Modeling of the Dehydrogenation Reaction to produce Olefins for the Petrochemical Industry

M.S.H.Mohamed* , M.SH.Hassan , H.A.Farag and Y.A, Eltawil

Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt. Emailaddress:marwahamedo@gmail.com*,medo_chem@yahoo.com abulfarag111@yahoo.com

Abstract Modeling of a heterogeneous industrial fixed bed reactor for selective dehydrogenation of heavy paraffin with Pt-Sn-Al₂O₃ catalyst (DEH-7 (UOP)) is the subject of current study. Using mass balance for appropriate element of reactor . In order to investigate reactor performance in time, the reactor model which is a set of partial differential equations (PDEs), ordinary differential equations and algebraic equations will be solved numerically. Variation of paraffin, olefin mole percent as a function of time and reactor radius is estimated by numerical solution of the mathematical model. And variation of temperature with reactor radius found by numerical solution of the mathematical model. Modeling results are compared with an industrial reactor data at different operating times.

The percentage loss of paraffin is 10.74% and the percentage increase of olefin about 13.18% and the total conversion of the process about 81,45% Comparing the actual industrial data for %paraffin, %olefin, temperature and pressure with those estimated by the model have shown that the developed model can predict the values to a high degree of accuracy maximum deviation was less than 3.5% for the case of pressure at the reactor outlet

Index Terms — Dehydrogenation, petrochemicals industry, Modeling, Olefins.

1 INTRODUCTION

Linear alkyl benzene (LAB) is a major compound for production of biodegradable detergents. Amreya Petroleum Refinery Company (A.P.R.C) has the first LAB plant which was built in Alexandria (Egypt). This plant processes a kerosene cut containing n-paraffin C₁₀- C₁₃ ^[4]. In this plant, the main process is the dehydrogenation of heavy paraffin to mono olefin which is performed by a catalytic radial flow reactor ⁽¹⁾.

The main reaction in catalytic dehydrogenation is the formation of mono-olefins (desirable product) from the corresponding feed paraffin Fig. (1) illustrates Paraffin dehydrogenation on modified platinum catalyst.



Fig. (1): Paraffin dehydrogenation on modified Pt catalyst^[5]

A study of the alumina support effect was presented by He et al.^[2]Results showed that the pore structure and the surface characteristic of the alumina supports strongly affect the catalytic performance. The support effect can be divided into three parts: (I) the BET and pore size distribution govern the Pt dispersion of the catalysts, resulting in influencing the dehydrogenation activity; (II)

 Hasan A. Farag is professor in chemical engineering Alexandria University, Egypt. E-mail: abulfarag111@yahoo.com the inherent acidity controls the acidity of the catalysts, bringing on the different product selectivity; (III) the pore volume provides the effective capability for carbon deposition, thus changing the lifetime of the catalysts Padmavathi et all³¹presented Kinetics of n-dodecane dehydrogenation on promoted platinum catalyst between 733 and 763°K .The reaction scheme includes three consecutive dehydrogenation reactions and also cracking of olefins to light paraffins. Various rate models based on Langmuir–Hinshelwood–Hougen–Watson (LHHW) and Eley Rideal mechanisms were derived for the three dehydrogenation reactions and subjected to model discrimination and parameter estimation by using Box's complex optimisation method.

The kinetics of simultaneous dehydrogenation of propane and isobutane over a commercial Pt-Sn-K/Al2O3catalyst is reported. The experiments were carried out in a laboratoryscale plug flow reactor over the temperature range of 560– 600 °C at atmospheric pressure. Several Langmuir-Hinshelwood mechanisms for C3 and iC4 were tested. Models were derived with the assumption of propane, isobutane and hydrogen adsorption on the same type of active site. A simple deactivation model was used for fitting the kinetic data, then the best fit for these reactions was found with the rate determining step (RDS) of surface reaction for propane and adsorption on the catalyst surface for isobutane.

Transient kinetic modelling of propane dehydrogenation

Marwa S. H. Mohamed is currently pursuing Doctorate degree program in chemical engineering in Alexandria university, Egypt. Email: <u>marwahamedo@gmail.com</u>

Mohamed.SH.Hassan is PhD in. Amreya Petroleum Refinery Company (Ahttp://www.ijser.org

Yehia A.El tawil is professor in chemical engineering Alexandria University, Egypt.

