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Some Experimental Observations of Mass Transfer Limitations in a Trickle-Bed Hydrotreating Pilot Reactor

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A systematic experimental work for evaluating isothermality of a pilot reactor, flow regime, axial dispersion, and mass transfer gradients between the catalyst surface and the bulk fluid in a trickle-bed hydrotreating reactor is presented. Experiments were carried out at the following operating conditions: 5.3 MPa total pressure, 356.2 mL mL⁻¹ hydrogen-to-oil ratio, 613–653 K reaction temperature, and 1.0–2.5 h⁻¹ liquid hourly space velocity. Commercial NiMo catalyst and feedstock were used for hydrotreating reactions. The catalyst (2.3 mm diameter) bed was diluted with silicon carbide (1.4 mm diameter) with an inert-to-catalyst volume ratio of 1. Various criteria reported in the literature were employed for evaluating axial dispersion in liquid and gas phases. Two typical tests were employed to determine mass transfer gradients: (I) changing the amount of catalyst loaded to the reactor and the feedstock flow rate at constant LHSV and (II) conducting experiments using different amounts of catalyst at variable LHSV.

Introduction

Trickle-bed reactors (TBR) are widely used in petroleum industry, especially for hydrotreating of middle distillates and heavy oil fractions. TBR consists of a fixed-bed of catalyst particles contacted by a concurrent downward gas–liquid flow carrying both reactants and products. In this reactor, conversion depends not only on the reaction kinetics but also on transport processes.¹

In the case of hydrotreating process (HDT), depending on the feed and reactor operating conditions, the reaction can be carried out in two or three phases. For middle distillates, hydrotreating is commonly accomplished in three phases (gas–liquid–solid, down-flow, and fixed-bed systems). When the heterogeneous gas–liquid–solid reaction takes place, various transport processes, such as flow dynamics, heat transfers, and mass transfers, can have significant effects on the global reaction rate.

According to the three-film theory,² the reactants must first be transferred from gas phase to liquid phase and then to the solid catalyst surface. The reactants then diffuse inside the porous structure of the catalyst and the reactions take place both on the external and internal surfaces of the catalyst.

In hydrotreating trickle-bed reactors the liquid hydrocarbon flows over the catalyst particles in films and

rivulets from one particle to the next, and the vapor (mostly hydrogen) flows continuously through the remaining voids. These conditions may cause poor catalyst utilization due to incomplete catalyst wetting, axial dispersion and mass transfer limitations.³

Due to economical reasons, catalyst screening and other experimental studies are usually conducted in small-scale reactors, because new catalyst formulations are not available in large quantity, and the amount of catalyst involved in experimental tests must be small.⁴

The differences between pilot and commercial reactors cause number of problems in testing catalyst having commercially applied size and shape, and the data obtained may not easily be transposed from the pilot reactor to the commercial reactor, because physical processes inside are not well-known and are apparently different.^{5–7} The reduction of the reactor length imposes the use of lower gas and liquid velocities in the catalyst bed which affect the bed hydrodynamics. Extended deviations from the ideal plug flow are observed in the liquid-flow through short beds built with catalyst particles of commercial size that affect the performance of the laboratory hydrotreaters.⁸

The following general characteristics are proposed as crucial by Perego et al.⁷ for the correct carrying out experiments for continuous operations in order to reduce deviation from ideal behavior: (I) isothermality, (II)

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(†) Santos, A. R.; Nigam, S. D. P. *Rev. Chem. Eng.* 1999, 12, 307–

304.

(‡) Karsten, H.; Hoffmann, U. *AIChE J.* 1999, 42, 1202.

(§) Carrozzini, J. D.; O'Connell, D. J. *Appl. Catal.* 1999, 42, 213.

(¶) Lefebvre, D.; Baccot, R.; Vermeil, M.; Schwach, G.; Pouch, I. *Ind. Eng. Chem. Res.* 1999, 37, 2442.

(||) Liu, S. T. *AIChE J.* 1994, 42, 3499.

