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# Catalytic cracking of kerosene on Z5 catalyst: Steady state modelling

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### Abstract

Catalytic cracking of  $C_{13}$  was carried out on a  $Z5CaO$  catalyst using a two stage single reaction to evaluate a 3-lump model of a steady state reaction setting  $C_2$  as the objective product. A total volume of  $0.0962m^3$  of kerozene was used over a ten (10) h period using two adjustable feed rates of 7.7 and  $8.3 \cdot 10^{-5}m^3/s$ . Between  $400 \pm 50^\circ C$  the reactor performance and the model result showed an excellent correlation of  $C_2$  output suggesting that the catalyst ratio and the temperature favored hexane-heptene fragmentation with a methyl radical as a result of the short space time (0.012s). It was observed that the increase in gas phase ( $M_{gas}$ ) was responsible for catalyst regeneration since the catalyst mass ( $M_{cat}$ ) was constant in the circulating volume. This condition helped the 3-lump model to operate as a two-stage steady state single reaction with a maximum usage of kerozene at a single pass with a 96% yield of ethylene.

## 1. Introduction

Demand for high grade olefin products especially ethylene in the industry especially in the production of base chemical, petrochemical pharmaceutical products is causing a high competition in demand for ethylene used mainly as raw material in the polyethylene industry and allied petrochemical processes. Ethylene is produced mainly from natural gas especially from pyrolysis of methane and de-hydrogenation of ethane which often accompany crude oil production as associated gases<sup>1</sup>. There had been various reports of oxy-pyrolysis<sup>2</sup>, pyrolysis<sup>3</sup>, chloro-methano-pyrolysis<sup>4</sup> and coal gasification<sup>4,11</sup> processes for production of ethylene. Other sources of ethylene include catalytic cracking of Linear and cyclic alkanes hydrocarbon.

Use of kerosene ( $C_{13} - C_{15}$  linear hydrocarbon) fraction from atmospheric distillation of crude petroleum is not common. This is because kerosene is a high demand consumer product, also kerosene is a flammable liquid hydrocarbon product. These among other factors preclude its use in catalytic cracking. Kerosene is a saturated linear hydrocarbon (Tridodecane). Kerosene is a stable product at ambient condition. Also, the fact that thermal and catalytic cracking of kerosene in a single stage - two step reactions can yield six moles of ethylene from kerosene without cake formation is an advantage that makes kerosene cracking a process that can be used to convert this product into a more valuable and highly demanded monomer.

Generally fluidized catalytic cracking, especially cracking of hydrocarbon, is carried out in a fixed bed reactor which may be connected with a regenerator<sup>6</sup> while in other type reactor, cracking reaction is carried out in a vertical vessel loaded at a particular point with catalyst. The upper portion of the vessel is often used as a disengagement unit for the catalyst. The main advantage of this type of reactor is that there is no coke deposition on the catalyst particles to render it inactive. Thus catalyst regeneration is carried out in-situ as a result of excess hydrogen produced during the cracking of hydrocarbon. These types of reactor remain the most significant concept to date especially the dilute phase cracking reaction with a short residence time using active zeolite<sup>5</sup>.

The complexity of the fluidize reactor, their importance in production of raw material for the petrochemical industry and the demand for novel method or rather maximum utilization of feedstock on one hand and the development of a simple and reliable kinetic and mathematical model to describe the steady state behaviour of a novel pilot riser type is the main objective of this present work.

## 2. Method

### 2.1. Formulation of a Steady State Model

The reactor reported here consist of a catalyst bed riser where all cracking reaction is taking place, an upper fluidized bed where the gaseous product is separated by particle disengagement. The product in one part disengages from the catalyst using the differential densities exhibited by the catalyst and the gaseous products. This type of riser is not common in the industry and most often is regarded as the fix bed. The difference between the fix bed and this riser is just the fact that the catalyst rises up to a height where the differential pressure (density) will serves as disengagement factor in the reactor<sup>8</sup>. The reactor specifications are presented in Table 1 below.

Table 1. Reaction Specifications.

S/No	Parameter	Values
1	Reactor Volume $V_R$ (m <sup>3</sup> )	0.02 m <sup>3</sup>
2	Reactor diameter $d_i$ (m)	0.2m
3	Residence time of reactant $t_r$	0.012s
4	Space velocity (S)	83.3s <sup>-1</sup>
5	Catalyst activity per pass	0.96
6	Catalyst weight (g)	45g
7	Catalyst bed height (m)	0.60m
8	Reaction temperature	400 ± 50°C
9	Reaction pressure	2.5atm
10	Energy input per hr	600KJ/h

If the reactor is modeled as a plug flow using the Weekman 3 – lumped kinetic model, then a parallel cracking of kerosene to hexane – heptene to ethylene and hydrogen gas and methyl radical (which subsequently forms ethylene) can be established.

