

Investigación

Analysis of Deactivation Models Based on Time-on-Stream (TOS) Theory for Fluid Catalytic Cracking Process

Jorge Ancheyta-Juárez^{*1,2} and Felipe López-Isunza³

¹ Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan, México 07730 D.F.,
Fax: (52) 5587-3967, E-mail: jancheyt@imp.mx

² Instituto Politécnico Nacional, UPALM, México 07738, D.F.

³ Universidad Autónoma Metropolitana-Iztapalapa, México 09340 D.F.

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Abstract. The deactivation of equilibrium catalyst for catalytic cracking of vacuum gas oil was studied via MAT experiments with industrial catalyst and feedstock using the 3-lump kinetic scheme proposed by Weekman [1] and five deactivation models reported in literature based on Time-on-Stream (TOS) Theory (Model 1, exponential law; Model 2, a second-order model; Model 3, power law; Model 4, hyperbolic function; Model 5, an empirical model). The five deactivation models can be derived from a general *m*-order expression. All the models can represent the experimental data except the second-order model.

Keywords: Catalysts, deactivation, models, cracking, gas oil.

Resumen. La desactivación de catalizadores de desintegración catalítica de gasóleos se estudió experimentalmente en una unidad MAT con catalizador y cargas recuperadas industrialmente usando el esquema cinético de 3 lumps propuestos por Weekman [1] y cinco modelos de desactivación reportados en la literatura basados en el tiempo de corrida (TOS) (1, modelo exponencial; 2, modelo de segundo orden; 3, modelo de ley de potencias; 4, modelo hiperbólico; 5, un modelo empírico). Los cinco modelos de desactivación se pueden derivar de una expresión general de orden *m*. Todos los modelos pueden representar los datos experimentales, excepto el modelo de segundo orden.

Palabras clave: Catalizadores, desactivación, modelos, desintegración, gasóleo.

1. Introduction

The Fluid Catalytic Cracking Process (FCC) is the major source of high octane gasoline. It is also the most widely used catalytic process [2]. An FCC unit comprises mainly two sections: a reactor, where heavy oil fractions come in contact with the catalyst and crack to light products with simultaneous deposition of coke on the catalyst, and a regenerator where this coke is burnt with air and the catalyst is returned to the reactor. During normal operation, catalyst activity is lost due to different processes like coking, nitrogen poisoning and adsorption of heavy aromatic molecules. The lost in activity due to these factors is restored in the regenerator and hence this is called temporary deactivation. Permanent deactivation is caused by metal deposits such as nickel and vanadium, and also due to sintering by the severe thermal conditions in the reactor and regenerator [3].

Coke deposition on catalyst in FCC processing is the main cause of catalyst deactivation. This process has been studied by different authors [1, 4-13]. Using the same mathematical function to explain the changes in catalyst activity with the time-on-stream (TOS), they have found different values for the deactivation kinetic parameters, mainly due to the use of feedstocks with different composition, experimental methods, catalyst, operating conditions and type of reactors [13].

Various mathematical models have been proposed using TOS theory. The parameters which typically change in these models are: the deactivation order and the functionality of activity respect to time-on-stream.

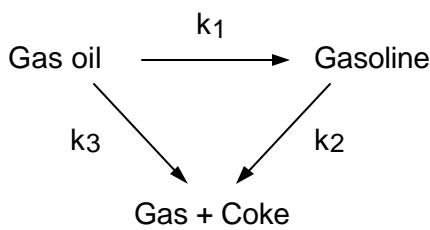
In the present work we used the experimental data obtained in a microactivity plant and five deactivation models reported in the literature to predict the deactivation kinetic parameters using the 3-lump kinetic model proposed by Weekman [1].

2. Kinetic Model

Various complex schemes have been proposed for catalytic cracking reactions [14-17]. However, the 3-lump scheme [1,18], which contains the minimum number of rate constants, is a widely used model. In the present work this model was also used together with different deactivation models. The simple scheme involves parallel cracking of gas oil to gasoline and gas plus coke, with consecutive cracking of the gasoline to gas plus coke (Figure 1).

For gas oil cracking the rate is assumed to be second order

$$\frac{dy_1}{dt} = -k_1 y_1^2 \mathbf{F} - k_3 y_1 \mathbf{F} = -(k_1 + k_3) y_1^2 \mathbf{F} = -k_o y_1^2 \mathbf{F} \quad (1)$$

**Fig. 1.** 3-lump kinetic model.

For gasoline cracking the rate is assumed to be first order

$$\frac{dy_2}{dt} = k_1 y_1^2 \mathbf{f} - k_2 y_2 \mathbf{f} = (k_1 y_1^2 - k_2 y_2) \mathbf{f} \quad (2)$$

The gas + coke yield is determined by the mass balance

$$y_3 = 1 - y_1 - y_2 \quad (3)$$

3. Deactivation Models

The TOS theory is based on the hypothesis that the concentration of active sites is simply a time-dependent power function of the remaining concentration of active sites and that all of them have the same strength (homogeneous surface) [19,20].