(||) Diamantidis, D.; Papayannakos, N. *Chem. Eng. Sci.* 1998, 53,

2469.

(||) Perego, C.; Perrella, S. *Catal. Today* 1999, 52, 111.

ideality of flow pattern (without axial dispersion and wall effects), and (3) no limiting interphase and intraphase concentration and temperature gradients. For trickle-bed reactors, the following care must be taken: (4) catalyst wetting.

Moreover, for the interpretation of kinetic data and the development of new catalysts it is necessary to perform experiments under conditions where transport resistances are negligible.

It is well-known that all these evaluations are needed before obtaining kinetic-quality data, however, not all published works take care of them, and hence, the reported results may be influenced by above-mentioned phenomena, and estimated kinetic parameters may also be inaccurate.

The main objective of this work is to present a systematic study for carrying out experiments in a trickle-bed pilot reactor using catalyst and feedstock both recovered from a commercial HDT plant in order to define the best operating conditions to ensure that hydrotreating reactions are conducted without deviation from ideality.

Techniques To Check the Absence of External Limitations and Mass Transfer Gradients. Gradients of concentration and temperature occur between the catalyst surface and the bulk fluid. The presence of these gradients also referred as external or interphase severely complicates the analysis of the catalyst performance.³

These gradients between bulk fluid C_f and catalyst surface C_s can be evaluated with the following general equation:⁴

$$(C_f - C_s) = \frac{(r)\rho Sc^{2/3}}{a_s j_b G} \quad (1)$$

where r is the reaction rate, ρ the density, Sc the Schmidt number ($Sc = \mu/\rho D$), a_s the external surface of the catalyst, j_b a Reynolds number ($Re = d_p G/\mu$) depending factor commonly determined as $j_b = f(Re^{-1/4})$, G the superficial mass flow velocity, μ the viscosity, D the diffusivity, and d_p the catalyst particle diameter.

If reactants and catalyst properties are kept constant, $(C_f - C_s)$ depends only on the value of G :

$$(C_f - C_s) = G^{-1/4} \quad (2)$$

Equation 2 means that concentration gradients can be reduced by increasing the flow rate of reactants keeping the commercial catalyst size.

On the basis of this principle, there are two common tests reported in the literature to check the presence of external gradients: both consider that, in the absence of transport limitations, the apparent kinetic rate must be independent of the linear velocity through the bed:^{1,9}

(1) Various experiments are carried out by increasing both reactant flow rate (i.e. linear velocity) and catalyst volume, while keeping constant their ratio (i.e. keeping constant the contact time). In this test, conversion is plotted vs reactant flow rate. If the mass or thermal

Table 1. Characterization of the Feedstock (SRGO)

specific gravity 20/4 °C	0.8687
Elemental Analysis, wt %	
C	85.08
H	13.00
O	0.250
N	0.054
S	1.616
aromatics, wt %	39.71
ASTM Distillation, K	
IBP/10 vol %	460/556
30/50 vol %	585/608
70/90 vol %	626/657
EBP	680

Table 2. Physical and Chemical Properties of the Commercial Catalyst

diameter, mm	2.3
length, mm	5.2
specific surface area, m ² /g	204
pore volume, cm ³ /g	0.50
bulk density, g/cm ³	0.78
MoO ₃ , wt %	9.5
NO _x , wt %	2.4
P, wt %	1.58

transfers do not limit the reaction rate, conversion will be constant.

(2) Catalyst volumes and reactant flow rates are varied. Conversions are plotted vs inverse of space velocity. If all points are on the same curve, then there are no external gradients.

Moreover, the problems of deviations, such as poor wetting of catalyst, wall effect, maldistribution, and axial dispersion, resulting from the ideal plug flow behavior caused by the testing catalyst having commercially applicable size and shape in small reactors, can be avoided by using the catalyst in its original form but diluted with nonporous inert particles.

Experimental Section

A straight-run gas oil (SRGO) and a commercial NiMo/Al₂O₃ catalyst were employed for activity testing studies. Properties of these samples are shown in Tables 1 and 2, respectively. Both samples were recovered from a commercial hydrotreating plant. Gas oil had high sulfur content (1.616 wt %) mainly due to its high end boiling point (EBP = 680 K), and the catalyst is a trilobe extrudate.

