EMPIRICAL HYDRODYNAMIC MODEL FOR DE-METALIZATION OF KIRKUK REDUCED CRUDE OIL IN TRICKLE-BED REACTOR [+]

Ammar S. Abbas [*]

Abstract:

Kirkuk reduced crude oil was hydro-demetallized over two particle size (0.2 - 0.3 and 0.2 - 0.5 cm) Ni-Mo/γ-Al_2O_3 catalyst beds. The catalyst bed length varied from 12.7 to 31.8 cm and the liquid hourly space velocity varied from 0.5 to 4.2 h^{-1}. Reaction temperature was kept constant at 360°C. Also, hydrogen pressure and hydrogen to reduced crude oil ratio were kept at 3.2 Mpa and 400 cm^3 cm^{-3}. The effects of catalyst particle size, catalyst bed porosity, catalyst bed length and superficial liquid reduced crude oil flow through trickle-bed reactor has been studied. The results show, that apparent rate constant increased with increasing liquid velocity and bed length while decreasing in apparent rate constant with increasing of bed porosity and particle size of the catalyst.

Two empirical hydrodynamic models described the behavior of apparent rate constant of the hydro-demetallization has been discussed. First, the classical empirical hydrodynamic model proposed by Garcia and Pazos [1]. Second, suggested model denoted as Reynolds empirical hydrodynamic model. Statistical analyses of these two models show that both models represented well the effect of particle size, bed length, bed porosity and liquid superficial velocity on the apparent rate constant of the hydro-demetallization reaction. But suggested Reynolds hydrodynamic model, was more accurate than classical hydrodynamic model.

المستخلص:

تمت عملية ازالة المعادن من نفط خام كركوك المختزل بواسطة مفاعلته فوق عامل مساعد Ni-Mo/γ-Al_2O_3 و لحجمين من الحبيبات للعامل المساعد(٠,٢ – ٠,٥ و ٠,٢ – ٠,٣ سم) في مفاعل ثلاثي الاطوار. تراوح طول حشوة العامل المساعد بين ١٢,٧ الى ٣١,٨ سم و تراوحت سرعة الفراغية لزيت الوقود بين ٠,٥ و ٤,٢ ساعة$^{-1}$. تم تثبيت درجة حرارة التفاعل عند ٣٦٠ درجة مئوية و ضغط هيدروجين ٣,٢ ميكا باسكال و نسبة هيدروجين الى زيت وقود ٤٠٠ سم^3 سم$^{-3}$.

تم دراسة تأثير كل من حجم حبيبات العامل المساعدو مسامية الحشوة و طول حشوة العامل المساعد و السرعة الظاهرية لنفط خام كركوك المختزل اشارت النتائج الى ان القيمة الظاهرية لثابت تفاعل ازالة المعادن يزداد مع زيادة كل من السرعة الظاهرية لنفط خام كركوك المختزل و طول حشوة العامل المساعد و انخفاض كل من مسامية الحشوة و حجم حبيبات العامل المساعد.

نوقش موديلين تجريبيين لوصف تصرف ثابت تفاعل ازالة المعادن. الاول موديل كلاسيكي مقترح من قبل كراسيا و بازوس (Garcia and Pazos, 1982) و الثاني مقترح من قبلنا و سمي بموديل رينولدز. اشارت النتائج الاحصائية لحلول الموديلين ان كلا الموديلين يصفان بصورة جيدة تصرف ثابت تفاعل ازالة المعادن مع تغير حجم حبيبات العامل المساعد و طول حشوة العامل المساعد و مسامية الحشوة و السرعة

[+] **Received on 15/11/2006 , Accepted on 27/5/2008**

[*] **Lecturer / Chemical Engineering Department/ College of Engineering - University of Baghdad**

الظاهرية لنفط خام كركوك المختزل. لكن دقة الموديل المقترح لهذا الوصف هي اكثر من الموديل الكلاسيكي.

Keywords:

Hydrodynamic model, hydrotreatment, empirical model, trickle bed reactor, de-metallization and reduced crude oil.

Introduction:

Hydrotreatment (HDT) is a catalytic process whereby crude oil fraction (or product), as the feedstock is passed with hydrogen, over or through a catalyst bed at elevated temperatures and pressures in order to remove impurities or development of physical properties[2].