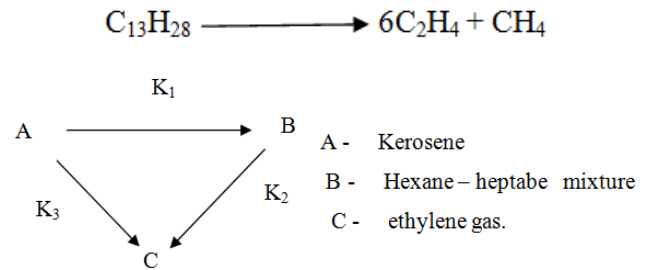


Fig. 1. Model route for cracking kerosene into ethylene.

If for hexane- heptene cracking, a second order reaction is assumed while for kerosene it is assumed that a first order reaction is predominant, then the rate of reagents' disappearance can be given as:-

$$R_A = (K_1 + K_3)C_{A1}^2\phi \frac{\theta_R}{(1-\theta)\rho_s} \quad (1)$$

$$R_B = (K_2C_{A2} - K_1C_{A1}^2)\rho \frac{\epsilon_R}{(1-\epsilon_R)\rho} \quad (2)$$

if the catalytic activity in the reactor  $\phi$  is defined by

$$\phi = \frac{c_n - x_c}{c_m} \quad (3)$$

Then the rate of formation of ethylene in the reactor can be denoted by  $R_{C2}$

$$R_{C2} = (K_3C_{A2}^2 + K_2C_{A2}) \frac{c_n - x_c}{c_m} \cdot \frac{\epsilon_R}{(1-\epsilon_R)\rho} \quad (4)$$

Thus the temperature dependence of the rate constants will be in agreement with Arrhenius relation.

### 2.2. Model Assumption

For effective evaluation of the reactor performance, the following conditions were presumed as constant.

- The residence time is only a few second; operation is under steady state condition.
- Adiabatic condition is observed during reaction
- The densities and heat capacity ( $\rho, C_p$ ) are constant, no catalyst exits from the reactor

Based on these assumptions it can be stated that both the energy and material balances will obey linear relation of the type:

$$\frac{dX_1}{dh} = -(\alpha_1 e^{-r_1/y} + \alpha_3 e^{-r_3/y})X_1^2, X_1(h = 0) = 1\gamma \quad (5)$$

$$\frac{dX_2}{dh} = (\alpha_1 e^{-r_1/y}X_1 - \alpha_2 e^{-r_2/y}X_2)\gamma, X_2(h = 0) = 0 \quad (6)$$

$$\frac{d\gamma}{dh} = -\left(\alpha_3 e^{-r_3/y}X_1 + \alpha_2 e^{-r_2/y}X_2\right)\gamma \frac{a}{c_m}, \gamma(h = 0) = \gamma_c \quad (7)$$

where  $Y_i = E/RT$

$$\alpha_1 = K_{01}\epsilon_R C_{A1F}\tau_R \quad (8a)$$

$$\alpha_2 = K_{02}\epsilon_R\tau_R \quad (8b)$$

$$\alpha_3 = K_{03} C_{A1F} \varepsilon_R \tau_R \quad (8c)$$

$$\tau_R = \frac{V_R}{q} \quad (8d)$$

$$a = \frac{q}{F_c}$$

The General energy balance equation for the riser type reactor is given as:

$$\frac{dH}{dh} = [(\alpha_1 \beta_1 e^{-\gamma_1/y} + \alpha_3 \beta_3 e^{-r_3/y}) X_1^2 + \alpha_2 \beta_2 e^{-r_2/y} X_2] \gamma H(h=0) H_0 \quad (9)$$

$$\text{where } \beta = \frac{(-\Delta H) C_{A1F}}{T_r \rho \delta C_{PAV}}$$

$C_{PAV}$  = average specific heat capacity of the stream, then:

$$C_{PAV} = \left[ \frac{C_{ps}}{a} + C_{p_{hept}} \right] \quad (10)$$

Thus, the heat balance at the point of intersection of feed stream ( $C_{13}$  and the catalyst) can be performed to obtain  $H_0$

$$H_0 = a_1 Y_G + a_2 Y_F - \beta_v \quad (11)$$

### 2.3. Solution of the Model Equations

The basic mathematical model consist of four ordinary differential equations (eqtns: 5, 6, 7, 9). Solving these differential equations we can obtain the values of "Xi, and Y". These values will form the basis for the disengagement algebraic equations. The values for the initial condition for these equations will be dependent on  $Y_a$ , and  $Y_G$ . This implied that an iterative method must be adopted to solve the set of equations describing the model.

