^2 + \Delta H_{\text{go-gl}} k_{\text{go-gl}} y_{\text{go}}^2 + \Delta H_{\text{go-ck}} k_{\text{go-ck}} y_{\text{go}}^2 + \Delta H_{\text{go-lpg}} k_{\text{go-lpg}} y_{\text{go}}^2 + \Delta H_{\text{go-dg}} k_{\text{go-dg}} y_{\text{go}}^2 + \Delta H_{\text{dz-ck}} k_{\text{dz-ck}} y_{\text{dz}} + \Delta H_{\text{dz-gl}} k_{\text{dz-gl}} y_{\text{dz}} + \Delta H_{\text{dz-lpg}} k_{\text{dz-lpg}} y_{\text{dz}} + \Delta H_{\text{dz-dg}} k_{\text{dz-dg}} y_{\text{dz}} + \Delta H_{\text{gl-lpg}} k_{\text{gl-lpg}} y_{\text{gl}} + \Delta H_{\text{gl-dg}} k_{\text{gl-dg}} y_{\text{gl}} + \Delta H_{\text{gl-ck}} k_{\text{gl-ck}} y_{\text{gl}} + \Delta H_{\text{lpg-dg}} k_{\text{lpg-dg}} y_{\text{lpg}} + \Delta H_{\text{lpg-ck}} k_{\text{lpg-ck}} y_{\text{lpg}} + \Delta H_{\text{dg-ck}} k_{\text{dg-ck}} y_{\text{dg}}) \phi_c$	(42)
<b>Riser equations from energy balance equation</b>		
<p>Temperature of catalyst along the riser height</p>	$\frac{dT_c}{dx} = \frac{\Omega h_p A_p}{F_c C_{pc}} (T_g - T_c)$	(43)
<p>Temperature of gas phase along the riser height</p>	$\frac{dT_g}{dx} = \frac{\Omega}{F_g C_{pg}} [h_p A_p (T_c - T_g) + \rho_c \varepsilon_c Q_{\text{react}}]$	(44)
<b>Riser hydrodynamic equations</b>		
<p>Gas volume fraction, <math>\varepsilon_g</math>, and catalyst volume fraction, <math>\varepsilon_c</math></p>	$\varepsilon_c = \frac{F_c}{v_c \rho_c \Omega}; \varepsilon_g = 1 - \varepsilon_c$	(45)
<p>Cross sectional area of the riser</p>	$\Omega = \frac{\pi D^2}{4}$	(46)
<p>Catalyst deactivation</p>	$\phi_c = \exp(-\alpha_c C_{ck})$	(47)
<p>Catalyst deactivation coefficient</p>	$\alpha_c = \alpha_{c0} \exp\left(\frac{-E_c}{R_g T_g}\right) (R_{AN})^{\alpha_{c*}}$	(48)

Coke on catalyst	$C_{ck} = C_{ckCL1} + \frac{F_g Y_{ck}}{F_c}$	(49)
Density of the gas phase	$\rho_g = \frac{F_g}{\varepsilon_g v_g \Omega}$	(50)
Riser pressure	$P_{RS} = \rho_g \frac{Z R_g T_g}{M_{wg}}$	(51)
Catalyst-to-oil ratio (C/O)	$C/O \text{ ratio} = \frac{F_c}{F_g}$	(52)
Pseudo-reduced temperature in the riser	$T_{pr} = \frac{T_g}{T_{pc}}$	(53)
Pseudo-reduced pressure in the riser	$P_{pr} = \frac{P_{RS}}{P_{pc}}$	(54)
Catalyst and gas velocity distribution across the riser	$\frac{dv_c}{dx} = - \left( G_c \frac{\Omega}{F_c} \frac{d\varepsilon_c}{dx} - \frac{C_f(v_g - v_c)\Omega}{F_c} + \frac{2f_{rc}v_c}{D} + \frac{g}{v_c} \right)$	(55)
Catalyst and gas velocity distribution across the riser	$\frac{dv_g}{dx} = - \left( \frac{\Omega}{F_g} \frac{dP_{RS}}{dx} - \frac{C_f(v_c - v_g)}{F_g} + \frac{2f_{rg}v_g}{D} + \frac{g}{v_g} \right)$	(56)
Stress modulus of the catalyst (Tsuo and Gidaspow, 1990)	$G_c = 10^{(-8.76\varepsilon_g + 5.43)}$	(57)
Catalyst temperature at the vaporization section	$T_{cFS} = T_{cCL1} - \frac{F_{lg}}{F_{cCL1} C_{pc}} \left[ C_{plg}(T_{gFS} - T_{lg}) + \frac{F_{ds} C_{pds}}{F_{lg}} (T_{gFS} - T_{ds}) + \Delta H_{vlg} \right]$	(58)
Gas phase temperature at the vaporization section	$T_{gFS} = \frac{B_{lg}}{A_{lg} - \log(P_{FS} Y_{goFS})} - C_{lg}$	(59)

Pressure at the vaporization	$P_{FS} = P_{RT} + \Delta P_{RS}$	(60)
Weight fraction of feed (gas oil) at the vaporization section	$y_{goFS} = \frac{F_{lg}}{F_{lg} + F_{ds}}$	(61)
Velocity of gas phase at the vaporization section	$v_{gFS} = \frac{F_{lg} + F_{ds}}{\rho_{gFS}(1 - \varepsilon_{cCL1})\Omega_{FS}}$	(62)
Velocity of entrained catalyst at the vaporization section	$v_{cFS} = \frac{F_{cCL1}}{\rho_c \varepsilon_{cCL1}\Omega_{FS}}$	(63)
Gas oil density at the vaporization section	$\rho_{gFS} = \frac{P_{FS}M_{wgFS}}{R_g T_{gFS}Z_{gFS}}$	(64)
Catalyst phase velocity	$v_{cRS}^{(0)} = v_{cFS}$	(65)
Gas phase velocity	$v_{gRS}^{(0)} = v_{gFS}$	(66)
Catalyst mass flowrate	$F_{cRS} = F_{cCL1}$	(67)
Gas phase mass flowrate	$F_{gRS} = F_{lg} + F_{ds}$	(68)
Heat of vaporization of gas oil	$\Delta H_{vlg} = 0.3843T_{MABP} + 1.0878 * 10^3 \exp\left(\frac{-M_{wm}}{100}\right) - 98.153$	(69)
Z factor of Heidaryan et al., (2010)	$Z = \ln \left[ \frac{A_1 + A_3 \ln(P_{pr}) + \frac{A_5}{T_{pr}} + A_7(\ln P_{pr})^2 + \frac{A_9}{T_{pr}^2} + \frac{A_{11}}{T_{pr}} \ln(P_{pr})}{1 + A_2 \ln(P_{pr}) + \frac{A_4}{T_{pr}} + A_6(\ln P_{pr})^2 + \frac{A_8}{T_{pr}^2} + \frac{A_{10}}{T_{pr}} \ln(P_{pr})} \right]$	(70)

217

218

### 219 **3. Parameter Estimation Techniques**

220 Parameter estimation is usually carried out for a particular model with the aim of optimising  
221 some parameters and in some cases estimating such parameters using experimental data. The  
222 optimal estimated parameters are obtained as the best match between the experimental data  
223 and the values calculated by the model (Dobre and Marcano, 2007). The use of suitable and  
224 accurate models in advance process analysis and optimization is very important. The  
225 accuracy of the model for a particular process depend on having the right parameters in use.  
226 However, accurate online information of some unknown parameters is difficult to obtain even  
227 with accurate models but can be estimated using parameter estimation. It was identified that  
228 parameter estimation is not an easy task in the development of process models, whether  
229 dynamic or steady state, and that fitting a model to a set of measurement is the challenge  
230 (Soroush, 1998).

231 There are many types of parameter estimation techniques and they are mainly based on the  
232 systems used. The parameter estimation by state estimation technique found common use in  
233 chemical and biochemical engineering in systems of dynamic models where each model  
234 represents an unknown parameter to be estimated (Tatiraju and Soroush, 1997, Soroush,  
235 1997, Soroush, 1998). Another parameter estimation technique is achieved through on-line  
236 optimization. This is a case where the estimates are derived from minimization of the sum of  
237 squared errors of the optimization problem through comparing the experimental and  
238 calculated results within some given range of constraints (Muske and Rawlings, 1995,  
239 Robertson et al., 1996). This method has gained acceptance in the parameter estimation of  
240 chemical processes (Jarullah et al., 2011) and it is the method used in this work. Another  
241 method is the parameter estimation by model inversion (Tatiraju and Soroush, 1998) which  
242 comprises a parameter estimate of left inverse of process model concurrently estimating least-  
243 squared errors via on-line measurements (Tatiraju and Soroush, 1998). The method of  
244 calorimetric technique for estimating kinetic parameters of process systems is achieved with  
245 the use of mass and energy balance models of the systems (Régnier et al., 1996).

246 Parameter estimation for kinetic and compositional values of processes is based on  
247 optimization techniques that are either Linear (LN) or non- linear (NLN) regressions. These  
248 estimations are readily carried out using computer programs and software (Nowee et al.,  
249 2007), which makes complex NLN models much easier to solve. There are many NLN  
250 optimization methods such as maximum likelihood estimation (Tjoa and Biegler, 1992)  
251 where it seeks a weighted least squares fit to the measurements with an underdetermined



252 process model. Other methods includes the Bayesian parameter estimation, which uses the  
253 Bayesian regularization back propagation (Ma and Weng, 2009). There is Newton-Raphson  
254 method (Souza et al., 2009) which is a robust technique for solving nonlinear problems.  
255 There is also the Genetic algorithm and its various types known to be common in academia  
256 and the industry due its insightfulness, easy applicability and effectiveness in solving highly  
257 nonlinear, mixed integer optimization problems that are typical of complex engineering  
258 systems such as the FCC unit (Hassan et al., 2005, Kordabadi and Jahanmiri, 2005, Wang et  
259 al., 2005). The Successive Quadratic Programming (SQP) (Tjoa and Biegler, 1992) are  
260 readily implementable with the help of computer programming packages and software. It is  
261 very much utilized by the gPROMS software (gPROMS, 2013) and it is proved to be very  
262 capable (Jarullah et al., 2011).

### 263 **3.1. Parameter estimation of kinetic parameters using gPROMS**

264 Parameter Estimation can be achieved for complex models using the parameter estimation  
265 platform of gPROMS software. However, it requires detailed gPROMS process model that  
266 captures the system's physical and chemical interactions like the riser model used in this  
267 study. The process model representing the system should have parameters that can be tuned  
268 to make the model predictions adequately aligned with real data. Such model parameters,  
269 particularly in this work, are heat of reactions, frequency factors and activation energies. The  
270 more accurate these parameters are, the closer the model's response to reality (gPROMS,  
271 2013). The method used in making these parameters to fit with laboratory or plant/industrial  
272 data is called parameter estimation.