Trickle bed reactors are extensively used in the oil industry for hydrotreatment of petroleum distillates, removal of impurities, such as sulfur and nitrogen, and hydro-cracking. These reactors are also being used for HDT of residue, where hydro-desulfurization (HDS) and hydro-demetallization (HDM) are the key reactions.

These reactions take place in the liquid phase, since much of the residual feed and product molecules do not vaporize at reactor pressure and temperature. The oil in the reactor is saturated with hydrogen gas because the partial pressure of hydrogen is very high and hydrogen is available in great excess [3]. The oil and hydrogen reactant molecules diffuse through the liquid oil filling the catalyst pores and adsorb on to the catalyst surface where the hydro-treating reactions take place. Large molecules tend to adsorb more strongly on to the catalyst surface than smaller molecules. This means that the large molecules tend to dominate the reactions on the catalyst when they can successfully diffuse into the catalyst pores. The product molecules must then desorb from the catalyst surface and diffuse out through the liquid that fills the catalyst pores.

Many studies have been made to determine the reaction order for residue demetallization with respect to metal concentration. All studied reports that the metal removal reactions (demetallization) are obey first order reaction rate expression. Kinetics of hydro-demetallization of distillates [4], Kirkuk reduced crude [5], Bai-Hasan reduced crude [6], Sharki Baghdad crude and reduced crude oils [7] and Basrah reduced crude oil and the deasphaltening fraction of Basrah reduced crude oil [8], are reported as1 first order rates.

Research work is usually carried out in small pilot units, where liquid linear velocities can be up to a hundred times lower than those used in commercial plants, at real space velocities. It is well recognized [9] that, at these low velocities, problems such as liquid channeling, liquid stagnant zones, poor catalyst wetting and back-mixing can occur. These phenomena must be corrected or their effect on reactor performance should be quantitatively estimated to obtain meaningful kinetic data.

Several papers have been published dealing with the behavior of trickle bed reactors. A review by Satterfield [9] and Shah [10] cover most of the published literature, Models based on back-mixing; hold-up and catalyst wetting theories have been proposed by several authors [11, 12, 13]. However, most of the information used to derive the theoretical equations, have been taken from the widely studied packing absorption towers, where flow regimes and particle sizes are rather different from those used in trickle bed reactors. Furthermore, there is evidence that back-mixing, liquid hold-up and catalyst wetted area depend on particle diameter, and its effect has

not been quantitatively measured or there seems to be a controversy about its influence.

Garcia and Pazos [1] studied the performance of small trickle bed reactors, at real space velocities used for HDS and HDM of heavy Venezuelan feeds and correlated two empirical expressions for the effect of the liquid velocity and the mean particle diameter on reactor behavior.

The purpose of this paper is to evaluate the effect of the mean particle diameter, bed length and real velocity of liquid feed on reactor behavior and the final objective is to obtain an empirical model, which considers the influence of the flow conditions and packing properties on rate constants.

Experimental Work:

Raw Materials

- **Reduced crude oil:** Kirkuk reduced crude oil fraction was used as feedstock. The properties of used reduced crude oil are shown in Table 1.
- **Catalyst:** Nickel Molybdenum over alumina was used as a hydrotreatment catalyst. The normal size of the catalyst was about 0.2 – 0.5 cm and has porosity of about, catalyst was also crushed to normal size about 0.2 – 0.3 cm to use in another group of experiments which smaller average particle size required. Catalyst properties are given in Table 2.

Table (1): Properties of reduced crude oil

Specific gravity at 15.6/15.6^{o} C	0.9826
API gravity, degree	12.5
Sulfur, wt%	4.25
Vanadium, ppm	120
Nickel, ppm	35
Iron, ppm	12

Table (2): Properties of commercial catalyst Ni-Mo/γ-Al_2O_3.and crushed catalyst