Hydrotreating experiments were performed at pilot scale. A detailed description of this pilot unit was reported in a previous work.¹⁰

The isothermal reactor, which was the central part of the HDT pilot plant, was made of a stainless steel tube. The overall length and internal diameter of the reactor were 143 and 2.54 cm, respectively. The length of reactor was divided in three zones as can be seen in Figure 1. Zone 1 was packed with inert particles and was used to heat up the mixture to the desired reaction temperature and to provide a uniform feedstock distribution. Zone 2 contained the NiMo/Al₂O₃ catalyst and the diluent. Zone 3 was also packed with inert particles. Between each section a wool glass plug was inserted in order to improve oil distribution.

The inert used for diluting the catalyst was silicon carbide with an average spherical particle size of 1.4 mm. The inert particle size is lower than that of the catalyst. The catalyst was diluted with equal volume of inert in order to maintain a ratio of the volume of catalyst to that of diluent at a constant value of 1.0.

(8) Smith, J. M. *Chemical Engineering Kinetics*, 3rd ed.; McGraw-Hill: New York, 1979.

(9) Hill, C. G. *An Introduction to Chemical Engineering Kinetics & Reactor Design*; John Wiley & Sons: New York, 1977.

(10) Marroquin, G.; Ancheyta, J. *Appl. Catal., A* 2001, 207, 407.

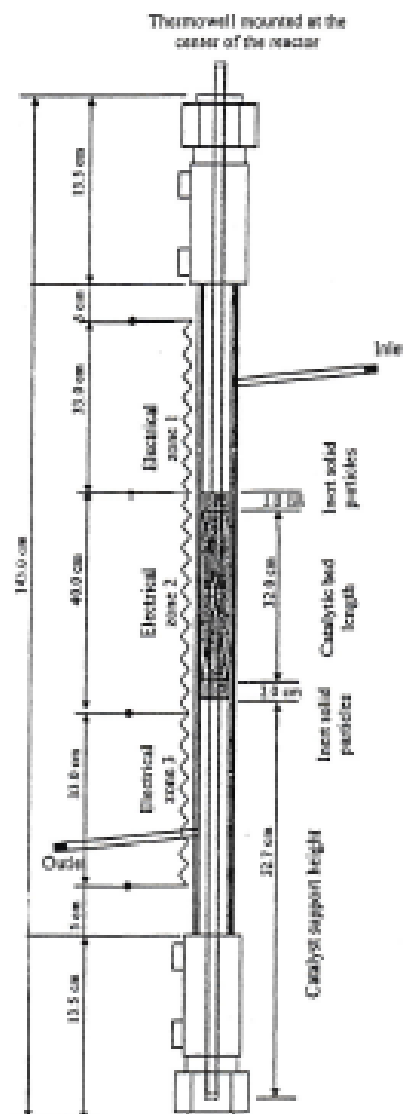


Figure 1. Isothermal trickle-bed pilot reactor.

The reactor temperature was maintained at the desired level by using a three-zone electric furnace, which provided an isothermal temperature along the active reactor section. Catalytic bed temperature was measured during the experiments by three thermocouples located in a thermowell mounted at the center of the reactor (0.66 cm external diameter). The temperature profile was measured at the middle of each experiment by a movable axial thermocouple located inside the reactor.

The catalyst and the diluent were loaded to the reactor with the following procedure: half of the total volume of catalyst was loaded in the reactor followed by the loading of the same volume of diluent. The reactor was vibrated gently for allowing the diluent to settle in the voids of the catalyst bed. The remaining catalyst and diluent were then loaded following the same procedure.

