

Kinetics of catalyst deactivation in dehydrogenation of higher normal paraffins over Pt-Sn/Al₂O₃ catalysts

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Abstract- The kinetics of the main reaction and deactivation of the catalyst in dehydrogenation of higher (C₁₀-C₁₄) normal paraffins over Pt-based catalyst was studied. A simple mathematical model for catalyst decay based on a reversible main reaction and concentration-independent, *n*th-order decay law was presented. The model was checked both through integral analysis of experimental data and nonlinear estimation functions of temperature-time data of a commercial plant, and model parameters were evaluated. The results of both approaches were consistent, that is, the deactivation rate law was found to be of second order. The activation energies of the dehydrogenation and catalyst decay were found to be 90 KJ/mol and 140 KJ/mol, respectively.

Keywords: Dehydrogenation of paraffins; Pt/Al₂O₃ catalyst; Kinetics; Catalyst deactivation.

1. Introduction

Linear alkylbenzene (LAB) is the dominant detergent intermediate since the early 1960s to produce biodegradable detergents [1]. The efficiency of linear alkylbenzene sulfonate as surfactant is clearly established, and it is one of the safest and most cost-effective products in widespread commercial use. The key step in the synthesis of linear alkylbenzene sulfonate is the selective dehydrogenation of higher normal paraffins (C₁₀-C₁₄) to the corresponding mono olefins. The dehydrogenation of paraffins to olefin is an endothermic reversible reaction:



The reaction is accompanied by volume expansion and is limited by chemical equilibrium. The equilibrium conversion increases at higher temperatures but side reactions, coke formation and catalyst deactivation are also accelerated. Dehydrogenation is thermodynamically less favorable than thermal cracking. Therefore, to achieve reasonable olefin yields, a catalyst should be used. It is carried out over promoted Pt/alumina catalyst in a radial-flow fixed-bed reactor with hydrogen as feed diluent. Commercial processes typically operate at conversion levels of 10-20%, close to thermodynamic equilibrium conversion.

Catalyst deactivation is an important issue in the petroleum refining and chemical industries. It plays an important part in process design and operation. The time scale of deactivation has profound consequences for process design [2, 3]. This deactivation time

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refers to the time after which a catalyst has lost so much of its initial activity that it must be regenerated or replaced.

In commercial C₁₀-C₁₄ *n*-paraffins dehydrogenation, the activity of catalyst drops slowly with time on stream. To maintain a constant conversion with the decaying catalyst, the reaction rate is increased steadily by increasing the feed temperature to the reactor. In this way, the useful catalyst life can be extended to more than a month.

Praserthdam et al. [4] studied the effect of reactants on coke formation during dehydrogenation on Pt-Sn-K/Al₂O₃ catalysts. They concluded that short alkane dehydrogenation provides coke in series and larger alkane dehydrogenation generates coke in series and consecutive modes.

The deactivation rate parameters can be obtained through applying experimental or occasionally commercial plant data to kinetic models. Krishnaswamy and Kittell [5] analyzed the temperature-time data of deactivating catalysts for constant conversion and developed a simple mathematical model based on a single irreversible primary reaction and *n*-th order, concentration-independent deactivation. The applicability of the model to hydrocracking and reforming pilot plant data was demonstrated. Some practical aspects of interpretation of temperature-time data for constant conversion policy in continuous reactors are given Pacheco and Petersen [6].

The theoretical analysis of variable-space-velocity concept to determine catalyst deactivation parameters are given by Levenspiel [7], and Petersen and Pacheco [8]. Sapre [9] used this approach to maintain constant conversion for a decaying catalyst. The variable-space-velocity experimental technique was demonstrated for the methanol to hydrocarbon process on ZSM-5 catalyst. The rate information was then used to determine the determine temperature-time policy for maintaining constant reactor outlet conversion at a fixed space velocity.

In this work, the deactivation of Pt-based catalysts in dehydrogenation of higher normal paraffins is studied by both approaches. The kinetic parameters are obtained by analysis of experimental data and compared with parameters obtained by optimization algorithms using commercial plant data.

2. Experimental

The catalyst performance tests were conducted in a stainless-steel, fixed-bed, isothermal reactor at 440 °C and 0.7 barg using industrial feedstock with a molar H₂/hydrocarbon ratio of six. The reactor was loaded with 10 ml of Pt-Sn/alumina catalyst diluted with 20 ml SiC. The reactor effluent was analyzed on an online gas chromatograph (Varian CV3800). HP/PONA column of 50m length, 0.2 mm diameter and 0.5μm fill thickness and FID detector were used for liquid product analysis. The industrial data were provided by a commercial plant for three sets of runs, with start of run and end of run temperatures of 470 and 495 °C, respectively.