Chemical Composition		Physical properties		
Loss, wt%	<3.0	Cylindrical catalyst of normal size 0.2 – 0.5 cm	Mean particle diameter, cm	0.31
NiO, wt%	3.0		Bulk density, g cm^{-3}	0.670
MoO, wt%	15.0		Surface area, m^2 g	210
SiO_2, wt%	1.1		Pore volume, cm^3 g	0.50
Na_2O, wt%	0.07	Cylindrical catalyst of normal size 0.2 – 0.3 cm	Mean particle diameter, cm	0.26
Fe, wt%	0.04		Bulk density, g cm^{-3}	0.690
SO_4, wt%	2.0		Surface area, m^2 g	210
Al_2O_3, wt%	Balance		Pore volume, cm^3 g	0.40

Hydrotreatment Experiments:

The hydrotreatment runs were preformed in a pilot plant continuous high-pressure unit employing an up-flow co-current. The reactor is stainless steel, and heat resisting steel with dimensions of 65 cm length 2 cm in diameter. The reactor was jacketed with 4 separately heat controlled block shells in order to ascertain isothermal operation.

The reactor products were cooled in a condenser-cooler and separated from hydrogen un-reacted and the hydrocarbon gases by passing into high and low-pressure separators. The gases were then vented to the exterior through a gas flow meter. The unit was supplied with a high pressure-dosing pump to introduce the feedstock into the unit. The reaction conditions employed are temperature of 360^{o} C, pressure of 3.2 Mpa, liquid hourly space velocity (LHSV) from 0.5 to 4.2 h^{-1} and hydrogen to reduced crude oil ratio of 400 cm^3/ cm^3. Products were collected only after steady-state operation was established and initial operating products were discarded.

The reactor was packed with 40, 60, 80 and 100 cm^3 of the commercial Ni-Mo/γ-Al_2O_3 catalyst of normal size 0.2 – 0.5 cm after drying at 120^{o} C for 2 h between two layers of inert material (glass beads with 0.4 cm diameter), which is give bed length of 12.7, 19.1, 25.5 and 31.8 cm and measured bed porosity of about 0.34. The above experiments were repeated by using reactor packed with 40, 60, 80 and 100 cm^3 of the commercial Ni-Mo/γ-Al_2O_3 catalyst of normal size 0.2 - 0.3 cm, which is give bed length of 12.7, 19.1, 25.5 and 31.8 cm and measured bed porosity of about 0.28.

Catalyst presulfiding was accomplished by a solution of 1.2 vol% of thiophene in one liter of reduced crude oil. The first 4 hours of presulfiding was carried out at 2.0 Mpa, 204^{o} C and LHSV of 3 h^{-1}. The next step in the catalyst activation was continued for 16 hours using the following operating conditions, 300^{o} C temperature, 1 h^{-1} LHSV, 2.1 Mpa pressure and 200 cm^3/ cm^3 hydrogen to reduced crude oil ratio.

Test Method:

The metals content of the feed reduced crude oil and experiment products were measured by using ATSM D-3327 standard method.

PYEUNICAM Sp-9 atomic adsorption spectra-photometer with 381.5 nm wave length and N_2O / acetone flame was used to measured vanadium content. While wave length of 232.0 and 248.6 nm and air / acetone flame were used to measured nickel and iron content, respectively. The lamp current was15 mA for all tests.

Results and Discussions:

Effect of Catalyst Bed Length, Liquid Velocity and Mean Particle Diameter

Several experiments were carried out at catalyst bed lengths ranging from 12.7 cm up to 31.8 cm to study its effect on vanadium removal. This is the largest component of metals in the feed (Table 1). The space velocity was also varied in each run, in the range of 0.5 - 4.2 h^{-1}. Tables 3 and 4 show the apparent rate constant (k_a,h^{-1}), determined from the first order expression for plug-flow equation [7, 8, 14, 15, 16], as a function of the liquid (superficial) velocity (u,cm h^{-1}) for vanadium removal reaction. Liquid velocity (u) is equal to the total liquid flow per reactor cross-sectional area per bed porosity (e).

In general, it can be observed from tables 3 and 4, which are showing the values of apparent rate constants versus liquid velocity for different bed porosity and catalyst particle size, that apparent rate constants increase substantially with the liquid

velocity, indicating a poor catalyst wetting and there was a very poor effect of the catalyst bed volume (bed length) on the apparent rate constant values.