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over a Pt–Sn–K/Al₂O₃ catalyst was studied by Lobera et al^[4] A complete kinetic model of propane dehydrogenation to produce propene over a Pt-Sn-K/Al₂O₃ catalyst was obtained.. A Langmuir-Hinshelwood mechanism provided the best fit for propane dehydrogenation, while a monolayer-multilayer mechanism was proposed for modelling the coke formation. In addition, the reaction rate of coke formation and its influence on catalyst deactivation and subsequent regeneration had been studied.

2 THEORETICAL BACK GROUND

In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame. During the catalytic reaction the following steps occur:

- 1. Transport of reactants and energy from the bulk fluid up to the catalyst pellet exterior surface.
- 2. Transport of reactants and energy from the external surface into the porous pellet.
- Adsorption, chemical reaction, and desorption of 3. products at the catalytic sites.

Transport of products from the catalyst interior to the external surface of the pellet, and transport of products into the bulk fluid

3 MODEL DEVELOPMENT

3.1 MASS BALANCE

Assumptions:

The different mass balances equations of the fixed bed reactor are based on the following hypothesis:

- 1. There are no axial gradients.
- 2. Endothermic reaction
- 3. Constant fluid velocity through the bed.
- 4. Radial flow.
- 5. Linear combination of the mass transfer resistances corresponding to the external mass transfer from the bulk gas phase to the particle surface.

dCn

Based on the previous assumptions the differential equations for the molar balance of the gas phase are: [8] Molar balance for paraffin:

$$\frac{\partial C_p}{\partial t} = \frac{C_p u}{r\varepsilon} + \frac{u}{\varepsilon} \frac{\partial C_p}{\partial r} + \frac{C_p}{\varepsilon} \frac{\partial u}{\partial r} + d_{load} * ac^*(-r_1)$$
(1)

Initial conditions:

At
$$t = 0$$

$$\frac{dCp}{dt} = C_p, \qquad \text{and at } t = t \qquad \frac{dCp}{dt} = 0$$

Boundary conditions: At r = r

$$\frac{dCp}{dr} = C_p, \quad \text{and at } r = 0 \quad \frac{dCp}{dr} = 0$$

Molar balance for olefin:

 $\frac{\partial C_o}{\partial t} = \frac{C_o u}{r\varepsilon} + \frac{u}{\varepsilon} \frac{\partial C_o}{\partial r} + \frac{C_o}{\varepsilon} \frac{\partial u}{\partial r} + d_{load} * ac^* (r_1 - r_2 - r_4)$ (2)Boundary conditions: At r = rdCo dCo

$$d\mathbf{r} = 0$$
, and at $\mathbf{r} = 0$ $d\mathbf{r} = \mathbf{C}_{c}$

Molar balance for hydrogen:

$$\frac{\partial C_{H}}{\partial t} = \frac{C_{H}u}{r\varepsilon} + \frac{u}{\varepsilon}\frac{\partial C_{H}}{\partial r} + \frac{C_{H}}{\varepsilon}\frac{\partial u}{\partial r} + d_{load} * ac$$

$$*(r_{1} + r_{2} + 2r_{3} - 2r_{4})$$
At t = 0
$$\frac{dC_{H}}{dt} = 0, \quad \text{and at } t = t \qquad \frac{dC_{H}}{dt} = C_{H}$$
Boundary conditions:
At r = r

At r = r

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$$\frac{dC_{H}}{dt} = 0, \quad \text{and at } r = 0 \quad \frac{dC_{H}}{dt} = C_{H}$$

Flow chart Solution Method



Fig. (2) represents the mass balance solution flow chart

4 RESULT AND DISCUSSION

4.1. THE PERCENTAGE OF PARAFFIN WITH THE RADIUS OF THE REACTOR:



Fig. (3) the variation of the percentage of paraffin with the radius of the reactor $% \left(f_{1}, f_{2}, f_{3}, f_$

Fig. (3) shows the variation of the percentage of paraffin with the radius of the reactor It is clear that the percentage of paraffin decreases with the decrease of the radius of the reactor as the feed flows from the outer to the inner diameter of the reactor (radial flow), because of the formation of the olefin and hydrogen.