273 gPROMS uses the Maximum Likelihood formulation technique for parameter estimation  
274 which estimates parameters in the physical model of the process and the variance model of  
275 the measuring instruments. The measuring instrument can be a sensor that is either constant  
276 variance for temperature measurement (thermocouple) with an accuracy of +/- 1K, or  
277 constant relative variance for measuring of concentration (composition analyser) with an  
278 error of +/- 2%, or both measuring instruments, in which case it is called the heteroscedastic  
279 variance, combining both constant variance and constant relative variance (gPROMS, 2013).

280 The riser process model as shown in Table 1 is a set of differential –algebraic equations  
281 (DAEs) with  $\xi$ ,  $\eta$  and  $\theta$  as vector parameters to be estimated. In this case,  
282  $[k_{o1}, k_{o2}, k_{o3}, k_{o4}, k_{o5}]$ ,  $[E_1, E_2, E_3, E_4, E_5]$  and  $[\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_5]$  for the case of the  
283 four-lump model which is used to test the technique employed in this work.

284 For the case of the six-lump model proposed in this work

$$\begin{aligned}
 & \left[ k_{dz-gl}, k_{dz-lpg}, k_{dz-dg}, k_{gl-lpg}, k_{gl-dg}, k_{gl-ck}, k_{lpg-dg}, k_{lpg-ck}, k_{dg-ck}, y_{dg}, k_{go-dz}, \right. \\
 & \quad \left. k_{go-gl}, k_{go-ck}, k_{go-lpg}, k_{go-dg}, k_{dz-ck} \right], \\
 & \left[ E_{dz-gl}, E_{dz-lpg}, E_{dz-dg}, E_{gl-lpg}, E_{gl-dg}, E_{gl-ck}, E_{lpg-dg}, E_{lpg-ck}, K_{dg-ck}, K_{go-dz}, \right] \text{ and} \\
 & \left[ \Delta H_{dz-gl}, \Delta H_{dz-lpg}, \Delta H_{dz-dg}, \Delta H_{gl-lpg}, \Delta H_{gl-dg}, \Delta H_{gl-ck}, \Delta H_{lpg-dg}, \Delta H_{lpg-ck}, \Delta H_{dg-ck}, \right. \\
 & \quad \left. \Delta H_{go-dz}, \Delta H_{go-gl}, \Delta H_{go-ck}, \Delta H_{go-lpg}, \Delta H_{go-dg}, \Delta H_{dz-ck} \right].
 \end{aligned}$$

288 When solving a Maximum Likelihood Parameter Estimation problem as in this case,  
 289 gPROMS determines the uncertain physical and variance model parameters values ( $\xi$ ,  $\eta$  and  
 290  $\theta$ ) which maximise the probability that the mathematical model will predict the measurement  
 291 values obtained from the experiments. Assuming independent, normally distributed  
 292 measurement errors  $\epsilon_{ijk}$ , with zero means and standard deviations,  $\sigma_{ijk}$ , the estimation is  
 293 achieved with the use of the following objective function:

$$\begin{aligned}
 & \Phi(\xi, \eta, \theta) = \frac{M}{2} \ln(2\pi) + \frac{1}{2} \min_{(\xi, \eta, \theta)} \left\{ \sum_{i=1}^{M\alpha} \sum_{i=1}^{M\beta_i} \sum_{i=1}^{M\gamma_{ij}} \left[ \ln(\sigma_{ijk}^2) + \frac{(y_{ijk}^{exp} - y_{ijk}^{cal})^2}{\sigma_{ijk}^2} \right] \right\} \\
 & (71)
 \end{aligned}$$

296 Where M is total number of measurements taken experimentally and  $\xi, \eta$  &  $\theta$  are set of  
 297 model parameters to be estimated. The acceptable values may be subject to given lower and  
 298 upper bounds:  $\xi^l \leq \xi \leq \xi^u$ ,  $\eta^l \leq \eta \leq \eta^u$ ,  $\theta^l \leq \theta \leq \theta^u$ .

### 299 3.2. Mathematical formulation for kinetic parameters estimation

300 The estimation of kinetic parameters using model based technique along with experimental  
 301 (generated from model and plant) data is carried out in this work. The method involves the  
 302 use of optimization technique in gPROMS to the minimize sum of squared errors (SSE)  
 303 between experimental values  $y_i^{exp}$  (generated by using a new technique from the model  
 304 having obtained input and output data from the plant) and calculated values  $y_i^{cal}$ . This  
 305 technique has two approaches: first, simulation for converging all the equality constraints and  
 306 satisfying the inequality constraints and the second, performing the optimization where the  
 307 objective function is as summarily written:

$$308 \quad Obj(SSE) = \sum_{M=1}^{M_t} (y_i^{exp} - y_i^{cal})^2 \quad (72)$$

309 Where  $y$  is the mass fraction of lumps and  $i$  refers to the various lumps in the riser.

310 The parameter estimation problem statement can be written as:

Given The fixed riser reactor configuration, feed quality and characteristics, catalyst properties and process operational conditions

Optimize The kinetics parameters; activation energies  $E_j$ , heat of reactions  $\Delta H_j$  and frequency factors  $k_{oj}$  at given process conditions

So as to minimize The sum of square errors (SSE)

Subject to Equality and inequality constraints

311

312 Mathematically;

313  $\min_{\xi, \eta, \theta} SSE$

314 s. t.

$f(x, z'(x), z(x), u(x), v) = 0$  (model equations, equality constraints)

315  $\xi^l \leq \xi \leq \xi^u$  (inequality constraints)

316  $\eta^l \leq \eta \leq \eta^u$  (inequality constraints)

317  $\theta^l \leq \theta \leq \theta^u$  (inequality constraints)

318 Where  $f(x, z'(x), z(x), u(x), v) = 0$  is model equation,  $x$  is height of the riser and the  
 319 independent variable,  $u(x)$  is the decision variable;  $\xi$  the frequency factors  $k_{oj}$  with  $\xi^u$  as  
 320 the upper and  $\xi^l$  as lower limits;  $\eta$  the activation energies  $E_j$ , with  $\eta^u$  as upper and  $\eta^l$  as  
 321 lower limits;  $\theta$  as the heat of reaction  $\Delta H_j$ , with  $\theta^u$  as upper and  $\theta^l$  as lower limits.  $z(x)$  is  
 322 the differential and algebraic equations while  $z'(x)$  their derivative.  $v$  is the constants  
 323 parameters.

324 Using industrial data, and FCC unit kinetic and hydrodynamic models, the unknown  
 325 parameters of the proposed six-lump model in Figure 2 are estimated. The parameters to be  
 326 estimated are the activation energies, frequency factors and heats of reaction. Here, 45  
 327 unknown parameters of the proposed kinetic scheme (15 heats of reaction,  $\Delta H_j$ ; 15 frequency  
 328 factors,  $k_{oj}$ ; and 15 activation energies,  $E_j$ ) will be estimated. The frequency factors and  
 329 activation energies of six lumped models available in the literature are presented in Table 2.  
 330 The authors did not present the heats of reaction for the various cracking reactions of the six  
 331 lumps and do not have all the parameters for the cracking reactions LPG to dry gas and coke,  
 332 and dry gas to coke because the authors assumed the reactions are negligible. In this study,  
 333 the exiting kinetic data in Table 2 will be used to set guess values, including lower and upper  
 334 bounds for each parameter on the gPROMS parameter estimation platform to estimate the 45  
 335 unknown parameters for the new kinetic scheme proposed in this study.

336

### 337 **3.2.1 Testing of parameter estimation technique**

338 Figure 4 shows a schematic diagram of the parameter estimation technique used in this work.  
339 It describes how input and output data from the plant were used in model simulation to  
340 generate online data across the discretised height of the riser which were used to represent  
341 experimental data in the gPROMS software for parameter estimation.