Tables below (3 and 4) show that the apparent rate constants were decrease as particle size decreases. This observation is in opposite of the natural behavior due to reduced in bed porosity from 0.34 to 0.28 as a result of decreasing of catalyst particle diameter. This observation was in agreement with the results of the performance of small hydrotreating of Venezuelan deasphalted oil in small trickle bed reactor (100 cm * 1.9 cm) by Garcia and Pazos [1], which were reported that the rate constant was increase with decreasing of catalyst diameter at constant bed porosity of 0.34, but this rate constant decreasing when the bed porosity reduced to 0.25.

Table (3): Apparent 1st order rate constant versus bed length and liquid velocity at temperature 360° C, catalyst particle size 0.31 cm and bed porosity 0.34

Bed length, cm	Liquid velocity, cm/h	Apparent 1st order rate constant (k_a), h^{-1}
12.7	18.7	0.19
12.7	41.2	0.38
12.7	112.4	0.88
12.7	157.4	1.16
19.1	28.1	0.29
19.1	67.4	0.61
19.1	157.4	1.24
19.1	202.3	1.53
25.5	37.5	0.39
25.5	74.9	0.70
25.5	217.3	1.70
25.5	314.7	2.31
31.8	56.2	0.57
31.8	112.4	1.02
31.8	196.7	1.62
31.8	365.3	2.71

Table (4): Apparent 1st order rate constant versus bed length and liquid velocity at temperature 360° C, catalyst particle size 0.26 cm and bed porosity 0.28

Bed length, cm	Liquid velocity, cm/h	Apparent 1st order rate constant (k_a), h^{-1}
12.7	22.7	0.19
12.7	86.4	0.61
12.7	136.5	0.89
12.7	163.8	1.04
19.1	34.1	0.30
19.1	68.2	0.53
19.1	143.3	0.99
19.1	259.3	1.63
25.5	45.5	0.40
25.5	109.2	0.83
25.5	263.9	1.73
25.5	364.0	2.26
31.8	56.9	0.50
31.8	125.1	0.96
31.8	295.7	1.96
31.8	443.6	2.75

The deviations of the experimental points, at constant liquid velocities, are due to the different catalyst bed lengths. This suggests the existence of back-mixing effects under these conditions. If flow dynamic problems were not present, a straight horizontal line should be obtained [10, 11, 12, 13, 17].

Classical Empirical Hydrodynamic Model :

Total experimental data (which is summarized in table 3 and 4) were correlated by combination of two hydrodynamic models suggested by Garcia and Pazos [1]. The combine suggested model assume apparent rate constant is proportional with liquid velocity (u), bed length (l), catalyst particle size (dp) and bed porosity (e) to the power of α, β, γ and δ, respectively.

$$k_a \propto u^{\alpha} l^{\beta} dp^{\gamma} e^{\delta} \qquad \text{----------} \quad (1)$$

In other words,

$$k_a = c u^{\alpha} l^{\beta} dp^{\gamma} e^{\delta} \qquad \text{----------} \quad (2)$$

Where: c is proportional constant.

Coefficients in equation 2 were determined, using conventional methods of multi-linear regression by least squares with results confidence level of 95 %. The following empirical model equation was obtained:

$$k_a = 0.015 u^{0.952} l^{0.05} dp^{-2.83} e^{3.43} \qquad \text{----------} \quad (3)$$

Equation 3 indicates that apparent rate constant can be improved by increasing the liquid velocity and the catalyst bed length. It is rather difficult to elucidate if this behavior is a consequence of the back-mixing effects or due to an increase in the liquid hold-up or catalyst effective wetted area. According to the hold-up [12] and wetted area models [13], catalyst activity is exclusively a function of liquid velocity, in the absence of back-mixing problems. However, $\beta > 0$ was obtained for a confidence level of 95%. This indicates an additional effect of the catalyst bed length, which can be interpreted by the presence of back-mixing effects.

The empirical model also represents that apparent rate constant is increasing with bed porosity ($\delta > 0$) and reduces of catalyst particle size ($\gamma < 0$), which is in a good agreement with the results of effect of catalyst particle size on performance of trickle-bed reactor used to hydro-desulfurization of Kuwait reduced crude oils by using 100 cm^3 of 0.3 to 1.3 cm catalyst particle size [18].