As the feed is a mixture of C₁₀ to C₁₄ normal paraffins, along with small amounts of other hydrocarbons (Table 1), to simplify the analysis through using a single X_{Ae} and the subsequent equations, the feed components were lumped as a representative component (*n*-C₁₁) for which the thermodynamic properties were obtained from the Chemical Properties Handbook [10]. This should be a reasonable assumption as the thermodynamic properties of normal paraffins change smoothly with the carbon number.

Table 1
Typical paraffin feedstock composition.

Component	Weight percent in the feed
<i>n</i> -C ₁₀	7
<i>n</i> -C ₁₁	38
<i>n</i> -C ₁₂	32
<i>n</i> -C ₁₃	21
<i>n</i> -C ₁₄	1
Others	1

3. Modeling

3.1 Integral Method of Analysis of Data

The dehydrogenation of alkanes on Pt-based catalysts has been found to show first-order dependence with respect to alkane and negative half- to zeroth-order dependence in hydrogen concentration [11]. Studies by Padmavathi et al. [12] on kinetics of *n*-dodecane dehydrogenation, included three consecutive dehydrogenation reactions and also cracking of olefins to light paraffins, show that a power law model with first order dependence in hydrogen concentration also fitted the experimental data well. Accordingly, to account for the above concentration dependences and reversibility of the reaction, the following rate expression should represent the kinetics

$$-r'_A = k_A C_A - k_{-A} C_B C_{H_2} = k_A \left(C_A - \frac{C_B C_{H_2}}{K_{eq}} \right) \quad (2)$$

Where $-r'_A$ is the net dehydrogenation rate, k_A and k_{-A} are the rate constants of the forward and backward reactions; respectively, K_{eq} is the equilibrium constant of paraffin dehydrogenation, C_A is the concentration of paraffin and C_B is the concentration of corresponding internal mono-olefin. To account for catalyst decay, the catalyst activity, a , is incorporated in the rate expression as:

$$-r'_A = k_A a \left(C_A - \frac{C_B C_{H_2}}{K_{eq}} \right) \quad (3)$$

Where the activity of the catalyst at time t and temperature T , is defined as:

$$a(t, T) = \frac{-r'_A(t, T)}{-r'_A(t=0, T)} = \frac{-r'_A}{-r'_{A0}} \quad (4)$$

Because of the high H₂/HC molar ratios (~6 mol/mol) commonly employed and the low conversions practiced, the concentration of hydrogen remains constant, in other words, the

method of excess is applicable. Similarly, the volume change of reaction can be neglected. Consequently, the reaction rate in terms of paraffin conversion, X_A , reduces to:

$$-r'_A = k_A C_{A0} a \left(1 - \frac{X_A}{X_{Ae}} \right) \quad (5)$$

Where X_{Ae} represent equilibrium paraffin conversion. Equation (4) shows that an increase in temperature results in an increase in the reaction rate both through increasing the rate constant and thermodynamic driving force.

For a fixed-bed plug-flow reactor under isothermal conditions in the case of a reversible kinetics:

$$X_{Ae} \ln \left(1 - \frac{X_A}{X_{Ae}} \right) = -k_A a t' \quad (6)$$

The decay law based on the concentration-independent is assumed to be of the following form:

$$-\frac{da}{dt} = k_d a^n \quad (7)$$

k_d is decay constant at temperature T and n is the order of deactivation. Integrating with $t=0$, $a=1$:

$$-\frac{1}{n-1} (a^{1-n} - 1) \Big|_1^a = k_d t \quad (8)$$

$$\frac{1}{n-1} (a^{1-n} - 1) = k_d t \Rightarrow a = [1 + (n-1)k_d t]^{\frac{1}{1-n}} \quad (9)$$

Substituting Eq. (9) to Eq. (6) and rearranging yields:

$$F(X_A) = \left[X_{Ae} \ln \left(1 - \frac{X_A}{X_{Ae}} \right) \right]^{1-n} = (-k_A t')^{(1-n)} - (n-1)(k_A t')^{(1-n)} k_d t \quad n \neq 1 \quad (10)$$

$$F(X_A) = \ln \left(-X_{Ae} \ln \left(1 - \frac{X_A}{X_{Ae}} \right) \right) = \ln k_A t' - k_d t \quad n = 1 \quad (11)$$

In which t' , the ratio of catalyst weight per volumetric feed flow rate, is a capacity factor known as the weight-time.