After the catalyst was loaded, the reactor pressure was increased from atmospheric to a value 30% higher than operating reactor pressure in order to ensure the airtightness

Table 3. Operating Conditions

Test 1				
	LHSV = 1.0 h ⁻¹			
catalyst weight (W), g	58.8	78.4	98.0	117.6
catalyst volume (V), mL	75	100	125	150
reactant flow, mL/h	75	100	125	150
superficial velocity, kg/m ² s	0.0357	0.0476	0.0595	0.0714
Test 2				
	W = 58.8 g, V = 75 mL			
LHSV, h ⁻¹	1.0	1.5	2.0	2.5
reactant flow, mL/h	75	112.5	150	187.5
superficial velocity, kg/m ² s	0.0357	0.0536	0.0714	0.0893
	W = 117.6 g, V = 150 mL			
LHSV, h ⁻¹	1.0	1.5	2.0	2.5
reactant flow, mL/h	150	225	300	375
Superficial velocity, kg/m ² s	0.0714	0.1072	0.1429	0.1786

of the system. This condition was kept during 2.5 h. Once the reactor was verified to be totally hermetic, the reactor pressure was reduced to the desired value. The temperature of the reactor was increased from ambient to 503 K at a heating rate of 30 K/h in the presence of hydrogen (99.8% purity) at a flow rate of 150 L/h.

The catalyst was in-situ sulfided with a desulfurized naphtha contaminated with 0.6 wt % carbon disulfide at the following operating conditions: pressure of 5.3 MPa, hydrogen-to-oil ratio of 355.2 mL mL⁻¹, temperature of 503 K, liquid hourly space velocity of 3 h⁻¹, during 12 h.

When sulfiding was completed, the feedstock was introduced and naphtha flow was stopped without stopping the hydrogen flow, and the reactor temperature and other conditions were adjusted to the desired start-of-run conditions.

All the experiments were carried out at constant reaction pressure and hydrogen-to-oil ratio without hydrogen recycle (5.3 MPa and 355.2 mL mL⁻¹, respectively). Three reaction temperatures were studied: 613, 633, and 653 K. Two experiments were performed for each condition.

To determine the concentration and temperature gradients, two experiments previously described were performed. In the first test, the amount of catalyst loaded to the reactor and the feedstock flow were changed proportionally in order to maintain constant the liquid hourly space velocity. This test was carried out at four space velocities (1.0, 1.5, 2.0, and 2.5 h⁻¹). In the second test, two experiments were conducted using different amounts of catalyst. For each amount of catalyst the feedstock flow was varied in order to have different space velocities. Operating conditions for these two tests are presented in Table 3. Only data at 1.0 h⁻¹ LHSV are shown in this table because other conditions change proportionally with space velocity.

Product samples were collected at 4–8 h intervals after allowing a 12 h stabilization period under each set of conditions. For each run, mass balances were in the range 100 ± 3%. Catalyst activity was checked by measuring the following properties of the products: total sulfur (ASTM D-4294), total nitrogen (ASTM D-4629), and aromatics content (ASTM D-5186).

Results and Discussion

Isothermality of the Pilot Reactor. The temperature profile along the reactor length was measured in each experiment by a movable axial thermocouple located inside the reactor in order to check that the reactor was kept isothermally stable.

Figure 2 shows two temperature profiles obtained at low and high severities (613 K reaction temperature and 1.0 h⁻¹ LHSV, and 653 K reaction temperature and 1.0 h⁻¹ LHSV, respectively). This figure includes the temperature profiles obtained with minimum ($V = 75$ mL)

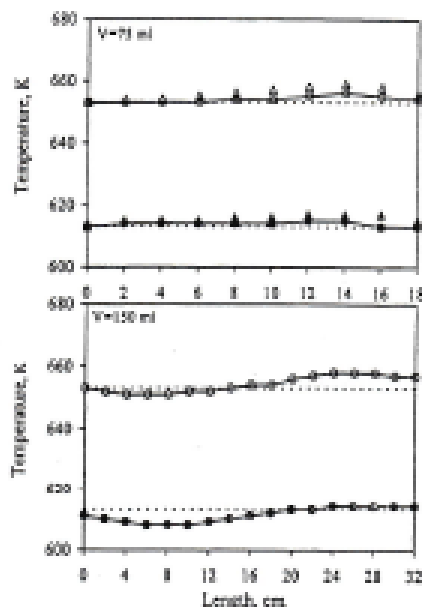


Figure 2. Temperature profiles along the pilot reactor: (□ and ■) with catalyst dilution, (Δ and ▲) without catalyst dilution; (□ and Δ) 653 K and 1.0 h^{-1} LHSV, (■ and ▲) 613 K and 2.5 h^{-1} LHSV; (---) programmed temperature.

and maximum ($V = 150 \text{ mL}$) amounts of catalyst loaded to the reactor.