Statistical calculation of the compute empirical hydrodynamic model and experimental data shows that the solution of the model (equation 1) is proportional correlated with the experimental data and the distribution of the experimental data around the model solution (variance) is about 0.7823, standard error of 16.2 % in 95 % confidence level, as summarized in Table 5.

Predicted values calculated from empirical model (equation 3) and experimental data is shown in figure 1.

Table (5): Statistical analysis of the model.

Experimental observations	32
Standard error, %	16.2
Variance	0.7823
Correlation coefficient	+ 0.8846
Confidence level, %	95

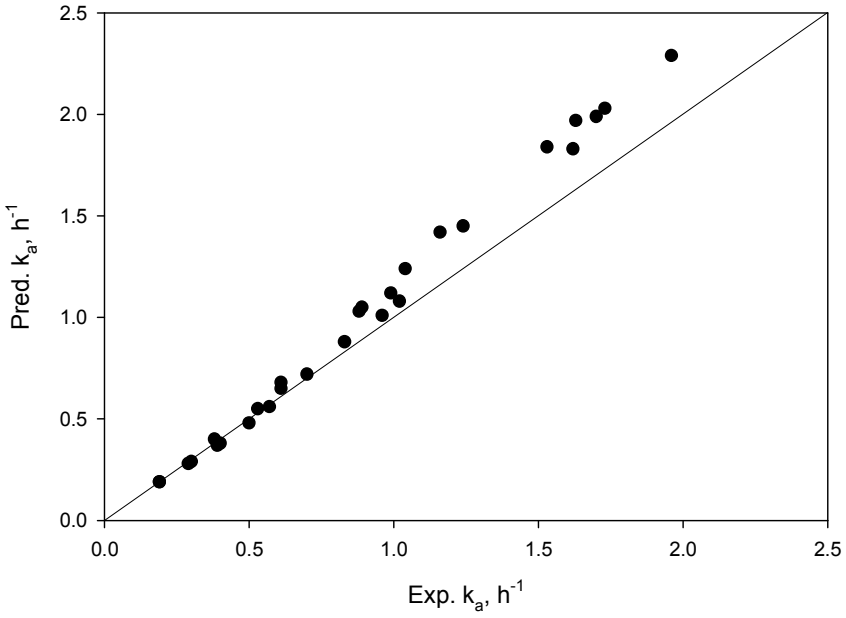

Fig. (1): Experimental and predicted values of apparent rate constant by using classical hydrodynamic model.

The standard error (16.2 %) is agreed very well with the standard error of about ±10% proposed by Kan and Greenfield [19]. The results of Garcia and Pazos [1] was in the range of ±20 %, this high value of standard error was due to evaluated the effects of liquid velocity, bed length, catalyst particle size and bed porosity in separate two equations and then comparison with their experimental data.

Reynolds Empirical Hydrodynamic Model (Suggested Model):

In order to find another empirical expression to describe the effects of liquid velocity, bed length, catalyst particle size and bed porosity with higher variance of data, empirical model denoted as Reynolds empirical hydrodynamic model has been suggested.

The suggested model assume that the apparent rate constant is proportional with Reynolds number (Re) of the liquid through the catalyst bed to power α and dimensionless ratio of reactor length to reactor diameter (l/dr) to power β, thus, the suggested model can be written as:

$$k_a = c\,\mathrm{Re}^{\alpha}\left(\frac{l}{dr}\right)^{\beta} \qquad \text{----------} \quad (4)$$

Where: $\mathrm{Re} = \frac{\rho u dp}{\mu}$, and c is the proportional constant.

Reduced crude oil density (ρ) 0.7931 g cm^{-3} and reduced crude oil viscosity (μ) 0.537g cm^{-1} s^{-1} were calculated at experiments conditions of 360° C temperature [20].

Values of Reynolds number Re, which is less than 5 (for particle size between 0.2 to 0.5 cm, bed porosity between 0.28 to 0.34, LHSV between 0.5 and 4.2 h^{-1} and bed length between 12.7 and 31.8 cm) were in good agreement with the results of Reynolds number values for hydrotreating in trickle-bed reactor, which were ranged between 0.08 and 80 for catalyst particle size ranged between 0.3 to 1.3 cm, bed porosity between 0.24 to 0.5, LHSV less than 10 and bed length less than 100 cm [1, 10, 17].