3.2 Time-Temperature Trajectory Analysis

Alternatively, the decay law and kinetic parameters can be obtained from temperature-time trajectory data by the methods outlined elsewhere [5, 6], however, the methodology is much more complicated here due to the reversibility of the main reaction [13].

Noting the high excess of hydrogen in the feed and the reversibility of reaction, the following rate laws were proposed for the main reaction and catalyst decay, respectively:

$$X_{Ae} \ln \left(1 - \frac{X_A}{X_{Ae}} \right) = -k_A a t' \quad (12)$$

So the following must be satisfied for constant paraffin conversion:

$$\frac{k_A(T)a(t,T)}{X_{Ae}(T)\ln(1-X_A(T)/X_{Ae}(T))} = \frac{k_{A0}}{X_{Ae}(T_0)\ln(1-X_A(t=0,T_0)/X_{Ae}(T_0))} \quad (13)$$

Eq. (13) is difficult to treat because in the reversible reaction an increase in temperature results in an increase both in the rate constants and thermodynamic driving force for the main reaction. Rearranging Eq. (13) gives:

$$k_A(T)a(t,T) = k_{A0} \frac{X_{Ae}(T)\ln(1-X_A(T)/X_{Ae}(T))}{X_{Ae}(T_0)\ln(1-X_A(t=0,T_0)/X_{Ae}(T_0))} = k_{A0} b(T) \quad (14)$$

With

$$b(T) = \frac{X_{Ae}(T)\ln(1-X_A(T)/X_{Ae}(T))}{X_{Ae}(T_0)\ln(1-X_A(t=0,T_0)/X_{Ae}(T_0))} \quad (15)$$

The parameter *b* accounts for the role of increased thermodynamic driving force on paraffin conversion at higher temperatures.

4. Results and discussion

A long-term time-on-stream performance of catalysts from experimental run is shown in figure 1. Activity decreases with a very slow rate as implied by decrease of conversion, because the selectivity remains rather constant (87-92%). A good measure of the overall performance of the catalyst during its lifetime can be concluded of which the line of olefins yield closely parallels paraffins conversion. The stable selectivity depicted in figure1 is typical of Sn-promoted platinum catalysts and can be explained in geometric term by the dilution of Pt ensembles by Sn. This dilution greatly reduces the activity toward reactions that require a large ensemble of Pt-atoms to constitute active sites, such as hydrogenolysis and coking. Additionally, the carbon deposited during reaction acts the role of inactive species that inhibits undesired reactions. Therefore, although coke deposition adversely affects catalyst activity, it exhibits some beneficial effects on olefin selectivity [14].

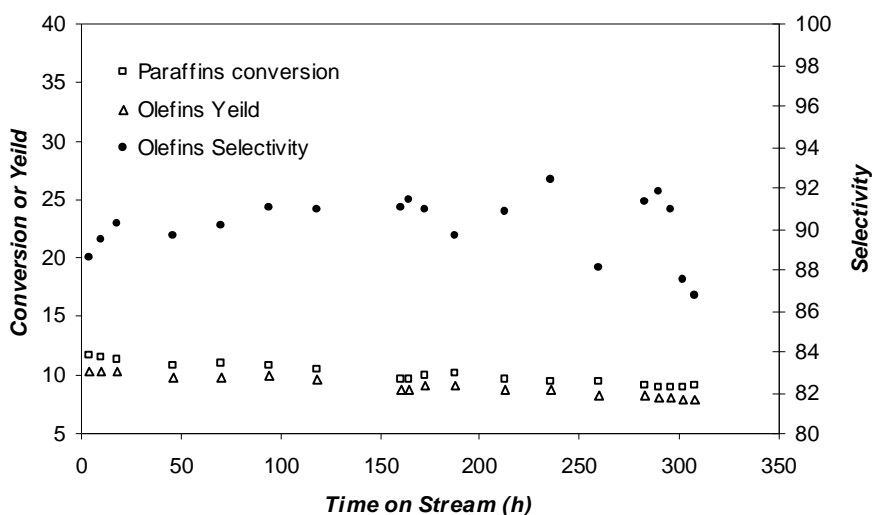


Figure1: Typical Time-on-Stream behavior for Catalyst dehydrogenation ($WHSV=22.2h^{-1}$, $H_2/HC=6$ mol/mol).