It is observed that for the maximum amount of catalyst the difference in temperature profile is slightly higher than that of minimum amount of catalyst. The greatest deviation from the desired temperature value found in these tests was $\pm 1 \text{ K}$ for minimum amount of catalyst and $\pm 2 \text{ K}$ for maximum amount of catalyst.

The low temperature differences inside the pilot reactor were achieved because of the use of catalyst bed dilution and the glass wool plugs, which improve oil distribution at low liquid mass velocities and the homogeneity of the temperature throughout the reactor.

We conducted some experiments without catalyst bed dilution using 75 mL of catalyst volume loaded to the reactor, but feedstock properties were slightly different to those employed in the diluted bed study. The results of temperature profile along the reactor length are also shown in Figure 2. It can be clearly observed that reactor temperature differences when the catalyst bed dilution is used are considerably reduced compared to those found with catalyst dilution, specially at high temperatures.

Flow Regime. Depending on the gas and liquid flow rates and the physical properties of the liquid, various flow regimes may exist in a trickle bed reactor. Normal laboratory and commercial reactors are operated in trickle or pulse flow. The prediction of the pulse/trickle flows boundary is generally of practical interest in trickle-bed reactors. For this reason before checking mass transfer limitations it is first necessary to determine if the liquid feedstock is total or partially vaporized, and which is the flow regime in the reactor.

The vaporization of the liquid feed can be calculated by using a commercial process simulator. The composi-

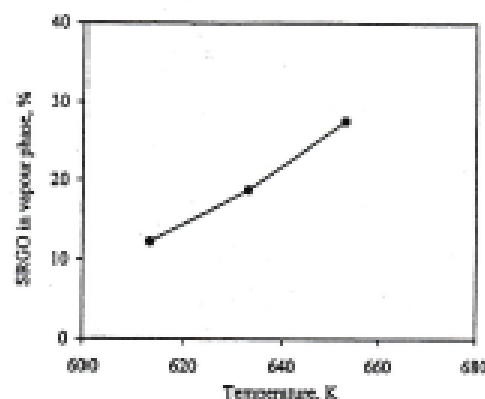


Figure 3. Evaluation of SRGO vaporization.

tion of the mixture (SRGO and hydrogen) is evaluated at the reaction operating conditions just before the reactants enter to the reactor.

On the other hand, the flow regime can be determined by plotting the superficial mass velocities or Reynolds numbers on both gas and liquid phases in maps of hydrodynamic flow regimes.^{11,12} These maps distinguish between a number of flow regimes in packed columns with downflow operation.

Figure 3 shows the results obtained with the commercial process simulator. Percentage of SRGO in vapor phase was calculated as the amount of SRGO vaporized divided by the amount of liquid SRGO before mixing with hydrogen. It can be clearly seen that the vaporized fraction of the liquid feedstock was greater than 12% and that it increased as the reaction temperature was also increased. That means that 88, 81, and 72% of the straight-run gas oil remain in liquid phase at 613, 633, and 653 K, respectively.

In our experiments the SRGO vaporized fraction will be almost the same along the pilot reactor because of reactor isothermality, while at commercial scale this SRGO vaporized fraction may increase along the reactor since $15\text{--}25 \text{ K}$ temperature gradients are commonly reported in industrial middle distillates HDS reactors.