Equation 4 was solved to obtained values of c, α and β by using experimental data with conventional methods of multi-linear regression by least squares with results confidence level of 95 %. The following empirical model equation was obtained:

$$k_a = 0.490\,\mathrm{Re}^{0.835}\left(\frac{l}{dr}\right)^{0.156} \qquad \text{----------} \quad (5)$$

The result power in equation 5 shows that, the apparent rate constant is increasing with Re and reactor dimensionless ratio (l/dr), which is ranged from about 6 to 16.

Statistical analysis was carried out for the Reynolds hydrodynamic model (suggested model-equation 5) and experimental data. The statistical analysis shows that the solution of the model is highly proportional correlated with the experimental data with correlation coefficient and the distribution of the experimental data around the model solution (variance) is approach to 1. Statistical analysis of the model in summarized in table 5.

Table (5): Statistical analysis of Reynolds hydrodynamic model.

Experimental observations	32
Standard error, %	2.30
Variance	0.9112
Correlation coefficient	+ 0.9901
Confidence level, %	95

Predicted values calculated from empirical model (equation 5) and experimental data is show in figure 2.

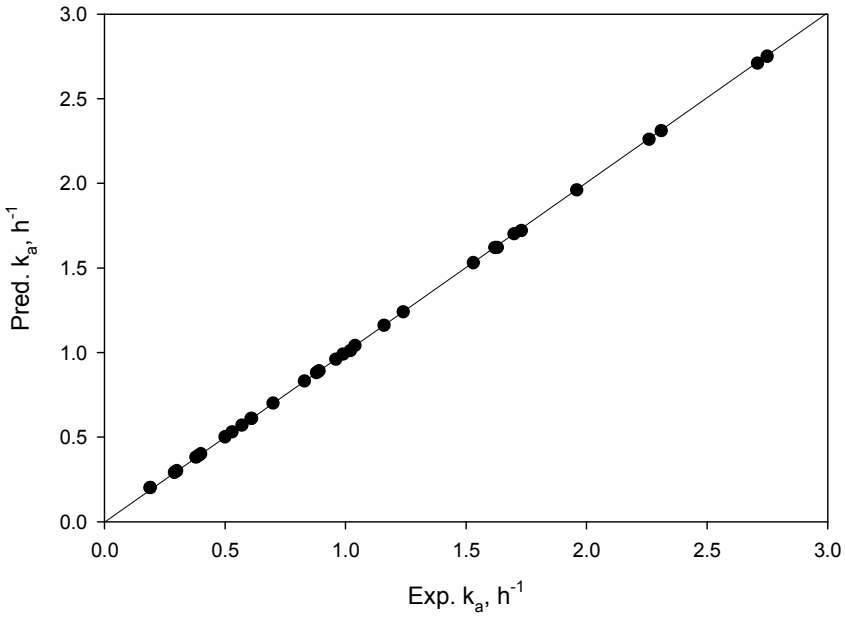

Fig. (2): Experimental and predicted values of apparent rate constant by using Reynolds hydrodynamic model.

The standard error and variance of Reynolds hydrodynamic model were 2.3 % and 0.9112 while the standard error and variance of classical hydrodynamic model were 16.2 % and 0.7823 for correlation coefficient of about + 0.9901 for Reynolds hydrodynamic model compared with +0.8846 for the classical hydrodynamic model. Thus, the suggested hydrodynamic model (Reynolds hydrodynamic model) is represent more accurate the apparent rate constant in the presence of back-mixing and catalyst effective wetted area phenomena than the classical hydrodynamic model, which was proposed by Kan and Greenfield [19] and used by Garcia and Pazos [1] to described the hydrotreating of the heavy Venezuelan deasphalted oil.