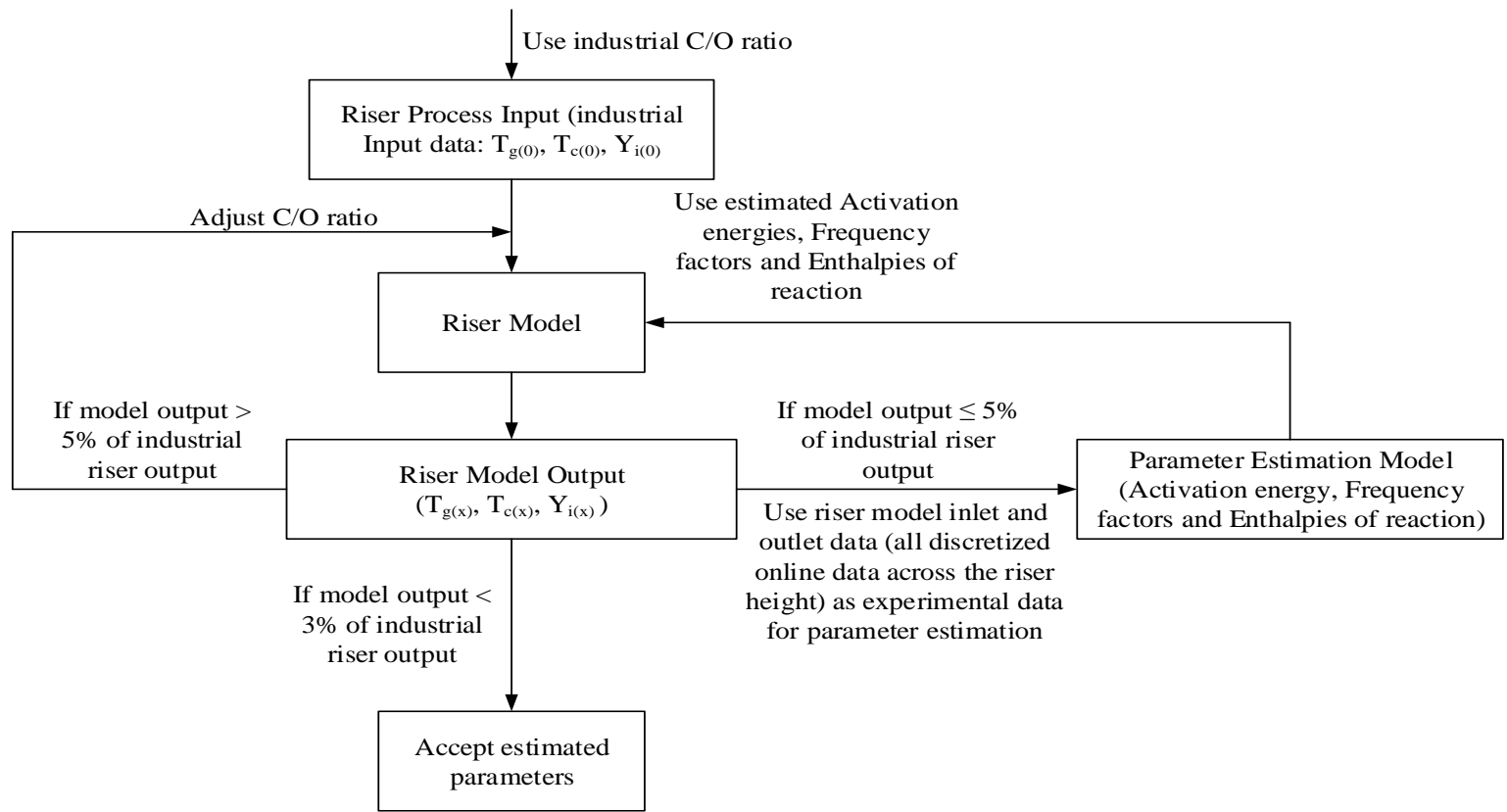
342 The feed condition is assumed 100% gas oil and the riser inlet temperatures of the feed  
343 (522.9 K) and the catalyst (904.7 K) from the regenerator. Gas oil input flow rate is 62.5 kg/s  
344 and that of the catalyst is 400.32 kg/s, which is a catalyst to oil ratio of 6.41. Parameter  
345 estimation in gPROMS require industrial data of the yields of all lumps of the riser which are  
346 used as experiments to estimate the unknown parameters. The available industrial data are the  
347 yields of the lumps at the exit of the riser, which are used as experimental data on the  
348 parameter estimation platform of gPROMS. The kinetic data in Table 2 are used with the  
349 riser model along with the only available industrial riser outputs, which are gas oil; 0.0478,  
350 diesel; 0.1857, gasoline; 0.4731, LPG; 0.1518, dry gas; 0.0483 and coke; 0.0891. The FCC  
351 process model is then simulated in gPROMS software to generate yields at discreet points of  
352 the riser height which gives more data that are then used on the parameter estimation  
353 platform of gPROMS. The newly estimated kinetic parameters are taken back into the riser  
354 model to obtain yields that are compared with the ones obtained from the industrial plant as  
355 described in Figure 4.

356 Table 2. Kinetic parameters of six-lumped model in the literature

Reaction	(Du et al., 2014)		(Xiong et al., 2015)		(Zhang et al., 2017)	
	Frequency Factor ( $k_{oi}$ )*(s <sup>-1</sup> )	Activation Energy (kJ/kmol) (E <sub>i</sub> )	Frequency Factor ( $k_{oi}$ )* (m <sup>3</sup> kg <sup>-1</sup> hr <sup>-1</sup> )	Activation Energy (E <sub>i</sub> ) (kJ/mol)	Frequency Factor ( $k_{oi}$ )*(s <sup>-1</sup> )	Activation Energy (kJ/kmol) (E <sub>i</sub> )
Gas Oil → Diesel	601.7	59.33	31328.5	47.6	$6.012 \times 10^4$	65.14
Gas Oil → Gasoline	$2.19 \times 10^5$	95.00	52064.7	43.4	$2.190 \times 10^5$	90.93
Gas Oil → Coke	28.91	177.2	574.4	30.0	$0.485 \times 10^3$	45.10
Gas Oil → LPG	16.96	38.05	6560.4	38.5	$9.053 \times 10^6$	70.53
Gas Oil → Dry Gas	1869	176.44	175.6	30.2	$1.870 \times 10^3$	69.34
Diesel → Coke	$2.7 \times 10^4$	174.4	46291.9	65.0	$6.760 \times 10^3$	61.40
Diesel → Gasoline	240.46	57.5	14683.7	54.1	$2.400 \times 10^3$	49.20
Diesel → LPG	46.08	141.95	40140.4	62.9	$4.680 \times 10^3$	68.65
Diesel → Dry Gas	1560	81.78	18604.8	66.7	$1.560 \times 10^4$	63.23
Gasoline → LPG	40.39	74.22	494068.4	80.5	$4.039 \times 10^4$	50.90
Gasoline → Dry Gas	1.6	135.34	245194.8	85.2	$9.420 \times 10^3$	36.81
Gasoline → Coke	1.22	44.26	241931.9	77.3	$0.515 \times 10^3$	37.23
LPG → Dry Gas	78.98	89.27	*	*	$1.081 \times 10^4$	65.80
LPG → Coke*						
Dry Gas → Coke*						

357 \*reactions not available in the authors kinetic schemes

358



359

360 Figure 4. Testing of parameter estimation technique

361 Since estimated parameters of a process can only be trusted if it is obtained from accurate  
362 models of that process, the riser mathematical model used for this parameter estimation was  
363 validated to ensure that it is not just accurate enough to simulate the riser, but it is able to  
364 estimate those kinetic parameters. Hence, to generate experimental data through simulation  
365 with the riser model, a known four-lump kinetic model of the riser (Han and Chung, 2001a,  
366 Han and Chung, 2001b) is used. From Figure 4, the procedure requires that the output data  
367 from the riser model simulation be compared with the actual plant riser outlet conditions. If  
368 the difference between the outputs from the simulation and plant data are less than or equal to  
369 5%, a reasonable limit of error, the values of the lumps and temperatures of the catalyst and  
370 gas phases at discrete heights of the riser are taken and used as experimental data on the  
371 parameter estimation platform of the gPROMS software. If the outputs from the simulation  
372 are more than 5%, the C/O ratio is adjusted to obtain riser output in the simulation almost the  
373 same as those of the plant. Once this happens, the values of the estimated parameters are  
374 deemed 'estimated' and are used in the riser model, which is expected to eventually predict  
375 the riser output to be the same as that of the plant. 5% level of error is accepted because the  
376 data generated will be subjected to some optimization during the parameter estimation  
377 process, where the level of error is further reduced as the estimated parameters are obtained.

### 378 **3.2.2 Testing of parameter estimation technique using four-lumped model**

379 A four-lumped kinetic model is chosen for testing the parameter estimation strategy because  
380 it is most widely used for FCC unit simulation. It also represents the major product  
381 classification of the FCC reactant and products, and have all the values of its kinetic  
382 parameters validated over the years. Additionally, using kinetic models with more than four  
383 lumps means more kinetic parameters to estimate. The less the lumps the fewer the kinetic  
384 parameters needed. The four lumped kinetic data in Table 3 are from the literature and have  
385 been used by many authors to simulate the FCC riser. In this section, these kinetic data of the  
386 four lumped kinetic model are used as guess values with upper and lower bounds, along with  
387 the riser mathematical model on the parameter estimation platform of gPROMS.

388 The mass and energy balance, and kinetic model equations used for the four-lump model are  
389 presented in Equations (1-14) together with the riser hydrodynamic Equations (44-70) in  
390 Table 1. The operational parameters and riser configuration used can be found in the same  
391 literature from where the riser model was adopted (Han and Chung, 2001a, Han and Chung,  
392 2001b). The riser conditions (temperatures and compositions) at discrete points along the

393 riser height obtained from the procedure in Figure 4 were used as experimental data in the  
 394 parameter estimation platform of the gPROMS software. The values are presented in Table 4.

395

396 Table 3. Kinetic parameters of four-lump model (Han and Chung, 2001b)

Reaction	Frequency Factor ( $k_i$ ) ( $s^{-1}$ )	Activation Energy (kJ/kmol) ( $E_i$ )	Heat of Reaction (kJ/kmol) $\Delta H_i$
Gas Oil $\rightarrow$ Gasoline	1457.50	57,359	195
Gas Oil $\rightarrow$ Gas	127.59	52,754	670
Gas Oil $\rightarrow$ Coke	1.98	31,820	745
Gasoline $\rightarrow$ Gas	256.81	65,733	530
Gasoline $\rightarrow$ Coke	0.000629	66,570	690

397

398 Table 4. Riser simulation results of the four-lump kinetic model

Riser Height (m)	Gas oil (wt. %)	Gasoline (wt. %)	Gases (wt. %)	Coke (wt. %)	Temperature of gas phase ( $T_g$ ) (K)	Temperature of catalyst phase ( $T_c$ ) (K)
0.0	1.0000	0.0000	0.0000	0.0000	679.0	911.6
5.0	0.5945	0.2918	0.0572	0.0295	808.5	833.7
10.0	0.4598	0.3937	0.0846	0.0313	807.6	817.6
15.0	0.3806	0.4403	0.1034	0.0352	802.2	809.1
20.0	0.3333	0.4741	0.1158	0.0348	796.8	801.3
25.0	0.2989	0.4929	0.1240	0.0409	794.6	797.8
*30.0	0.2750	0.5075	0.1365	0.0426	791.1	793.7
**30.0	0.2835	0.5137	0.1332	0.0354	791.5	791.9
% diff.	3.00	1.21	2.48	20.34	0.05	0.23

399 \*this row is riser exit condition obtained from the procedure in Figure 4, then used as  
 400 experimental data

401 \*\*this row riser exit condition obtained from literature (Han and Chung, 2001a, Han and  
 402 Chung, 2001b)

403

404 From Table 4, the percentage errors are within some level of acceptability, 5% and below as  
 405 described in Figure 4. Percentage difference for the coke lump was much because the value  
 406 of coke was assumed zero in the feed, which is not always the case. The values of the lumps  
 407 from the simulation are used as true representation of the online-discretised data along the  
 408 riser height. They are used as experimental data input in the parameter estimation platform of  
 409 the gPROMS software and used for the estimation of the four-lump kinetic parameters. The  
 410 four-lump kinetic parameters estimated are compared in Tables 6, 7 and 8 with the existing



411 four lumped kinetic data from the literature (Han and Chung, 2001a, Han and Chung, 2001b).  
412 As can be seen, the ability of the technique in predicting the exiting kinetic parameters is  
413 good. Hence, the parameter estimation technique is used to estimate the kinetic parameters of  
414 the new six-lumped kinetic model proposed in this work.