## 3. Results and Discussion

**Table 2.** Comparison between the model result and the experimental Results.

Conditions observed	Items	Model result	Experimental Result	% error
$C_{13}$ feed rate	F(kg/s)	0.550	0.4282	-0.1218
Cat feed rate	$F_{cat}$ (kg/s)	0.0412	0.0405	-0.0007
$C_{13}$ concentration	$X_i$	0.3426	0.3854	0.428
		2.12	2.10	0.9434
$C_2$ yield	$E_y$	8.216	7.3944	-0.8216
Cat activity	$\phi$	0.826	0.904	0.076
Rise in reactor temperature °C	T	2.16	2.06	4.63

The experimental set up has been earlier reported (Adeyinka and Otaraku, 2014b). The reactor output and the model result comparison shown in Table 2, while the reactor design specification is shown in Table 2. A 3 lump model for aluminum/silica catalyst had been reported (el Nashaie and elShishini, 1993) while Pt-Cu/ $Al_2O_3$ - has been

reported earlier (Adeyinka et al, 2014a; Kraemer, et al, 1990). Based on the 3- lump model, a laboratory scale required a parameter variation for ease of temperature and concentration manipulation.

From the kinetic formulation for this work coke formation was assumed to be negligible hence alkenes hydrocarbon was the main target with  $C_2$  and  $C_3$  as the major products. Between  $400 \pm 50^\circ C$  the reactor performance and the model result showed an excellent correlation of  $C_2$  output suggesting that the catalyst ratio and the temperature favored hexane-heptene fragmentation with a methyl radical as a result of the short space time (0.012s). It was observed that the increase in gas phase (Mgas) was responsible for catalyst regeneration since the catalyst mass (Mcat) was constant in the circulating volume. This condition helped the 3-lump model to operate as a two-stage steady state single reaction with a maximum usage of kerosene at a single pass with a 96% yield of ethylene. With increase in temperature, fragmentation of  $C_{13}$  will lead to HC modification which subsequently is the basis of gas-phase reaction at the gas – cat adsorption surface. The gas adsorption rate which is a function of the partial pressure of the fragmented HC thus becomes the limiting factor and consequently the rate determining factor for non-adsorbed gas (Adeyinka et al, 2014a; Weekman1986). The model equation was used to simulate the reactor performance. Plant behaviour and product yield showed that the model showed a good representation of the plant performance.

## 4. Catalyst Performance Evaluation

The performance of the catalyst in the reaction can be evaluated using the ratio of  $C_{13}$  in the gas phase (Mkgas) and that adsorbed on the catalyst surface (Mkcat). With increase in temperature Mkgas decreases with adsorption of Mkgas into Mkcat. This implied higher cat – cracking which consequently was responsible for a shift in pressure below 718K. At 718K when the Mkgas is in equilibrium with Mkcat, it was observed that the best kinetic operating condition can be established at this temperature.

## 5. Comparison of Model Result and Experimental Data

Table 3 below shows the comparison between the model result and the experimental data. The only adjustable parameter chosen is the feed flow rate at constant temperature and pressure to measure equilibrium attainment and stabilization for kinetic evaluation (Hollewand and Gladden, 1992; Weekman, and Nace, 1990). Also since the increase in gas phase (M.kgas) will affect Mkcat, then the catalyst circulation rate or available cat surface cannot be constant.

**Table 3.** Comparison of model and experimental result for a steady-state catalytic cracking of kerosene.

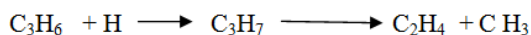
## CASE I

Runs	Feed Volume (m <sup>3</sup> )	Flow rate (m <sup>3</sup> )	Experimental yield	Model yield	Deviation	%
1	0.004	6.7 x10 <sup>-5</sup>	6.4x10 <sup>-5</sup> m <sup>3</sup>	6.3x10 <sup>-5</sup> m <sup>3</sup>	0.1x10 <sup>-5</sup> m <sup>3</sup>	0.16
2	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	0.2x10 <sup>-3</sup> m <sup>3</sup>	0.45
3	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
4	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
5	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
6	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
7	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
8	0.0046	7.7 x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
9	0.0051	7.7x10 <sup>-5</sup>	4.42x10 <sup>-3</sup> m <sup>3</sup>	4.4x10 <sup>-3</sup> m <sup>3</sup>	.02x10 <sup>-3</sup> m <sup>3</sup>	0.45
10	0.0050	8.3x10 <sup>-5</sup>	4.8x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-3</sup> m <sup>3</sup>	.05x10 <sup>-3</sup> m <sup>3</sup>	1.05