Equation (4) is integrated with the limits $t_c = 0$, $\mathbf{f} = 1$, for

$$-\frac{d\mathbf{f}}{dt_c} = k_d \mathbf{f}^m \quad (4)$$

$m \neq 1$, to give :

Using equations (4) and (5), the following reported mo-

$$\mathbf{f} = [1 + k_d(m-1)t_c]^{-\frac{1}{m-1}} \quad (5)$$

odels can be obtained.

Model 1. The integration of equation (4) in the case where the deactivation order (m) is taken equal to 1, gives the exponential law [1,18].

Model 2. Considering the deactivation order equal to 2, a se-

$$\mathbf{f} = e^{-k_d t_c} \quad (6)$$

cond-order model can be obtained from equation (5) [9].

Model 3. If a higher order is considered ($m > 2$) and for times-

$$\mathbf{f} = \frac{1}{1 + k_d t_c} \quad (7)$$

on-stream long enough, the term $k_d(m-1)t_c$, becomes larger than 1. Consequently, equation (5) is equivalent to the power law [18].

$$\mathbf{f} = [k_d(m-1)]^{-\frac{1}{m-1}} t_c^{-\frac{1}{m-1}} \quad (8)$$

$$\mathbf{f} = A t_c^{-N} \quad (9)$$

where the constants A and N are :

$$A = [k_d(m-1)]^{-\frac{1}{m-1}} \quad (10)$$

$$N = \frac{1}{m-1} \quad (11)$$

The most used typical form of the power law is $\mathbf{f} = t_c^{-N}$, however, the kinetic parameters evaluated with this function include the deactivation constant in the overall kinetic constant $k_0 A$, a combined cracking and decay constant [21].

$$\mathbf{f} = (1 + G t_c)^{-N} \quad (12)$$

Model 4. Making $G = k_d(m-1)$ and $N = 1/(m-1)$, equation (5) becomes the hyperbolic function [11,19].

Model 5. In the empirical deactivation model proposed by Oliveira and Biscaira [22] for gasoline cracking (equation (13)), which is basically the model suggested by Jacob *et al.* [23] without including the gas oil partial pressure effect (equation (14)), if the constant g is equal to 1, b becomes in k_d similar to Model 2.

$$\mathbf{f} = \frac{1}{1 + b t_c^g} \quad (13)$$

$$\mathbf{f} = \frac{a}{p^g (1 + b t_c^g)} \quad (14)$$

4. Experimental

The microactivity test reactor (MAT) is an important tool to measure the activity of FCC catalysts and can also be used for kinetic analysis of the cracking reactions [24]. The MAT technique is a normalized ASTM procedure for a standard feedstock (ASTM D3907-92). Its main features are: 4 g fixed-bed of catalyst, reaction temperature of 482°C, catalyst-to-oil ratio of 3, WHSV of 16 h⁻¹ and contact time of 75 s. Modified MAT test have been developed in order to cover a wider range of experimental conditions, temperature 482-560°C, catalyst contact time 5-300 s, WHSV of 6-100 [13,25], in the search for testing conditions representative of commercial operation recommended experiments at cat-to-oil of 3, temperature of 516°C, 37.5 s contact time and 32 h⁻¹ of WHSV.

In this study a set of experimental data obtained in a fixed-bed MAT reactor was used to evaluate the kinetic parameters for catalyst deactivation. Experimental runs were performed at a reaction temperature of 500°C and constant cat-to-oil ratio of 5 using an industrial vacuum gas oil over a commercial equilibrium catalyst, both recovered from an indus-

Table 1. Feedstock properties.

Properties	Vacuum gas oil
API gravity	25.5
Aniline point, C	78
Molecular Weight	352
K uop	11.86
Sulfur, wt%	1.98
Nitrogen, ppmw	877
Refractive index @ 20 C	1.5085
Nickel, ppmw	0.1
Vanadium, ppmw	0.8
ASTM Distillation, C	
IBP	235
30 vol%	409
50 vol%	433
70 vol%	467
90 vol%	517
FBP	568

Table 2. Catalyst properties.

Properties	Catalyst
<i>Physical properties</i>	
Surface area, m^2/g	155
Average bulk density, kg/m^3	890
<i>Chemical properties</i>	
Al ₂ O ₃ , wt%	34.8
Re ₂ O ₃ , wt%	1.5
Na, wt%	0.4
Fe, wt%	0.51
Ni, ppmw	503
V, ppmw	2200
Cu, ppmw	20
C*, wt%	0.17

* Initial coke content.

trial FCC plant. Feedstock and catalyst properties are presented in Tables 1 and 2 respectively.