415

### 416 **3.2.3 Parameter estimation technique using six-lumped model**

417 The overall rate and Arrhenius equations written for the six-lumped model (Equations 21-42)  
418 as shown in Table 1, were used with the riser hydrodynamic equations. The kinetic  
419 parameters; frequency factors, activation energies and heat of reactions were estimated using  
420 guessed values between minimum and maximum of the respective kinetic parameter values in  
421 Table 2. In addition, the guess values of the kinetic data used for the cracking of LPG to dry  
422 gas and coke, and dry gas to coke on the parameter estimation platform were assumed to be  
423 between the minimum and maximum of the kinetic data presented in Table 2. Similarly,  
424 simulated results were generated for the six-lump model using the kinetic and hydrodynamic  
425 equations following the same parameter estimation technique described in Figure 4. These  
426 simulated riser exit compositions are then used as experimental data on the parameter  
427 estimation platform of the gPROMS software. The values shown in Table 5 were generated  
428 using the real plant configurations and industrial riser input and output conditions (Table A3  
429 of the Appendix) on the PROMS riser simulation.

430 This technique for parameter estimation provides a way to develop new kinetic schemes with  
431 just plant data. Once a plant inlet and outlet values (yields and process conditions) are known,  
432 along with a robust process model, which describes the process adequately, experimental  
433 results can be generated from the process model and be used for parameter estimation. This is  
434 a major novel contribution of this work. Another contribution is the development of a new  
435 kinetic scheme. Comparing Figures 1 and 2, the cracking reactions of dry gas to coke, and  
436 LPG to coke were added to Figure 1 to obtain a new six-lumped kinetic scheme shown in  
437 Figure 2. Most authors assumed that those reactions added were usually negligible, because it  
438 is usually difficult to measure them. With parameter estimation, it can be seen that they exit.  
439 This technique proved to be useful because the parameters estimated were used in the process  
440 model to predict the plants data with minimal percentage of errors as shown in Figures 5, 6, 7  
441 and 8. This technique is applicable to both laboratory and plant size processes which is an  
442 advantage.

443

444 **4. Results and Discussions**

445 The estimated kinetic parameters and the industrial riser simulation results are presented in  
 446 this section with the view to demonstrate the accuracy of the technique used in the simulation  
 447 of the plant where real data was obtained. The simulation also demonstrates the capability of  
 448 the gPROMS software which is used here for solving the FCC riser complex nonlinear DAEs  
 449 by validating the results against those of the plant. The estimated parameters for the four-  
 450 lump kinetics and six-lump kinetics are also presented.

451 The results of the parameter estimation for the four-lump model denoted with asterisks in  
 452 Tables 6-8, gives very close estimates as compared with similar values of kinetic data by Han  
 453 and Chung (2001b) with double asterisks, giving the assurance that the process model can be  
 454 used for the purpose of parameter estimation. The results are presented in Tables 6-8.

455 Table 5. Riser simulation results of the six-lump kinetic model

Riser Height (m)	Gas oil (wt. %)	Diesel (wt. %)	Gasoline (wt. %)	LPG (wt. %)	Dry gas (wt. %)	Coke (wt. %)	Temp. (Tg) (K)	Temp. (Tc) (K)
**0.0	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	523.0	904.7
5.0	0.3479	0.2185	0.2312	0.1073	0.0339	0.0612	706.0	775.5
10.0	0.1537	0.2652	0.3245	0.1385	0.0434	0.0748	734.5	748.2
15.0	0.0971	0.2613	0.3686	0.1476	0.0462	0.0792	738.4	742.2
20.0	0.0724	0.2487	0.3982	0.1516	0.0475	0.0817	738.3	740.2
25.0	0.0587	0.2349	0.4210	0.1538	0.0482	0.0834	737.7	739.1
30.0	0.0499	0.2217	0.4398	0.1552	0.0487	0.0847	737.0	738.2
35.0	0.0438	0.2095	0.4556	0.1562	0.0491	0.0857	736.5	737.5
40.0	0.0393	0.1983	0.4694	0.1570	0.0494	0.0866	736.0	736.9
45.0	0.0358	0.1881	0.4815	0.1576	0.0496	0.0873	735.5	736.4
47.0	0.0346	0.1843	0.4860	0.1578	0.0497	0.0876	735.3	736.2
47.1	0.0346	0.1841	0.4862	0.1578	0.0497	0.0709	735.3	736.2
**47.1	0.0478	0.1857	0.4731	0.1518	0.0483	0.0891	773.2	NA
% error	38.24	0.86	2.69	3.81	2.80	1.70	5.15	

456 \*\*values in this row are riser conditions from the industrial plant

457

458

459

460 Table 6: Heat of Reaction for four-lump model

Reaction	Heat of Reaction** (kJ/kmol) $\Delta H_i$	Heat of Reaction* (kJ/kmol) $\Delta H_i$	% Difference
Gas Oil $\rightarrow$ Gasoline	195	189	3.17
Gas Oil $\rightarrow$ Gas	670	664	0.90
Gas Oil $\rightarrow$ Coke	745	739	0.81
Gasoline $\rightarrow$ Gas	530	524	1.14
Gasoline $\rightarrow$ Coke	690	684	0.87

461 \*Heat of reaction obtained from the procedure in Figure 4.

462 \*\* Heat of reaction from literature (Han and Chung, 2001a, Han and Chung, 2001b)

463 Table 7: Frequency factor for four-lump model

Reaction	Frequency Factor** ( $k_i$ ) ( $s^{-1}$ )	Frequency Factor* ( $k_i$ ) ( $s^{-1}$ )	% Difference
Gas Oil $\rightarrow$ Gasoline	1457.50	1468.5	0.74
Gas Oil $\rightarrow$ Gas	127.59	134.269	4.97
Gas Oil $\rightarrow$ Coke	1.98	1.99911	0.95
Gasoline $\rightarrow$ Gas	256.81	253.315	1.38
Gasoline $\rightarrow$ Coke	0.000629	0.00052	20.96

464 \* Frequency Factor obtained from the procedure in Figure 4.

465 \*\* Frequency Factor from literature (Han and Chung, 2001a, Han and Chung, 2001b)

466

467 Table 8: Activation energy for four-lump model

Reaction	Activation Energy** (kJ/kmol) ( $E_i$ )	Activation Energy* (kJ/kmol) ( $E_i$ )	% Difference
Gas Oil $\rightarrow$ Gasoline	57,359	57,348	0.01
Gas Oil $\rightarrow$ Gas	52,754	52,765	0.02
Gas Oil $\rightarrow$ Coke	31,820	31,809	0.03
Gasoline $\rightarrow$ Gas	65,733	65,723	0.01
Gasoline $\rightarrow$ Coke	66,570	66,581	0.01

468 \* Activation Energy obtained from the procedure in Figure 4.

469 \*\* Activation Energy from literature (Han and Chung, 2001a, Han and Chung, 2001b)

470

471 The differences are 3% and less, except for the percentage differences between the frequency  
 472 factors of the reaction of gas oil to gas, which is 4.97% and gasoline cracking into coke,  
 473 which has a difference of about 20% as shown in Table 7. Although this difference appeared  
 474 to be very large, it may not be very significant. The reason being that the frequency factor  
 475 itself is very small, and even though the activation energy and heat of reaction for the  
 476 reaction may be large, the frequency factor multiplies the exponential term in the Arrhenius  
 477 equation, which makes the yield of coke very small. It was also found that even when the

478 heat of reaction was assumed 1000 kJ/kmol, the yield of coke is still small because of the  
479 value of the frequency factor.

480 Using the new kinetic parameters estimated for the riser simulation with four-lumped model,  
481 the riser exit conditions are presented in Table 9. Their percentage errors are all less than 3%,  
482 an acceptable level of marginal error. This low percentage differences in Table 6, 7 and 8  
483 shows that the technique used for the parameter estimation as described in Figure 4, is  
484 capable of estimating process parameters with very high accuracy. Since the difference of  
485 mostly about 3% and less is seen between the estimated parameters and the literature  
486 parameters. This confirms the adequacy of the riser model, the parameter estimation  
487 technique proposed in Figure 4 and the new kinetic data for parameter estimation.

488 Table 9. Riser exit results of the four-lump kinetic model using the new estimated parameters

Riser Height (m)	Gas oil (wt. %)	Gasoline (wt. %)	Gases (wt. %)	Coke (wt. %)	Temp. (T <sub>g</sub> ) (K)	Temp. (T <sub>c</sub> ) (K)
*30	0.2835	0.5137	0.1332	0.0354	791.5	791.9
**30	0.2803	0.5134	0.1366	0.0354	791.7	792.1
% diff.	1.14	0.06	2.49	0.0000	0.03	0.03

489 \*riser exit conditions for the Han and Chung (2001a, b) kinetics

490 \*\*riser exit conditions for the new estimated kinetic parameters

491

492 Table 10 shows the new six-lump estimated parameters. Being the first of such six-lumped  
493 kinetic model that considered the cracking of LPG and dry gas to coke, as well as the  
494 cracking of dry gas to coke. In Table 10, the frequency factors, activation energies and heats  
495 of reaction of the cracking reactions of LPG to dry gas and coke, and dry gas to coke, for the  
496 six lumped kinetic model are presented. These data were not available in the open literature,  
497 which is a contribution of this work. Overall, a new six lumped kinetic data (Table 10) is  
498 presented in this work. For the purpose of validation, the newly estimated kinetic data in  
499 Table 10 is simulated with the riser process model, and exit values were compared with the  
500 exit conditions of industrial riser.

501 The process model was run on the gPROMS simulation platform using the new six-lump  
502 kinetic parameters with the new kinetic scheme in Figure 2. At C/O ratio of 6.405, the feed  
503 (gas oil at 62.5 kg/s) meets the regenerated catalyst (400.32 kg/s) at the feed vaporization  
504 section of the riser unit and cracks to produce lumps; diesel, gasoline, LPG, dry gas and coke.

505 The cracking reaction starts at gas oil inlet temperature of 523.0 K and catalyst inlet  
506 temperature of 904 K. The profiles of the products are shown in Figure 4.