Conclusions:

1. Apparent rate constant for the de-metallization reaction of reduced crude oil is affected by bed properties and liquid velocity. The apparent rate constant is increasing with liquid velocity and bed porosity and decreasing with increasing catalyst particle size.
2. Back-mixing effects are important when short catalyst bed used. However, the catalyst utilization, and hence the wetted area, increases with decreasing particle size.
3. Classical empirical hydrodynamic model represent the apparent rate constant for hydro-demetallization of reduced crude oil with standard error of 16.2 %, variance of 0.7823 and correlation coefficient of 0.8846.
4. Suggested Reynolds empirical hydrodynamic model shows that the apparent rate constant is vary proportionally with the Reynolds number of the liquid flow through catalyst bed to the power one, with standard error of 2.3 %, variance of 0.9112 and correlation coefficient of 0.9901.
5. Suggested hydrodynamic model (Reynolds hydrodynamic model) is represent more accurate the apparent rate constant in the presence of back-mixing and catalyst effective wetted area phenomena than the classical hydrodynamic model.

Nomenclature:

C	Proportional constants in equations 2 and 4
Dp	Catalyst (average) particle size, cm
Dr	Reactor diameter, cm
E	Catalyst bed porosity, dimensionless
HDM	Hydro-demetallization
HDS	Hydro-desulfurization
HDT	Hydrotreatment
k_a	Apparent hydro-demetallization rate constant, h^{-1}
L	Catalyst bed length, cm
Re	Reynolds number ($\rho udp/\mu$), dimensionless
U	Liquid (superficial) velocity, cm h^{-1}

Greek Letters:

A B Γ Δ	Constants (coefficients) in equations 1, 2, and 4, dimensionless
M	Reduced crude oil viscosity, g cm^{-1} s^{-1}
P	Reduced crude oil density, g cm^{-3}

References:

1. Garica W. and J. M. Pazos, *Chem. Engeng. Sci.* **37**(10): 1361, 1982.
2. Speight, J. G., *The Desulfurization of heavy oils and residue*. New York: John Wiley and Sons Inc., 1981.
3. Meyers, R. A., *Handbook of petroleum refining processes*. New York: McGraw-Hill, 1996.
4. Chu, C. I. and I. Wang, *Ind. Engng. Chem. Proc. Des. Dev*. (2): 338, 1981.
5. Mohammed, A-H A-K and K. Hankish, *J. Petrol. Res*. (2): 37 1985.
6. Abbas A. A., A-H. A-K Mohammed, A. B-A Ahmed and K. Abbas, *Fuel Sci. Tech. Int*. (4): 307, 1990.
7. Hummadi, K. K., *Petroleum residue hydrogenating-catalyst preparation and activity*. Ph. D. Thesis, University of Baghdad, 1999.
8. Abbas, A. S., *Low sulfur feedstock from Basrah reduced crude oil for coke production*. M. Sc. Thesis, University of Baghdad, 1999.
9. Satterfield, C. N., *A.I.Ch.E. J*. **21**:209, 1975.
10. Shah, Y. T., *Gas – liquid – solid reactor design*. New York: McGraw-Hill, 2002.
11. Mears, D. E., *Chem. Engeng. Sci.* **26**: 1361, 1971.
12. Henry, H. C. and J. B. Gilbert, *Ind. Engng. Chem. Proc. Des. Dev.* **12**: 328, 1973.
13. Mears, D. E., *Advan. Chem. Ser.* **133**: 218, 1974.
14. Chang, C. D. and A. J. Silvertri, *Ind. Engng. Chem. Proc. Des. Dev.* **13**: 315, 1974.
15. Oleck, S. M. and H. S. Sherry, *Ind. Engng. Chem. Proc. Des. Dev.* **13**: 315, 1977.
16. Pazos, J. M., L. Aquino and J. Pachano, *Amer. Chem. Soc.* **26**(2): 456, 1981.

17. Montagna, A. A. and Y. T. Shah, *Ind. Engng. Chem. Proc. Des. Dev.* **14**(4):479, 1975.
18. Montagna, A. A., Y. T. Shah and J. A. Paraskos, *Ind. Engng. Chem. Proc. Des. Dev.* **16**(1): 152, 1977.
19. Kan, K. M. and P. F. Greenfield, *Ind. Engng. Chem. Proc. Des. Dev.* **18**: 740, 1979.
20. Nelson, W. L., *Petroleum refinery engineering*. New York: McGraw-Hill, 1956.