In each experiment, a new portion of equilibrium catalyst was used. The catalyst-to-oil ratio was kept at a constant value by keeping the amount of gas oil injected (0.8 ± 0.005 g) in order to obtain different space velocities. Gas-chromatographic techniques were used for analysis of both the liquid and the gaseous products. The fraction of gasoline was defined by the cut point at 220° C. The product yields were calculated as weight percent of the reactant. A mass balance was performed for each run in the range $100 \pm 5\%$ and the conversion in weight percent was evaluated as the sum of C₅ + gasoline, C₁-C₄ gases, hydrogen and coke.

5. Results and Discussion

The data used in the regression analysis were the unconverted gas oil, gasoline and gas plus coke yields in the range of

Table 3. Kinetic and deactivation parameters.

Parameter	Model 1	Model 2	Model 3	Model 4	Model 5
k_0 (wt. frac. s^{-1})	0.2446	0.7460	0.3649*	0.9214	0.9164
k_1 (wt. frac. s^{-1})	0.1951	0.6001	0.2811*	0.7358	0.7317
k_2 (s^{-1})	0.0095	0.1459	0.0078*	0.0362	0.0359
k_3 (wt. frac. s^{-1})	0.0495	0.1259	0.0838*	0.1836	0.1847
m	1	2	2.268	1.635	—
k_d (s^{-1})	0.0875	1.2864	—	0.9269	—
N	—	—	0.7888	1.5741	—
G	—	—	—	0.5889	—
b	—	—	—	—	0.9335
g	—	—	—	—	1.3575
k_1/k_0	0.7977	0.8044	0.7703	0.7986	0.7985

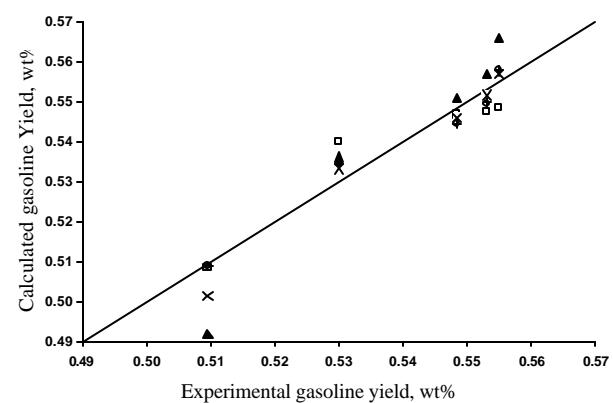
* $ki^* = k_i A$; A as in equation (10).

WHSV of 6.1-48.3 h^{-1} . The values of the kinetic and deactivation parameters were determined using a Marquardt non-linear regression technique and are shown in Table 3.

Figures 2 and 3 show the calculated and experimental yields using each deactivation model for gasoline and gas plus coke, respectively.

It can be observed from these figures that Models 4 and 5 represent the product yields equally well ($r > 0.982$ for gasoline and $r > 0.995$ for gases + coke yields). This is also shown in Table 1 where the corresponding kinetic parameters and the gasoline selectivity given by the k_1 / k_0 ratio are about the same. The second-order model (Model 2) does not yield a good prediction of experimental results in the range of times-on-stream studied in this work ($r \approx 0.96$ for gasoline and gases + coke yields).

The two most popular functions of deactivation catalyst, the exponential law and the power law given by Models 1 and 3 respectively, can reasonably represent the experimental data ($r \approx 0.975$ for gasoline and gases + coke yields). However, Models 4 and 5 are slightly superior to Models 1 and 3. It seems that Models 1 and 3 should be used for short times-on-

**Fig. 2.** Experimental and calculated gasoline yield.

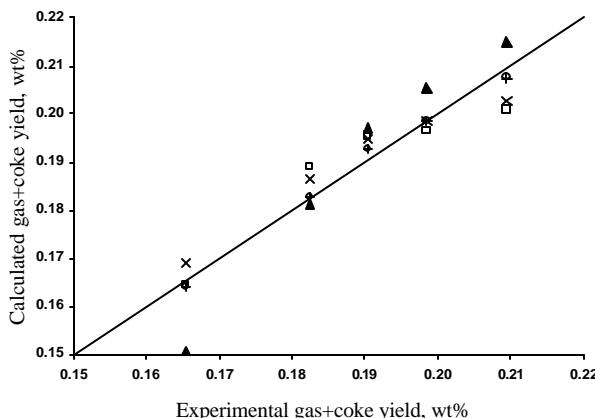


Fig. 3. Experimental and calculated gas plus coke yield.

stream as was predicted by Kraemer [21] in two different experimental units for the time range less than 20 s, and Models 4 and 5 for high times-on-stream (> 20 s).