For the second approach, we employed a trickle-bed simulator developed by Larachi et al.¹³ The flow regimes obtained with this simulator are shown in Figure 4. It should be mentioned that the equations which identify the boundaries of different flow regimes have been developed for other systems (i.e. air–water, glass spheres), and they cannot be totally applied to the system reported in this work (hydrogen–SRGO, trilobe extrudate catalyst). However, if we observe Figure 4 with more detail we can see that our experiments zone is clearly within trickle-bed regime and it is very far from other regimes. Hence, for the gas and liquid superficial mass velocities obtained in this work, the flow regime is trickle.

Ideality of Flow Pattern. Commercial catalyst samples and real feedstocks are commonly employed for

(11) Ramachandran, P. A.; Chaudhari, R. V. *Three-Phase Catalytic Reactors*; Gordon & Breach Science Publishers: Langhorne, PA, 1992.

(12) Fukushima, S.; Kusaka, K. *J. Chem. Eng. Jpn.* 1977, 10, 461.

(13) Larachi, F.; Grandjean, B.; Rivet, I.; Benoit, Z.; Andre, A.; Wild, G.; Chen, M. *Trickle-Bed Simulation*; Université Laval: Québec, Canada, 1999.

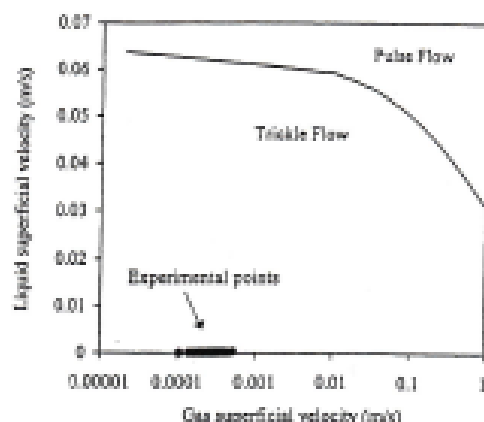


Figure 4. Flow regime maps.

Table 4. Comparison of Operating Conditions in Pilot and Commercial HDT Plants

characteristics	pilot plant	commercial plant
pressure, MPa	5.3	5.3
temperature, °C	613–653	633
LHSV, h ⁻¹	1.0–2.5	2.5
H ₂ -to-oil ratio, mL mL ⁻¹	356.2	356.2
temperature drop, K	± 2	15–20
catalyst volume	75–150 mL	65.67 m ³
liquid flow rate	75–375 mL/h	165625 L/h
catalytic bed length (L)	16.8–32.2 cm	9 m
reactor inside diameter (D)	2.34 cm	3.048 m
catalyst particle diameter (d _p), mm	2.3	2.3
L/d _p ratio	93–108	3913
D/d _p ratio	11.0	1325
superficial liquid mass velocity (u _L), kg/m ² s	0.0357–0.1788	5.429
superficial gas mass velocity (u _G), kg/m ² s	0.0012–0.0061	0.1850
Re in liquid phase (Re _L)	0.228–1.360	38.0
Re in gas phase (Re _G)	0.191–0.956	28.4
Pe in liquid phase (Pe _L)	0.023–0.163	0.235
Pe in gas phase (Pe _G)	3.613–5.718	0.112

conducting experiments in pilot reactors, however, the reactor small-scale length to catalyst particle diameter ratio (L/d_p) is very low as compared to that of commercial reactors as can be seen in Table 4. It can also be observed from this table that our pilot-scale reactor is about 25–50 times shorter than an industrial HDT reactor, and hence, superficial mass velocities and Reynolds numbers for both liquid and gas phases are smaller than a commercial reactor in the same order of magnitude. For these reasons low liquid velocities are used in small-scale reactors in order to match the LHSV of commercial plants, which implies that gas-liquid and liquid-solid mass transfers are much better in the latter one.

Because of the lower resistance to liquid flow at the wall, the linear velocity next to the wall is greater than that found at the center of the reactor. This variation in linear velocity causes an increase in axial dispersion. The extent of this axial dispersion effect depends mainly on the bed length and the conversion.