507 The amount of the gas oil at the exit of the riser is 0.0346 (kg lump/kg feed) which is 3.46%  
508 of gas oil left unreacted. It also means that, about 96.54% of gas oil reacted and above 80%  
509 of the reacted fraction was consumed in the first 12 m of the riser. In some risers, most of the  
510 conversion takes place in the first 10 m. This may not be the same for some short risers.  
511 Some of the risers are 30 m high and others are less (Han and Chung, 2001b, John et al.,  
512 2017b, John et al., 2017a). Here, the riser is 47.1 m high. The amount of diesel at the exit of  
513 the riser is 0.1842 (kg lump/kg feed) which is 18.42% of total products formed. The product  
514 gasoline formed is 0.4863 (kg lump/kg feed), that is 48.63% of total products formed. Other  
515 products formed are LPG; 0.1577 (kg lump/kg feed) which is 15.77% of products formed,  
516 dry gas; 0.0497 (kg lump/kg feed) which is 4.97% of total products formed, and coke; 0.0876  
517 (kg lump/kg feed), 8.76% of total product formed in the riser. These outputs from the riser  
518 are compared with the riser plant data in Table 11. The diesel and gasoline profiles increases  
519 from 0 (kg lump/kg feed) at the inlet of the riser to its maximum yield of 0.4863 (kg lump/kg  
520 feed) at the riser exit for gasoline and a maximum of 0.2660 (kg lump/kg feed) for diesel in  
521 the first 11 m. However, the mass fraction of diesel increases initially and then decreases  
522 gradually to 0.1858 (kg lump/kg feed) at the end of the riser. This fraction of diesel decreased  
523 after 11 m due to a secondary reaction, which is common for intermediates in a series –  
524 parallel reactions. The endothermic heat was sufficient to convert the diesel into gasoline and  
525 other intermediates. The other products of the riser; LPG, dry gas and coke all started from  
526 zero weight fraction as well and rose to their maximum at approximately 11 m height, but  
527 essentially levels out at the exit of the riser. The profiles of the lumps in the riser qualitatively  
528 compare favorably with the profiles of riser products in the literature (John et al., 2017a, John  
529 et al., 2017b, Du et al., 2014, Han and Chung, 2001b).

530

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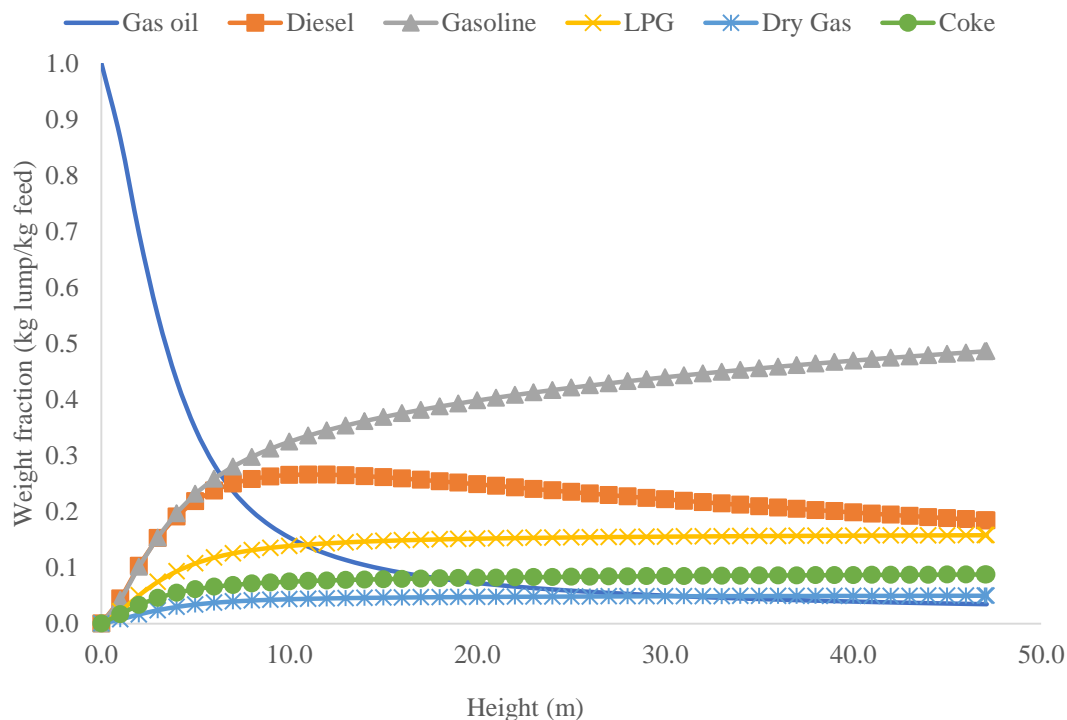
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537 Table 10. Kinetic parameters of six-lump model estimated

<b>Reaction</b>	<b>Frequency Factor (<math>k_i</math>) (<math>s^{-1}</math>)</b>	<b>Activation Energy (kJ/kmol) (<math>E_i</math>)</b>	<b>Heat of Reaction (kJ/kmol) <math>\Delta H_i</math></b>
Gas Oil $\rightarrow$ Diesel	7957.29	53,927.7	190.709
Gas Oil $\rightarrow$ Gasoline	14,433.4	57,186.6	128.45
Gas Oil $\rightarrow$ Coke	40.253	32,433.6	458.345
Gas Oil $\rightarrow$ LPG	2337.1	51,308.6	209.192
Gas Oil $\rightarrow$ Dry Gas	449.917	48,620.4	44.543
Diesel $\rightarrow$ Coke	75.282	61,159.4	305.925
Diesel $\rightarrow$ Gasoline	197.933	48,114.5	513.568
Diesel $\rightarrow$ LPG	3.506	67,792.9	90.894
Diesel $\rightarrow$ Dry Gas	3.395	64,266.6	204.381
Gasoline $\rightarrow$ LPG	2.189	56,194.4	225.082
Gasoline $\rightarrow$ Dry Gas	1.658	63,319.1	19.667
Gasoline $\rightarrow$ Coke	2.031	61,785.1	117.212
LPG $\rightarrow$ Dry Gas	3.411	55,513.0	17.618
LPG $\rightarrow$ Coke	0.601	52,548.2	11.839
Dry Gas $\rightarrow$ Coke	2.196	53,046.0	52.863



540

541 Figure 5. Profile of gas oil cracking in the riser

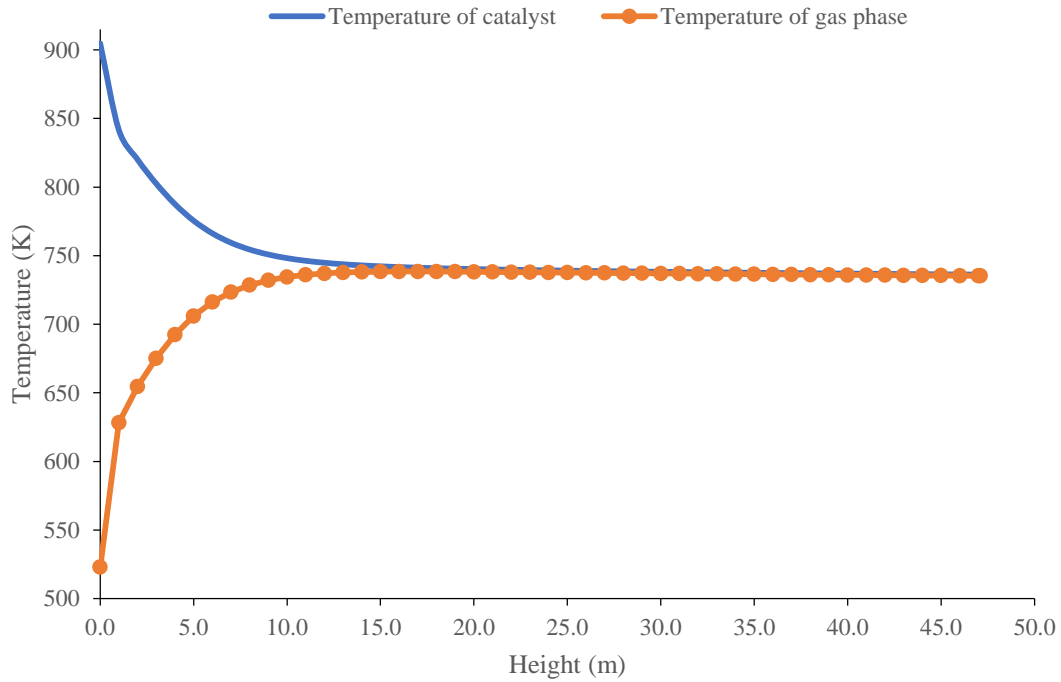
542

543 Figure 5 shows the temperature profiles of the gas and catalyst phases as a function of riser  
 544 height. The temperature of the catalyst-phase starts from about 933 K in the feed vaporization  
 545 section and decreases for the first 11 m from 904.7 K at the entrance of the riser and then  
 546 essentially levels out to 736.2 K at the riser exit.

547 The temperature profile of the gas phase starts from 478.15 K, which is also the temperature  
 548 of the gas oil coming into the vaporization section. This temperature was quickly raised by  
 549 the incoming hot regenerated catalyst to about 522.9 K as can be seen at the riser inlet in  
 550 Figure 5. This gas phase temperature rises from 522.9 K to a peak 738.5 K in the first 17 m of  
 551 the riser and levels out in the remaining portion of the riser. The difference in both  
 552 temperature profiles represents the endothermic reaction in the riser with a temperature  
 553 difference of 382.2 °C at the riser inlet to 0.95 °C at the exit. This difference aid the  
 554 completion of the cracking reaction and represents the heat of removal shown in Figure 9,  
 555 which is accounted for in this work with the help of the estimated heat of reactions obtained  
 556 and shown in Table 10. The temperature profiles obtained in this work are qualitatively  
 557 similar to those obtained in many literatures (Han and Chung, 2001b, Du et al., 2014, John et  
 558 al., 2017b, John et al., 2017a).

559 To determine the accuracy and validate the capability of this gPROMS model, refinery  
 560 operational data are used to compare with the results of this simulation work. The results are  
 561 shown in Table 11.