4.1 Kinetic Parameters

The kinetic expression given above can be tested against experimental data (time-conversion data) using integral method of analysis [7] with various values of order of deactivation (n) in Eqs. (10) and (11). Figure 2 shows a typical plot with $n=2$, suggesting a second order decay law. As it is observed, the kinetic models adequately predict the trend in the reduction of conversion and deactivation. This confirms the validity of a second-order decay law for the range of interest. The slope and intercept can be used to estimate the rate constants. From the slope and intercept of Figure 2, one obtains $k_d=0.0032$ h^{-1} and $k_1 t' = 0.31$. Considering the operating conditions ($t' = 0.0047$ $kg \cdot h/m^3$), the rate constant is found to be $k_1 = 66.18$ $m^3/kg \cdot h$.

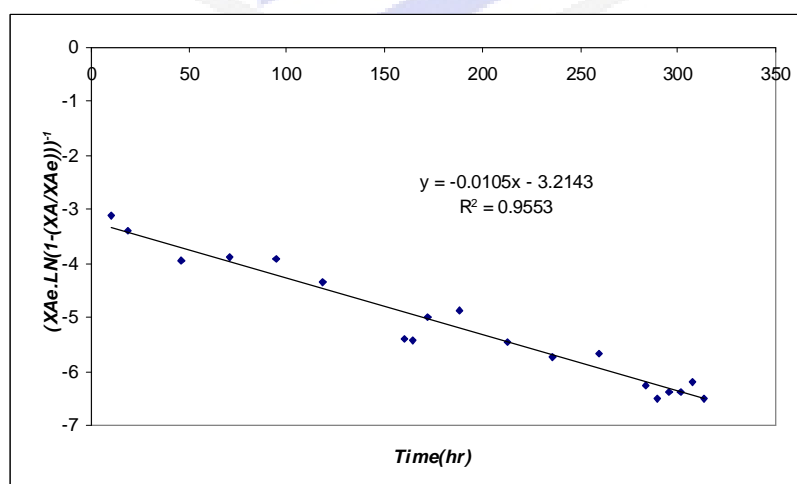


Figure2: Integral analysis of experimental conversion-time data with $n=2$.

Alternatively using three sets of time-temperature data obtained from a commercial plant, the catalyst deactivation parameters can be obtained through fitting the model by application of different optimization algorithms; that is, non-linear curve fitting, Nelder-Mead and genetic algorithms. Figure 3 show results obtained from proposed model and experimental

data in reversible condition. Most of the experimental data show goodness of fit with model data.

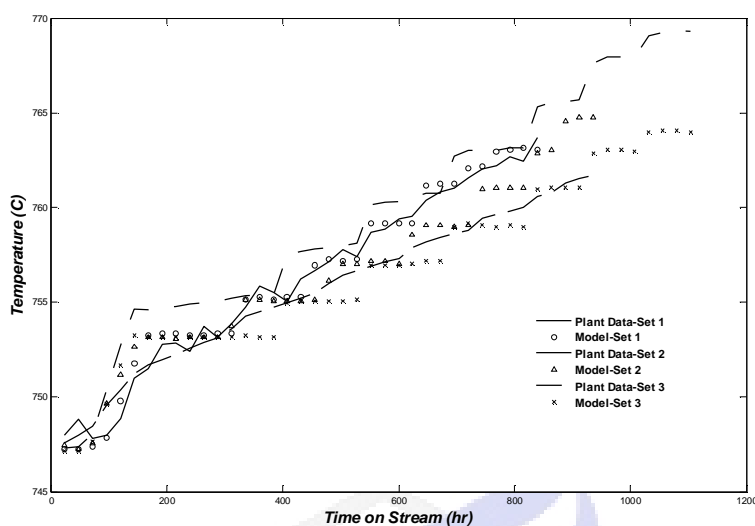


Figure 3: Time-temperature data obtained from parameters estimated with Genetic algorithm method in reversible reaction.

Again, a second order decay law is obtained. Table 2 shows the kinetic parameters obtained by this approach, where E_A and E_d represent the activation energies of the dehydrogenation and catalyst decay, respectively, and k_{d0} is the pre-exponential coefficient in the Arrhenius law for catalyst deactivation constant. Using kinetic parameters obtained by reversible kinetics, average values for order of deactivation, the activation energies of dehydrogenation and catalyst decay are 2.1, 90 kJ/mol and 140 kJ/mol, respectively.