## CASE II

Runs	Feed Volume (m <sup>3</sup> )	Flow rate (m <sup>3</sup> )	Experimental yield	Model yield	Deviation	%
11	0.005	8.3 x 10 <sup>-5</sup>	4.8 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.05x10 <sup>-4</sup>	1.05
12	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.78 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.03	1.03
13	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.76 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.01	0.012
14	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.8 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.05	1.05
15	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.8 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.05	1.05
16	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.7 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	-0.05	-1.05
17	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.72 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	-0.97	-0.11
18	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.8 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.05	1.05
19	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.75 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.00	0.00
20	0.005	8.3x10 <sup>-5</sup> m <sup>3</sup> /s	4.75 x10 <sup>-3</sup> m <sup>3</sup>	4.75x10 <sup>-4</sup> m <sup>3</sup>	0.00	0.00

The results herein suggest that the model and experimental data validates its possible application for a possible industrial scale operation with a maximum error of 1.1% of prediction. The simple nature of the energy and material balance determination using this model is an advantage over challenges of reactor modeling (Rajesh et al, 2005 and Ali et al, 2001). The availability of Mkcat thus become a determining factor hence the yield of alkenes especially C<sub>2</sub> conversion in the reaction. Since fragmentation and presence of C<sub>3</sub> from kerosene is temperature dependent, at 718K C<sub>3</sub> in the gas phase are liable to fragment to CH<sub>3</sub> (methyl radical) and ethylene from where the electron pivoting radical that sustains the equilibrium is generated (Adeyinka & Muganlinskii 1995; George and Abdullahi 2004).



## 6. Conclusion

A mathematical model was used to simulate the steady state performance of a fluidized catalytic cracking operating in a two-stage single reaction riser reactor. Two sets of feed rates were compared with test results and the experimental performance of the pilot rig showing a good agreement with the model formulated to evaluate the reaction. The results herein suggest that the model and experimental data validates its possible application for a possible industrial scale operation with a maximum error of 1.1% of prediction. The simple nature of the energy and material balance determination using this model is an

advantage over challenges of reactor modeling especially in a two-stage steady state single reaction with near zero impurity tolerance for high grade product yield.

## Nomenclature

a	kerosene to catalyst ratio
A	Kerozene
B	heptene-hexane mixture
C	ethylene concentration
C <sub>A1</sub>	heptene concentration
C <sub>A2</sub>	hexane concentration
C <sub>m</sub>	total active site
C <sub>p</sub>	specific heat capacity Kcal/kg
E	activation energy Kcal/kg
h	heat of formation of ethylene Kcal/kg
H	enthalpy of formation of C <sub>7</sub>
H <sub>O</sub>	enthalpy of formation of C <sub>2</sub>
K <sub>01</sub>	frequency factor for hexane conversion
K <sub>02</sub>	frequency factor for heptene conversion
K <sub>03</sub>	frequency factor for kerozene conversion
K <sub>cat</sub>	catalyst adsorption rate
K <sub>gas</sub>	gas adsorption rate on catalyst
M <sub>cat</sub>	mass of catalyst
M <sub>gas</sub>	mass of gas products
R	universal gas constant
R <sub>A</sub>	rate of C13 conversion
R <sub>B</sub>	rate of heptene-hexane conversion
R <sub>C</sub>	rate of ethylene production
T	temperature
T <sub>r</sub>	reaction temperature
V <sub>R</sub>	reactor volume

$X_i$	ethylene volume
$Y$	heptane temperature
$Y_a$	ethylene temperature
$Y_G$	catalyst temperature
$x_a$	Yield or fractional conversion
$S_{ov}$	Surface area of cat (unit surface available for reacting)
$q$	bubble phase air flow rate
$\rho$	density of kerosene ( $\text{kg/m}^3$ )
$C_A$	concentration of kerosene
$C_{A0}$	Initial concentration of kerosene
$K$	Overall reaction rate constant ( $\text{S}^{-1}$ )
$\phi$	catalytic deactivation coefficient
$\beta$	surface adsorption
$W$	Mass of catalyst
$F_{A0}$	Molar flow rate of kerozene
$V_R$	Total reactor volume
$-r_A$	rate of kerozene conversion
$Q$	Volumetric flow rate
$Y_a$	gram of cat adsorbed per gram of catalyst
$R_A$	Rate for monomolecular reaction
$K_1$	rate constant for ethylene propylene
$K_3$	rate constant for overall ethylene – propylene yield.
$\rho_{cat}$	density of catalyst ( $\text{g/cm}^3$ )
$u$	gas velocity
$\varepsilon$	expansion factor
$\tau$	space time for the reaction (s)
$\phi$	deactivation function
$\tilde{n}_{0A}$	mole number of reacting kerosene in the reactor

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