562



563

564 Figure 6. Temperature profiles across the riser.

565

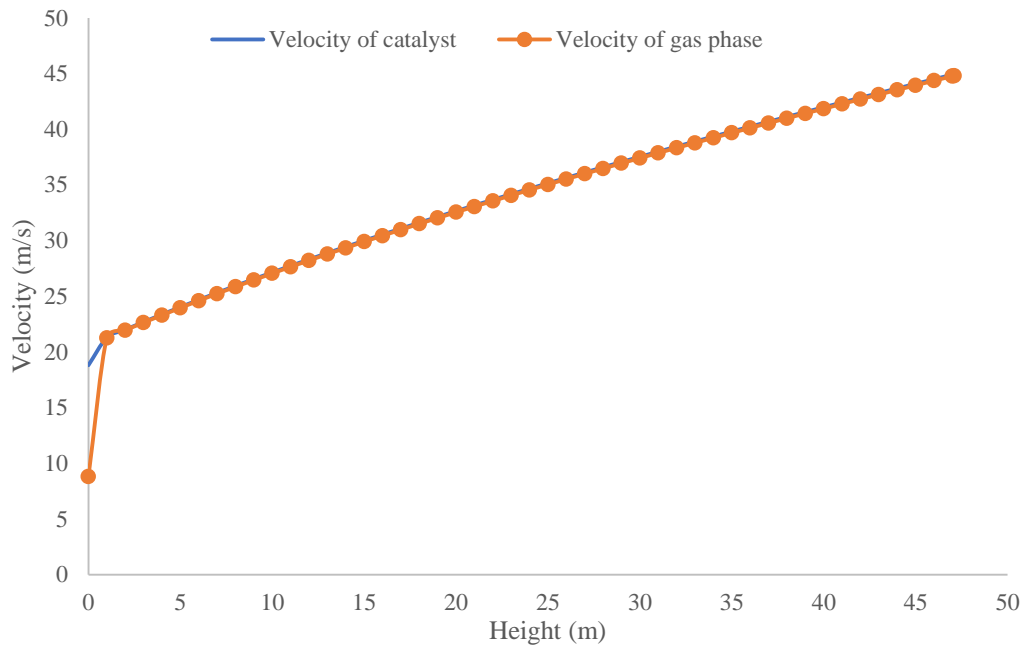
566 Table 11: Riser simulation results compared with plant data

Parameter	Input	Riser output	Plant data	% difference
Gas oil Temperature (K)	478.15	735.3	773.2	5.15
Catalyst Temperature (K)	905	736.2		
Gas oil Mass flowrate (kg/s)	62.5	62.5	62.5	
Catalyst Mass flowrate (kg/s)	400.32	400.32	400.32	
Mass fraction of Gas oil (wt. %)	1.0	0.0346	0.0478	38.15
Mass fraction of Diesel (wt. %)	0.0	0.1842	0.1857	0.81
Mass fraction of Gasoline (wt. %)	0.0	0.4863	0.4731	2.71
Mass fraction of LPG (wt. %)	0.0	0.1577	0.1518	3.74
Mass fraction of Dry gas (wt. %)	0.0	0.0497	0.0483	2.28
Mass fraction of Coke (wt. %)	0.0	0.0876	0.0891	1.71



567 The temperature of the catalyst is 905 K at the inlet of the riser and gradually decreased to  
568 736.2 K at the riser exit due to endothermic cracking reactions. The decrease in the catalyst  
569 temperature increased the temperature of the gas phase from 478.2 K at the riser inlet to  
570 735.3 K at the exit. For the gas phase temperature at the riser exit, there is a 5.15% difference  
571 between the riser exit temperature in this simulation 735.30 K and that of the plant (773.20  
572 K). The 5.15% difference can be acceptable considering that the yield of products is not only  
573 dependent on reaction temperature but as well as the hydrodynamics of the riser, C/O ratio,  
574 catalyst type, nature of feed and many other operational variables. This temperature  
575 difference between plant data and the simulation result is evident in the increased conversion  
576 found in this simulation, showing that more heat of the endothermic reaction was utilized.  
577 The feed conversion in this work is higher than that obtained in the plant, with a 38.15%  
578 increase on the fraction of feed converted. This increase is far above the 3% difference  
579 required for the estimated parameter to be accepted. However, most of the values of the six-  
580 lump are less than 3% and so the results are acceptable. The most valuable products are the  
581 diesel and gasoline and the parameter estimated was able to predict the plant values with  
582 about an average of over 98% accuracy. The percentage difference compared with the plant  
583 data for the diesel is 0.81% and for gasoline, it is 2.71%. The percentage difference between  
584 the value for the lighter products LPG and dry gas are 3.74% and 2.28% respectively, which  
585 are also acceptable values within margin of difference. The major products are diesel and  
586 gasoline and are within acceptable margin of error. Although the difference between the  
587 predicted values and plant data for gas oil value at the exit of the riser is large, it can be  
588 corrected by optimizing the C/O ratio and other operational variables of the unit. The  
589 percentage differences in Table 11 shows that the estimated kinetic parameters are accurate  
590 and can be used for the simulation of the riser of FCC unit.

591 Figure 7 shows the velocity profiles of the gas and catalyst phase along the riser height. The  
592 velocity profile of catalyst rose from 18.8 m/s at entrance of the riser to 44.94 m/s at the exit.  
593 The velocity profile of the gas phase rose sharply from 8.79 m/s to 21.25 m/s in the first 1 m  
594 of the riser, and eventually rose to 44.81 m/s at the exit of the riser. This gives a slip velocity  
595 of 10.01 m/s at the entrance to 0.13 m/s at the exit, making an average slip velocity of 0.29  
596 m/s across the riser. The slip velocity is very close to 0.25 m/s presented in the literature (Han  
597 and Chung, 2001b).

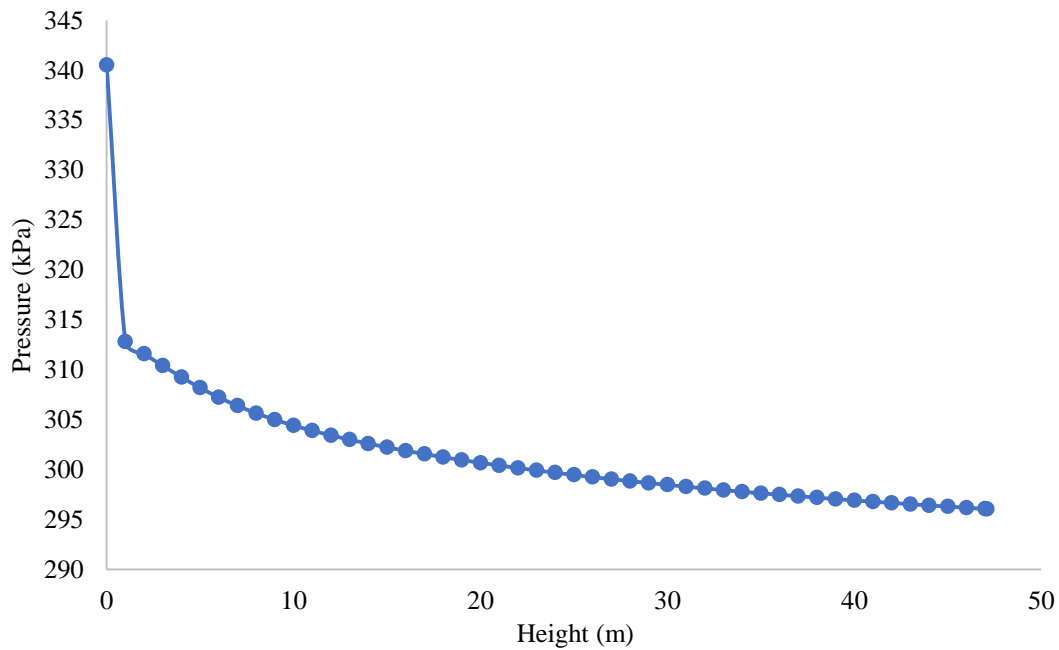


598

599 Figure 7. Velocity profiles across the riser

600 Figure 8 shows that the profile of pressure in the riser decreases from 340.5 kPa at the  
 601 entrance to 296.1 kPa at the exit. The pressure drop is thus 44.9 kPa and could be as high as  
 602 163 kPa industrial risers (Chang et al., 2012).

603



604

605 Figure 8. Pressure profile along the riser

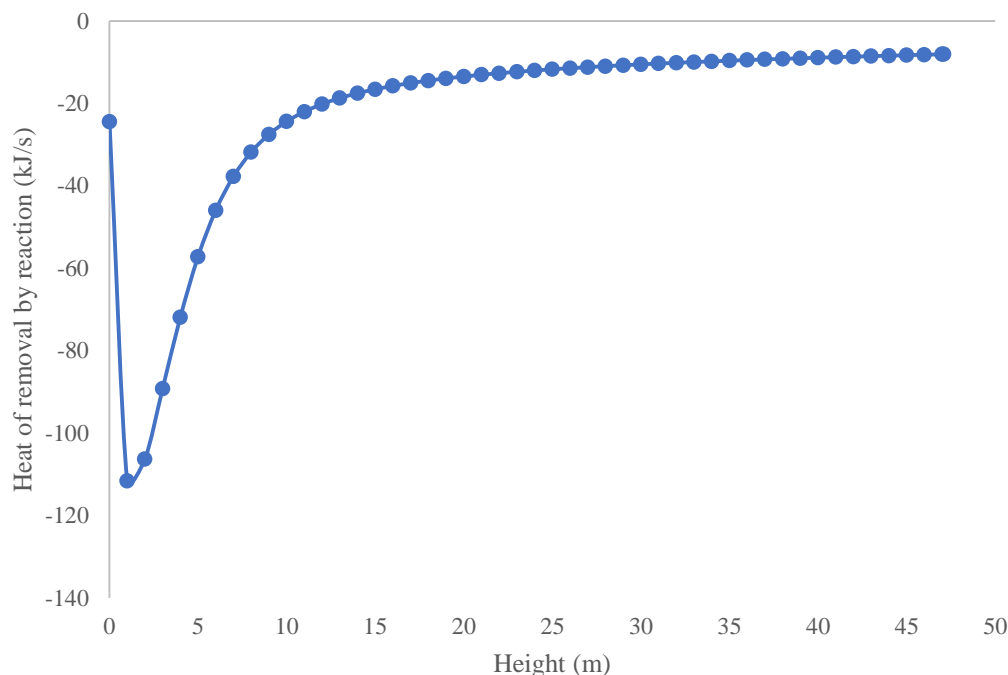
606 Although the model simulation predicts the pressure drop, it is only limited to the riser and  
607 the effect of the regenerator pressure was not considered which could be a reason for the  
608 variation of pressure drop in this study compared with other predicted pressure drops (Chang  
609 et al., 2012, Han and Chung, 2001b). Another reason could be that, since the pressure of the  
610 riser in the plant is measured at the end of the disengaging section, which is not captured in  
611 this simulation, more pressure drop is expected to be recorded in the plant. In addition,  
612 product streams are many times used for quenching of the cracking reactions at the riser end,  
613 which affects the pressure in the disengaging section. Though, the pressure drop is  
614 quantitatively different from the pressure drop of the plant (30 kPa), the profile is  
615 qualitatively similar to the ones in the literature (Han and Chung, 2001b).