Table 4 shows a comparison of the global gas oil cracking kinetic constant and the deactivation parameters obtained in the present work with those reported in the literature for Models 1, 3 and 4. There is no information available in the literature for the catalyst deactivation in gas oil cracking reactions using Model 5, only for the cracking of gasoline [22].

It can be seen that there are wide differences in the absolute values of kinetic and deactivation constants reported by various authors and the results obtained in this work compare well with some of them.

Figure 4 shows a comparison of calculated and experimental conversion using the five deactivation models. It is evident that Models 4 and 5 are acceptable and they can predict practically the same conversion ($r > 0.996$) and Model 2 is highly inaccurate for conversion prediction ($r \approx 0.98$).

Models 1 and 3 can predict equally well the conversion at short TOS (small conversions) and they become less accurate at high conversions ($r \approx 0.986$), specially Model 1.

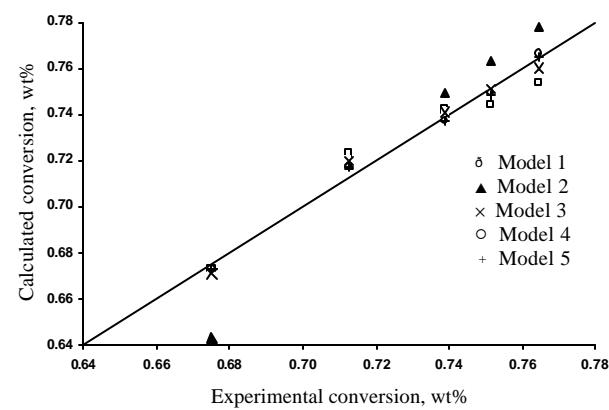


Fig. 4. Experimental and calculated conversion.

6. Conclusions

It was found that deactivation of equilibrium catalyst by coke deposition during catalytic cracking of vacuum gas oil can be reasonably and equally well represented using the hyperbolic function (Model 4) and an empirical model (Model 5), in fact, Model 5 has not been used before for this purpose.

The exponential and power laws (Models 1 and 3 respectively) were slightly inferior to Models 4 and 5, however they can represent the catalyst deactivation sufficiently well. The second-order model (Model 2) was highly inaccurate in the range of times-on-stream studied in the present work.

Models 1 and 3 have been widely used by various authors due to the fact that both require only one parameter to be estimated, k_d in Model 1 and N in Model 3. However, in order to obtain more accurate yield predictions when studies are performed at high times-on-stream, models which introduce two deactivation parameters, such as Models 4 and 5, should be included in kinetic estimations.

Table 4. Deactivation constants obtained by various authors.

Temperature (°C)	Model 1 k_0	Model 3 k_d	Model 4 N	Model 4 m	Model 4 m	Model 5 k_d
482 [1]	0.0063	0.012				
482 [4]			0.72			
482 [5]	0.0028-0.011	0.005-0.011				
510-538 [7]	0.36-0.70	0.13-0.21				
520 [9]	0.19x	1.58				
500 [26]	0.23	4.47				
510-550 [27]			0.10-0.22			
500-550 [28]			0.12-0.42			
500 [16]		0.089		4.48		
500-540 [11]				2.23-2.36		0.37-0.87
500 [This work]	0.2446	0.0875	0.7888	2.268	1.635	0.9269

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Nomenclature

<i>M</i>		Deactivation order
<i>t_c</i>	[s]	Time-on-stream
<i>k_d</i>	[s ⁻¹]	Deactivation constant
<i>k₀</i>	[wt frac ⁻¹ s ⁻¹]	Global gas oil cracking kinetic constant
<i>k₁</i>	[wt frac ⁻¹ s ⁻¹]	Gasoline formation kinetic constant
<i>k₂</i>	[s ⁻¹]	Gasoline cracking kinetic constant
<i>k₃</i>	[wt frac ⁻¹ s ⁻¹]	Gas oil to gases plus coke kinetic constant
<i>p</i>	[atm]	Partial pressure
<i>r</i>	[adim]	Correlation coefficient
<i>t</i>	[s]	Time
WHSV	[h ⁻¹]	Weight Hourly Space Velocity
<i>y₁</i>	[wt%]	Gas oil yield
<i>y₂</i>	[wt%]	Gasoline oil yield
<i>y₃</i>	[wt%]	Gases plus coke yield

Greek Symbols

<i>f</i>	Catalyst decay function
<i>a, b, g</i>	Constants

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