One empirical criterion frequently used to check the existence or not of back-mixing is examination of L/d_p ratio. Upon neglecting back-mixing effects this ratio should be at least 50 ($L/d_p > 50$) for two-phase fixed-bed reactors, and at least 100 ($L/d_p > 100$) for trickle-bed reactors.⁷ In our case the L/d_p ratio varied between 93 and 180 taking into account the inert and catalyst particle diameters. It means that axial dispersion may be neglected. It should be mentioned that this empirical approach does not distinguish the difference in axial dispersion for liquid and gas phases.

The following criterion is also commonly employed for the estimation of the minimum bed length to particle diameter ratio necessary for neglecting the back-mixing effects:¹⁴

$$\frac{L}{d_p} > \frac{20n}{Pe} \ln \frac{C_f}{C_p} \quad (3)$$

where n is the reaction order, Pe is the Peclet number, which can be estimated as a function of Reynolds number, and C_f and C_p are the sulfur concentrations in the feed and in the product, respectively.

Equation 3 can present different values depending on the correlation used for estimating the Peclet number. One criterion to select the Peclet number correlation is to use that which gives the highest back-mixing, hence the smallest Peclet number value. In this case we utilized the following most used equations reported by Hochman and Effron for calculating Peclet number in both liquid and gas phases:^{11,12}

$$Pe_L = 0.034 Re_L^{0.5} 10^{0.003 Re_L} \quad (4)$$

$$Pe_G = 1.8 Re_G^{0.7} 10^{-0.002 Re_G} \quad (5)$$

The values of the right-hand side of eq 3 are shown in Figure 5 for gas and liquid phases as a function of reaction temperature and space-velocity. For calculation for liquid phase, concentrations of sulfur in liquid feed and product were used; In the absence of data of C_f and C_p in the gas phase, the same values of these concentrations found in liquid phase were utilized. In both cases second reaction order was considered ($n = 2$). It should be mentioned that the higher the right-hand side of eq 3 values the higher the axial dispersion.

The following general observations can be made from Figure 5: (1) axial dispersion increases as the reaction temperature is increased, (2) the effect of LHSV and the amount of catalyst loaded to the reactor is different for both gas and liquid phases, and (3) axial dispersion is higher in liquid phase compared to gas phase.

At constant LHSV, when the reaction temperature is increased, the liquid vaporization also increases as is shown in Figure 3. It means that the amount of SRGO in liquid phase entering to the reactor is less at high temperature than low temperature, and hence the catalyst particles wetting is also less at high temperature. If LHSV is increased, that is an increase in liquid flow rate, the catalyst wetting is gradually improved.

(14) Meares, D. *Ind. Eng. Chem. Anal. Ed.* 1971, 43, 541.

(15) Turekian, M. G. *Catalytic Reactor Design*; McGraw-Hill: New York, 1983.

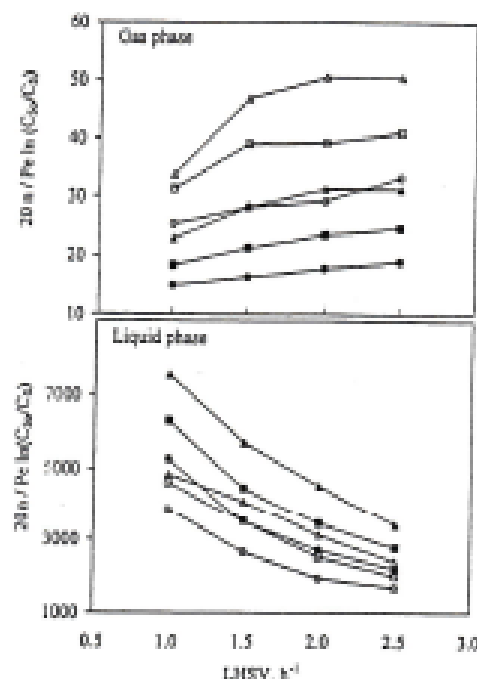


Figure 5. Axial dispersion in liquid and gas phases. (○, △, and □) Maximum amount of catalyst, (●, ▲, and ■) minimum amount of catalyst, (○ and ●) 613 K, (frames) 633 K, (△ and ▲) 653 K.