616 The heat released with the catalyst from the regenerator reimburses the heat requirements for  
617 the endothermic cracking reactions in the riser which causes the unit to operate, overall,  
618 under conditions of thermal balance. The same heat coming with the regenerated catalyst is  
619 useful for heating and evaporating the feed; gas oil, as it moves pneumatically upward into  
620 the riser. This process brings about heat removal due to the endothermic heats of the cracking  
621 reactions (Arbel et al., 1995) which strongly affects the overall heat balance in the FCC unit.  
622 This heat removal is measured as a function of the enthalpies of the various cracking lumps.  
623 It is possible to measure the heat removal as shown in Figure 9 from the estimated heats of  
624 reactions in Table 10.

625 At the entrance of the riser, much heat is removed because of the fast cracking reaction and  
626 vaporization. Also, most of the products are formed in the first few meters of the riser. After  
627 about 10 m of the riser, heat removal is almost constant for the remaining parts of the riser.

628 The simulation in this work was carried out at C/O ratio of 6.405 which means the gas oil  
629 mass flowrate at 62.5 kg/s and the regenerated catalyst mass flowrate at 400.32 kg/s. The C/O  
630 ratio was changed from 6.405 to 5.405 and compared with the plant data, though, the plant  
631 data was obtained at C/O ratio of 6.405. In the absence of the plant data at the varied C/O  
632 ratio of 5.405, its outputs are compared with the plant data at 6.405. The results are shown in  
633 Table 12.

634 In varying the C/O ratios, only the mass flowrate of the gas oil was varied while the mass  
635 flowrate of catalyst was kept constant. This is because mass flowrate of gas oil can be  
636 directly manipulated unlike the mass flow rate of catalyst which depends on many other  
637 variables including fresh catalyst addition.



639

640 Figure 9. Profile of heat removal along the riser

641 At 74.06 kg/s, a C/O ratio of 5.406, it is a 15.61% increase on mass flowrate of gas oil. This  
 642 lower C/O ratio compared to 6.405 of the plant brought about 11.15% increase in the  
 643 converted fraction of gas oil from 0.0478 to 0.0538 kg-lump/kg-feed. This increased  
 644 conversion leads to 17.80% increase in diesel yield from 0.1857 to 0.2259 kg-lump/kg-feed.  
 645 However, there is a significant decrease in the yield of gasoline from 0.4731 to 0.4305 kg-  
 646 lump/kg-feed (9.90% decrease). This is because the riser exit temperature for this simulation  
 647 being 712.7 K, 8.49% lower than the riser exit temperature of the plant (773.2 K), and favors  
 648 the cracking of heavier products like diesel compared with gasoline. This difference also  
 649 caused considerable percentage decrease in the lighter products and coke.

650 At 62.5 kg/s, the same mass flowrate of gas oil of the plant, the C/O ratio is 6.406. The  
 651 converted fraction of gas oil is 0.0478 kg-lump/kg-feed for the plant and 0.0346 kg-lump/kg-  
 652 feed for this simulation. This is equivalent to 38.15% increase on the conversion of gas oil.  
 653 This increase has caused a 0.81% increase of 0.1857 kg-lump/kg-feed of diesel for plant to  
 654 0.1842 kg-lump/kg-feed for this simulation at C/O ratio of 6.406. Likewise, the increase  
 655 caused a 2.71% increase of 0.4731 kg-lump/kg-feed of gasoline for the plant, to 0.4863 kg-  
 656 lump/kg-feed for this simulation at C/O ratio of 6.406. This shows that at C/O ratio of 6.406,

657 the percentage conversion of the gas oil is 38.15%, which is higher than 11.15% at C/O ratio  
 658 of 5.406.

659 The two simulation outputs shown in Table 12 are obtained at C/O ratios of 5.405 and 6.405.  
 660 Comparing their percentage differences with the plant data, there is a decrease of 8.49 % in  
 661 gas oil temperature at C/O = 5.405, while, there is a decrease of 5.15 % in gas oil temperature  
 662 at C/O = 6.405. This shows that increase in C/O ratio could increase the gas phase  
 663 temperature, which eventually favours conversion as seen; a 38.15 % increase in conversion  
 664 at C/O = 6.405 as against 11.15 % increase at C/O = 5.405. However, increase in C/O ratio  
 665 from 5.406 to 6.406 gives a lower diesel yield (17.8 % at C/O = 5.404 and 0.81 % at C/O =  
 666 6.404) and higher gasoline yield (a decrease of 9.90 % at C/O = 5.404 and 2.71 % at C/O =  
 667 6.404). This means that higher C/O ratios may favor increased gas oil conversion but results  
 668 in decrease yield of diesel.

669

670 Table 12: Compare riser output results for different C/O ratio

Riser Parameter	Plant	Simulation Output @ C/O = 5.405	% Diff. @ C/O = 5.405	Simulation Output @ C/O = 6.405	% Diff. @ C/O = 6.405
Catalyst-to-oil ratio (C/O)	6.405	5.405		6.405*	
Catalyst Mass flowrate (kg/s)	400.32	400.32	0.0	400.32	0.0
Gas oil Mass flowrate (kg/s)	62.50	74.06	15.61	62.50	0
Gas oil Temperature (K)	773.2	712.7	-8.49	735.3	-5.15
Catalyst Temperature (K)	N/A	713.6	N/A	736.2	N/A
Mass fraction of Gas oil (wt. %)	0.0478	0.0538	11.15	0.0346	38.15
Mass fraction of Diesel (wt. %)	0.1857	0.2259	17.80	0.1842	0.81
Mass fraction of Gasoline (wt. %)	0.4731	0.4305	-9.90	0.4863	2.71
Mass fraction of LPG (wt. %)	0.1518	0.1550	2.06	0.1577	3.74
Mass fraction of Dry gas (wt. %)	0.0483	0.0488	1.02	0.0497	2.28
Mass fraction of Coke (wt. %)	0.0891	0.0861	-3.48	0.0876	1.71

671

672 Therefore, the plant needs to be operated at lower C/O ratio for increased diesel yield, while  
673 increased C/O ratio favors the yield of gasoline. In addition, if the production objective is to  
674 produce gasoline, then higher C/O ratio is appropriate. Increased C/O ratio also increase the  
675 temperature of the riser which favors secondary reactions. This is one of the reasons for  
676 gasoline yield to increase with increase in C/O ratio. This variation of the C/O ratio, a major  
677 influence on the FCC unit, follows a typical FCC riser behaviour (León-Becerril et al., 2004,  
678 John et al., 2017b).

679

## 680 **5. Conclusions**

681 In this work, a steady state detailed industrial FCC riser process model is simulated to carry  
682 out parameter estimation of a new six-lump kinetic model of gas oil cracking. The new six-  
683 lump model was implemented on gPROMS software to crack gas oil into diesel, gasoline,  
684 LPG, dry gas and coke. The following conclusions can be made:

- 685 • A new kinetics scheme has been developed which includes the cracking of LPG to  
686 coke and dry gas, as well as the cracking of dry gas into coke.
- 687 • New activation energies, frequency factors and heat of reactions for a new six-lump  
688 kinetic model were estimated.
- 689 • The estimated parameters predicts the major industrial riser fractions; diesel is 0.1842  
690 kg-lump/kg-feed with a 0.81% error while gasoline is 0.4863 kg-lump/kg-feed with a  
691 2.71% error compared with the plant data.
- 692 • With the help of the new kinetic parameters, the heat of cracking reaction was  
693 estimated for the six lumped model for the first time.
- 694 • The estimated parameters can be used to simulate any type of FCC riser with a six-  
695 lump model since C/O ratios were varied and the results showed agreement with the  
696 typical riser profiles.

697

## 698 **Notation**

A	Surface area, m <sup>2</sup>
$A_{ptc}$	Effective interface heat transfer area per unit volume, m <sup>2</sup> /m <sup>3</sup>
C	Mole concentration, kg mole/m <sup>3</sup>
$C_{pg}$	Gas heat capacity, kJ/kg K

$C_{ps}$	Solid heat capacity, kJ/kg K
D	Diameter, m
$d_c$	Catalyst average diameter, m
E	Activation energy, kJ/kg mole
F	Mass flow rate, kg/s
H	Specific enthalpy, kJ/kg
$\Delta H$	Heat of reaction kJ/kg
$\Delta H_{vlg}$	heat of vaporization of liquid feedstock in the feed vaporization section, kJ/kg
h	Enthalpy of reaction kJ/kg
$h_p$	Interface heat transfer coefficient between the catalyst and gas phases
$h_T$	Interface heat transfer coefficient, kJ/m <sup>2</sup> s K
$k_{i0}$	Frequency factor in the Arrhenius expression, 1/s
$k_i$	Rate coefficient of the four-lump cracking reaction, 1/s
$K_g$	Thermal conductivity of hydrocarbons
L	Length, m
$M_w$	Molecular weight
P	Pressure , kPa
$P_{pr}$	Reduced pressure
$Q_{react}$	Rate of heat generation or heat removal by reaction, kJ/s
R	Overall rate of reaction
$R_g$	Ideal gas constant, 8.3143 kPa m <sup>3</sup> /-kg mole K or kJ/kg mole K
RAN	Aromatics-to-Naphthenes ratio in liquid feedstock
$S_c$	Average sphericity of catalyst particles
$S_g$	Total mass interchange rate between the emulsion and bubble phases, 1/s
T	Temperature, K
$T_{pr}$	Reduced temperature
u	superficial velocity, m/s
V	Volume, m <sup>3</sup>

$y$	Weight fraction
$Z$	Gas compressibility factor or Z factor

### Greek

$\Omega$	Cross-sectional area (units)
$\rho$	Density, kg/m <sup>3</sup>
$\emptyset$	Catalyst deactivation function
$\varepsilon$	Voidage
$\alpha$	Catalyst deactivation coefficient
$\alpha_c^*$	exponent for representing $\alpha$
$\mu_g$	viscosity (units)
$\Phi$	Maximum likelihood objective function
$M\alpha$	Number of experiments performed
$M\beta_i$	Number of variables measured in the $i$ th experiment
$M\gamma_{ij}$	Number of measurements of the $j$ th variable in the $i$ th experiment
	Variance of the $k$ th measurement of variable $j$ in experiment $i$ .
$\sigma_{ijk}^2$	This is determined by the measured variable's variance model $k$ th measured value of variable $j$ in experiment $i$
$\hat{y}_{ijk}$	$k$ th (model-)predicted value of variable $j$ in experiment $i$
$y_{ijk}$	

### Subscript

cc	Coke on catalyst
CL1	Cyclone 1
ck	Coke
dg	Dry gas
Ds	Disperse steam
dz	Diesel
FS	Feed vaporization section
g	Acceleration m/s <sup>2</sup>



gl	gasoline
go	Gas oil
gs	gas
j	Reaction path
MABP	Molal average boiling temperature, K
MeABP	Mean average boiling temperature, K
pc	pseudo-critical
pr	pseudo-reduced
Rs	Riser
RT	Disengager-stripping section

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706 **Appendix A**

707 Table A.1 and Equations A.1 – A.24 are correlations of physical and transport parameters  
 708 adopted from the literature (Han and Chung, 2001a, Han and Chung, 2001b).