Table 2: Estimated parameters (E_A , E_d , n , k_{d0})

	E_A (j/mole)	E_d (j/mole)	n	k_{d0} (hr ⁻¹)
Set1				
N.M	99431.6382	166458.2000	1.97	1.45E+08
G.A.	89304.4717	152937.6583	2.20	1.53E+07
Set2				
N.M	109042.2260	140907.1650	1.96	5.93E+06
G.A.	87292.2192	161574.0530	2.12	7.11E+07
Set3				
N.M	89712.2195	111028.1028	2.31	2.18E+04
G.A.	73187.6755	148437.1100	1.88	6.34E+06

4.2 Mass Transfer Effects

In this study, external and internal mass diffusion effects for Pt/Sn catalyst in C₁₀-C₁₄ dehydrogenation reaction were investigated. Mears and Weisz-Prater criterions show importance of external and internal mass transfer resistance over catalyst. If $C_M \ll 0.15$ and $C_{WP} \ll 1$, external and internal mass transfer resistance will be negligible, respectively. The effective diffusivity and mass transfer coefficient can be estimated from appropriate correlation given in the literature. In this way, one observes based on maximum reaction rate

for Pt/Sn catalyst in C₁₀-C₁₄ dehydrogenation C_M = 0.007 and C_{WP} = 0.05, external and internal mass transfer resistance at operating conditions (P = 1.7 bar, T = 480 °C) are negligible and working under the kinetic regime is confirmed.

The Weisz-Prater parameter, however, is not small enough to ensure negligible intra particle diffusion limitation throughout operation. Coking might cause significant diffusion limitation. The presumed series-parallel deactivation implies that uniform coking deposition occurs. On the other hand, significant diffusion limitation (for example, through pre-mouth plugging) could result in a shifting-order decay law which is not confirmed by experimental observations. Consequently, mass transfer limitations should be negligible throughout the useful life of the catalyst in both scales and the reaction rate and kinetic parameters represent the intrinsic ones. This reduce the complexities often arise in scale-up due to the difference in extent of resistances in the two scales.

4.3 Final Remarks

It is noteworthy to compare the results obtained by integral analysis with those of Table 2. Table 3 shows the results corrected to the same temperature using activation and deactivation energies of table 2 and parameters obtained from integral analysis, where k_{A0} is the pre-exponential coefficient in the Arrhenius law for main reaction constant. They depict a fair consistency. The difference observed might be due to the fact that the reactors were considered as isothermal. This is the case for the lab-scale reactor. It is also nearly the case for the commercial reactor, because of the low level of conversion and the high volume of diluent present. However, because of the endothermicity of the reaction, the average bed temperatures should be slightly lower than the feed temperatures being used in calculations.

Table 3. Estimated kinetic parameters form experimental catalyst performance data

Experimental Data		Industrial Data	
K_{A0}	k_{d0}	K_{A0}	k_{d0}
1.35E+08	1.72E+08	1.67E+08	8.53E+07

5. Conclusions

A simple mathematical model for catalyst decay in dehydrogenation of linear paraffins was developed. Using industrial plant time-temperature trajectory data, the kinetic parameters were obtained by utilizing nonlinear estimation functions. The kinetic model and parameters from time-conversion experimental data validated those obtained by nonlinear estimation functions applied to commercial plant data. A nearly second order decay law was obtained for catalyst deactivation. Since the plant data were used to fit the model, the results are directly applicable to the commercial plant.

Notation

A	alkane
a	catalyst activity
B	olefin
C_i	concentration of species i , mol/m ³
C_M	Mears' criterion
C_{WP}	Weisz-Prater criterion
E_A	activation energy for the main reaction, kJ/mol
E_d	activation energy for catalyst decay, kJ/mol
k_A	reaction rate constant, m ³ /(kg·h)
k_d	rate constant for catalyst decay, h ⁻¹
k_{d0}	decay constant at temperature T_0 , h ⁻¹
K_{eq}	concentration equilibrium constant, mol/m ³
r'_A	rate of disappearance of A per mass of catalyst, mol/(kg·h)
R	gas constant (m ³ Pa/(kmol K))
T	temperature, K
W	weight of catalyst in the reactor, kg
X	conversion of key component, A
<i>Greek letters</i>	
β	parameter defined by Eq. 8
τ	a capacity factor (catalyst weight per volumetric feed flow rate), kg·h /m ³

Subscripts

0	initial conditions
A	alkane
B	olefin

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