It is obvious that the decrease in the percentage of the paraffin is about 10.74 it is clear that the conversion from the paraffin to the olefin is low. The deviation between the industrial and simulated values is about 0.0046%

4.2. The percentage of olefins with the radius of the reactor:



Fig. (4) shows The variation of the percentage of olefin with the radius of the reactor. It is clear that the percentage of the olefin increases with decreasing the radius of the reactor across the catalytic bed and that is because of the dehydrogenation reaction. It is obvious that the increase in the percentage of the olefin is moderate, about 13.18% and it is clear that the actual conversion from the paraffin to the olefin is 81.45%. The deviation between the industrial and simulated values is about 0..076%

4.3. The percentage of hydrogen with the radius of the reactor



Fig. (5): The variation of the percentage of hydrogen with the radius of the reactor.

Figure (5) shows the variation of the percentage of hydrogen with the radius of the reactor. It is clear that the percentage of the hydrogen decreases with decreasing of the radius of the reactor across the catalytic fixed bed and it is obvious that the decrease in the percentage of the hydrogen is slight (about 0.05 %) that is because the concentration of hydrogen is a function of the dehydrogenation rate and cracking rate of olefin to light paraffin. That is to say when olefin cracking takes place, the cracked molecules need hydrogen for converting into light paraffin, as shown below:

$$(R - C = C - R + H_2) \rightarrow R - \stackrel{H}{C} - H + R - \stackrel{H}{C} - H \\ | H H H H H H H H H H$$

This explains why the percentage hydrogen decreases with decreasing of the radius of the reactor across the catalytic fixed bed. Hydrogen production is high at the entrance of the catalytic bed. Hydrogen generation decreases toward the end of the reactor because of olefin cracking ^{[6].} The deviation between the industrial and simulated values

is about 0.046 %

4.3. The pressure drop with the radial feed flow





4.3. The percentage of the pressure with the radius of the reactor





molar flow rate across the catalytic fixed bed. The deviation between the industrial and simulated values is (about 1.281 %) which is close to model anticipations and confirms model prediction

5-Conclusion

- 1. A mathematical model for a unit of heavy paraffin dehydrogenation has been developed in this study.
- 2. The formulation of the model equations is based on the principles of mass and momentum balance appropriate to the type of system.
- 3. The proposed model has been solved numerically using method of line (MOL).
- 4. Variations of % paraffin, % olefin and with time and reactor radius have been investigated in this research.
- 5. The model has been validated with typical plant industrial data and gave very low deviations.

6 – Nomenclature

Nomenclature	
ac	catalyst activity
C _{AS}	the concentration of occupied sites
Ci	gas concentration of component i (mol/m3)
CS	the total number of sites (occupied or not)
d_{load}	density of catalyst loading (Kg/m ³)
f	friction factor
ki	reaction rate constant, $i=1{-}3 \ (mol\ Pa^2/(h\ g\ cat))$
ki	reaction rate constant, $i = 4 \pmod{\frac{Pa}{h}} g$ (cat))
Ki	equilibrium constant for step i
$\begin{array}{lll} K_P, & K_O, & K_D, \\ K_A, & K_H \end{array}$	adsorption equilibrium
k_{d0}	frequency factor (h ⁻¹)
\mathbf{K}_{eff}	Vapor Thermal Conductivity
L=Z	height of reactor (m)
Ν	degree of catalyst activity
Ni	mole of component i (mol)
Р	pressure of feed (Pa)
Pi	partial pressure of component i (Pa)
R	radius of reactor (m)

ri	rate of reaction i (mol/(g cat s))
t	time (s)
Т	temperature (K)
u	velocity of feed (m/s)
W	weight of catalyst (kg)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	conversion of paraffin, olefin, hydrogen, diene, aromatic and light paraffin respectively
ρ	density of feed (kg/m ³)
3	porosity factor
μ	viscosity (kg/(m s))
Subscript	
Р	Paraffin
0	Olefin

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