709 Table A.1: Distillation Coefficients

Volume % distilled	a	b
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110

710

711 Heat capacity of gas,  $C_{pg}$ , is

712 
$$C_{pg} = \beta_1 + \beta_2 T_g + \beta_3 T_g^2 \quad (A.1)$$

713 Where  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  catalyst decay constant given as

714 
$$\beta_1 = -1.492343 + 0.124432K_f + \beta_4 \left( 1.23519 - \frac{1.04025}{S_g} \right) \quad (A.2)$$

715 
$$\beta_2 = (-7.53624 \times 10^{-4}) \left[ 2.9247 - (1.5524 - 0.05543K_f)K_f + \beta_4 \left( 6.0283 - \frac{5.0694}{S_g} \right) \right] \quad (A.3)$$

716

717 
$$\beta_3 = (1.356523 \times 10^{-6})(1.6946 + 0.0884\beta_4) \quad (A.4)$$

718 
$$\beta_4 = \left[ \left( \frac{12.8}{K_f} - 1 \right) \left( 1 - \frac{10}{K_f} \right) (S_g - 0.885)(S_g - 0.7)(10^4) \right]^2 \text{ For } 10 < K_f < 12.8 \quad (A.5)$$

719 Else  $\beta_4 = 0$  for all other cases

720  $K_f$  is the Watson characterization factor written as

721 
$$K_f = \frac{(1.8T_{MeABP})^{\frac{1}{3}}}{S_g} \quad (A.6)$$

722

723

724 The molecular weight  $M_{wg}$  of the gas can be calculated using

$$M_{wg} = 42.965 \left[ \exp(2.097 \times 10^{-4} T_{MeABP} - 7.787 S_g + 2.085 \times 10^{-3} T_{MeABP} S_g) \right] (T_{MeABP}^{1.26007} S_g^{4.98308})$$

725 (A.7)

$$T_{MeABP} = T_{VABP} - 0.5556 \exp[-0.9440 - 0.0087(1.8 T_{VABP} - 491.67)^{0.6667} + 2.9972(SI)^{0.3333}]$$

726 Where  $T_{VABP}$ , the volume average boiling temperature and SI is slope given as

$$727 \quad SI = 0.0125(T_{90ASTM} - T_{10ASTM}) \quad (A.9)$$

$$730 \quad T_{VABP} = 0.2(T_{10ASTM} + T_{30ASTM} + T_{50ASTM} + T_{70ASTM} + T_{90ASTM}) \quad (A.10)$$

731 The ASTM D86 distillation temperatures are calculated using

$$732 \quad T_{10ASTM} = a_{10}^{-\frac{1}{b_{10}}} (T_{10TBP})^{\frac{1}{b_{10}}} \quad (A.11)$$

$$733 \quad T_{30ASTM} = a_{30}^{-\frac{1}{b_{30}}} (T_{30TBP})^{\frac{1}{b_{30}}} \quad (A.12)$$

$$734 \quad T_{50ASTM} = a_{50}^{-\frac{1}{b_{50}}} (T_{50TBP})^{\frac{1}{b_{50}}} \quad (A.13)$$

$$735 \quad T_{70ASTM} = a_{70}^{-\frac{1}{b_{70}}} (T_{70TBP})^{\frac{1}{b_{70}}} \quad (A.14)$$

$$736 \quad T_{90ASTM} = a_{90}^{-\frac{1}{b_{90}}} (T_{90TBP})^{\frac{1}{b_{90}}} \quad (A.15)$$

737 Where  $a_i$  and  $b_i$  are distillation coefficients (Table A.1) and  $T_{iTBP}$  is the initial TBP  
738 distillation temperature.

739 Interface heat transfer coefficient between the catalyst and gas phases,  $h_p$ ,

$$740 \quad h_p = 0.03 \frac{K_g}{d_c^{\frac{2}{3}}} \left[ \frac{|(v_g - v_c)| \rho_g \epsilon_g}{\mu_g} \right]^{\frac{1}{3}} \quad (A.16)$$

741 Thermal conductivity of hydrocarbons

$$742 \quad K_g = 1 \times 10^{-6} (1.9469 - 0.374 M_{wm} + 1.4815 \times 10^{-3} M_{wm}^2 + 0.1028 T_g) \quad (A.17)$$

743

744  $M_{WM}$  is the mean molecular weight of the combined catalyst and gas

$$745 \quad M_{WM} = \frac{1}{\left(\frac{y_{go}}{M_{wgo}} + \frac{y_{gl}}{M_{wgl}} + \frac{y_{dz}}{M_{wdz}} + \frac{y_{lpg}}{M_{wlp}} + \frac{y_{dg}}{M_{wdg}} + \frac{y_{ck}}{M_{ck}}\right)} \quad (\text{A.18})$$

$$746 \quad M_{wgo} = M_{wg} \quad (\text{A.19})$$

$$747 \quad M_{wdg} = 0.0146M_{wH_2} + 0.4161M_{wC_1} + 0.5693M_{wC_2} \quad (\text{A.20})$$

$$748 \quad M_{lpg} = 0.3441M_{wC_3} + 0.6559M_{wC_4} \quad (\text{A.21})$$

749 The viscosity of the gas

$$750 \quad \mu_g = 3.515 \times 10^{-8} \mu_{pr} \frac{\sqrt{M_{WM} P_{pc}^{\frac{2}{3}}}}{T_{pc}^{\frac{1}{6}}} \quad (\text{A.22})$$

$$751 \quad \mu_{pr} = 0.435 \exp\left[\left(1.3316 - T_{pr}^{0.6921}\right)P_{pr}\right] T_{pr} + 0.0155 \quad (\text{A.23})$$

$$752 \quad T_{pc} = 17.1419 \left[ \exp\left(-9.3145 \times 10^{-4} T_{MeABP} - 0.5444 S_g + 6.4791 \times 10^{-4} T_{MeABP} S_g\right) \right. \\ \left. \times T_{MeAB}^{-0.4844} S_g^{4.0846} \right] \quad (\text{A.24})$$

$$753 \quad P_{pc} = 4.6352 \times 10^6 \left[ \exp\left(-8.505 \times 10^{-3} T_{MeABP} - 4.8014 S_g + 5.749 \times 10^{-3} T_{MeABP} S_g\right) \right. \\ \left. \times T_{MeAB}^{-0.4844} S_g^{4.0846} \right] \quad (\text{A.25})$$

755 Table A.2: Tuned coefficients for  $0.2 \leq P_{pr} \leq 3$  (Heidaryan et al., 2010)

Coefficient	Tuned Coefficient
A1	2.827793
A2	-0.4688191
A3	-1.262288
A4	-1.536524
A5	-4.535045
A6	0.06895104
A7	0.1903869
A8	0.6200089
A9	1.838479
A10	0.4052367
A11	1.073574

756

757 Table A.3 summarizes the variables, feed and catalyst characteristic and other parameters  
 758 used in this simulation. Most of the parameters were obtained from the FCC unit in Sudan  
 759 and the literature (Han and Chung, 2001b, Ahari et al., 2008, John et al., 2017b).

760 Table A.3: Specifications of constant parameters and differential variables at  $x = 0$ .

Variable	Value
Riser Height, $x$ (m)	47.1
$T_g(0)$ (Temperature of gas oil, K)	478.15
$T_c(0)$ (Temperature of gas catalyst, K)	905
D Riser Diameter (m)	1.36
$F_c$ (Catalyst mass flowrate, kg/s)	400.32
$F_g$ (Gas oil mass flowrate, kg/s)	62.5
$y_{go}(0)$ Mass fraction of gas oil (kg lump/kg feed)	1.0
$y_{gl}(0)$ Mass fraction of gasoline (kg lump/kg feed)	0.0
$y_{dz}(0)$ Mass fraction of diesel (kg lump/kg feed)	0.0
$y_{dg}(0)$ Mass fraction of dry gas (kg lump/kg feed)	0.0
$y_{lpg}(0)$ Mass fraction of LPG (kg lump/kg feed)	0.0
$y_{ck}(0)$ Mass fraction of coke (kg lump/kg feed)	0.0
$M_{wgo}$ Molecular weight gas oil (kg/k mol)	371
$M_{wgl}$ Molecular weight gasoline (kg/k mol)	106.7
$M_{wdz}$ Molecular weight diesel (kg/k mol)	178.6
$M_{wck}$ Molecular weight coke (kg/k mol)	14.4
$d_c$ (Average particle diameter, m)	0.000065
$S_c$ (Average sphericity of catalyst particles)	0.72
$S_g$ (Specific gravity)	0.9019
$C_{ckCL1}$ (Coke on catalyst, kg coke/kg catalyst)	0.001
$\alpha_{c0}$ (pre-exponential factor of $\alpha_c$ )	1.1e-5
$\alpha_{c*}$ (Catalyst deactivation coefficient)	0.1177
$C_{pc}$ (Heat capacity of catalyst, kJ/kg K)	1.15
$\rho_c$ (Density of catalyst, kg/m <sup>3</sup> )	720
$R_{AN}$ (Aromatics/Naphthenes in liquid feedstock)	2.1
$T_{10TBP}$ TBP distilled 10 volume%, °C	368
$T_{30TBP}$ , TBP distilled 30 volume %, °C	453
$T_{50TBP}$ , TBP distilled 50 volume %, °C	472
$T_{70TBP}$ TBP distilled 70 volume %, °C	528
$T_{90TBP}$ TBP distilled 90 volume %, °C	644

$E_c$ Catalyst Activation Energy (kJ/kg mol)	49,000
$M_{wH_2}$ Molecular weights of hydrogen (kg/k mol)	2
$M_{wC_1}$ Molecular weights of methane (kg/k mol)	16
$M_{wC_2}$ Molecular weights of ethane (kg/k mol)	30
$M_{wC_3}$ Molecular weights of propane (kg/k mol)	44
$M_{wC_4}$ Molecular weights of butane (kg/k mol)	58
g, acceleration due to gravity ( $m/s^2$ )	9.8
R, ideal gas constant (kPa m <sup>3</sup> /kg mole K)	8.3143

761

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