Axial dispersion in liquid phase is reduced as the LHSV is increased, which is owed to an increase in liquid flow rate. The same results are observed when the amount of catalyst is changed, since low axial dispersion is obtained with the maximum amount of catalyst loaded to the reactor, in which higher liquid flow rates were used compared to the minimum amount of catalyst. Phase gas exhibited an opposite behavior, which is a consequence of the observed liquid behavior, since in trickle-bed reactors the liquid phase is the dispersed phase and the gas phase is the continuous phase.

L/d_p values for all the amounts of catalyst loaded to the pilot reactor, including inert particles, are in the range 93–108. If we compare these L/d_p values with the $2Dm \ln C_0/C$ values given in Figure 5, we can clearly observe that axial dispersion in gas phase is unimportant. This observation confirms that for trickle-bed regime the important phase in the reactor is the liquid.

It should be remembered that eqs 4 and 5, which were employed for evaluating Pe_L and Pe_G , respectively, give the smallest values of Peclet number. We have tried with other correlations¹¹ and higher values of Pe and hence low axial dispersion were determined. It suggests that election of correlation for evaluating of Peclet number is very important since very different values can be obtained. Anyway, all observations mentioned about the dependency of both phases behavior with respect to operating conditions are valid.

Our results agree very well with those reported by Korsten and Hoffmann.² They employed a hydrocracking pilot reactor with 3 cm inside diameter and 125 cm

length, a NiMo/Al₂O₃ catalyst with a particle diameter of 1.72 mm, and superficial velocity of 0.0572 kg/cm²s, which are very close to those used in the our work (2.54 cm, 143 cm, 2.3 mm, and 0.0357–0.1786 kg/cm²s, respectively). These authors have carried out some experiments of residence-time distribution and they have also concluded that deviations from plug flow can be neglected for both phases.

On the bases of these results and literature reports as well as on experimental evidence discussed in the following section, we can conclude that at the conditions used in the present study our reactor behaves very close to plug flow.

Mass Transfer Gradients. Experiments were conducted with different amounts of catalyst, space velocities, and reaction temperatures according to the techniques described in a previous section in order to verify the presence of mass transfer gradients.

Figure 6 shows the results of hydrosulfurization (HDS), hydrodenitrogenation (HDN) and aromatics saturation (HDA) vs reactant flow rate at different reaction temperatures and two constant LHSV (1.0 and 2.5 h⁻¹). Two experiments were carried out at the same conditions, and the tendency line given in Figure 6 was plotted with average values.

It is seen from this figure that in the range of flow rates of 7.5–150 mL/h, sulfur, nitrogen and aromatics conversions are very similar at the same reaction temperature for a space velocity, especially at low HDS, which indicates that conversion do not change when reactant flow is modified, and hence, external mass gradients are not present.

The results of HDS, HDN, and HDA vs the inverse of LHSV are presented in Figure 7. It is observed that the curves at different temperature are very close. These experimental data also indicate that external diffusional gradients are very low.

Figures 6 and 7 correspond to the two common tests used to check the presence of external gradients described in previous section. Results showed in these figures are very important because it means that experimental studies can be carried out in the pilot plant without mass transfer limitations (interphase). Of course, additional experiments have to be performed to study internal gradients (intrapphase), which consist of determining the conversion for particles of different size at constant space velocity. If conversion is constant indicates that the system is under chemical kinetic control.⁷

Comparison of Results with and without Catalyst Bed Dilution. It is well-known that incomplete catalyst wetting is substantially avoided by diluting the laboratory beds with an inert material. This inert material should be nonporous and preferably smaller than the catalyst. When catalyst dilution is used, hydrodynamics is largely dictated by the packing of inert, whereas the catalytic phenomena are governed by the catalyst particle of the same shape and size as used in industrial plants.² The use of small particle size inert diluent lodged among the catalyst particles helps in narrowing the liquid flow channels and improves the liquid holdup, increasing residence time and improving conversion.

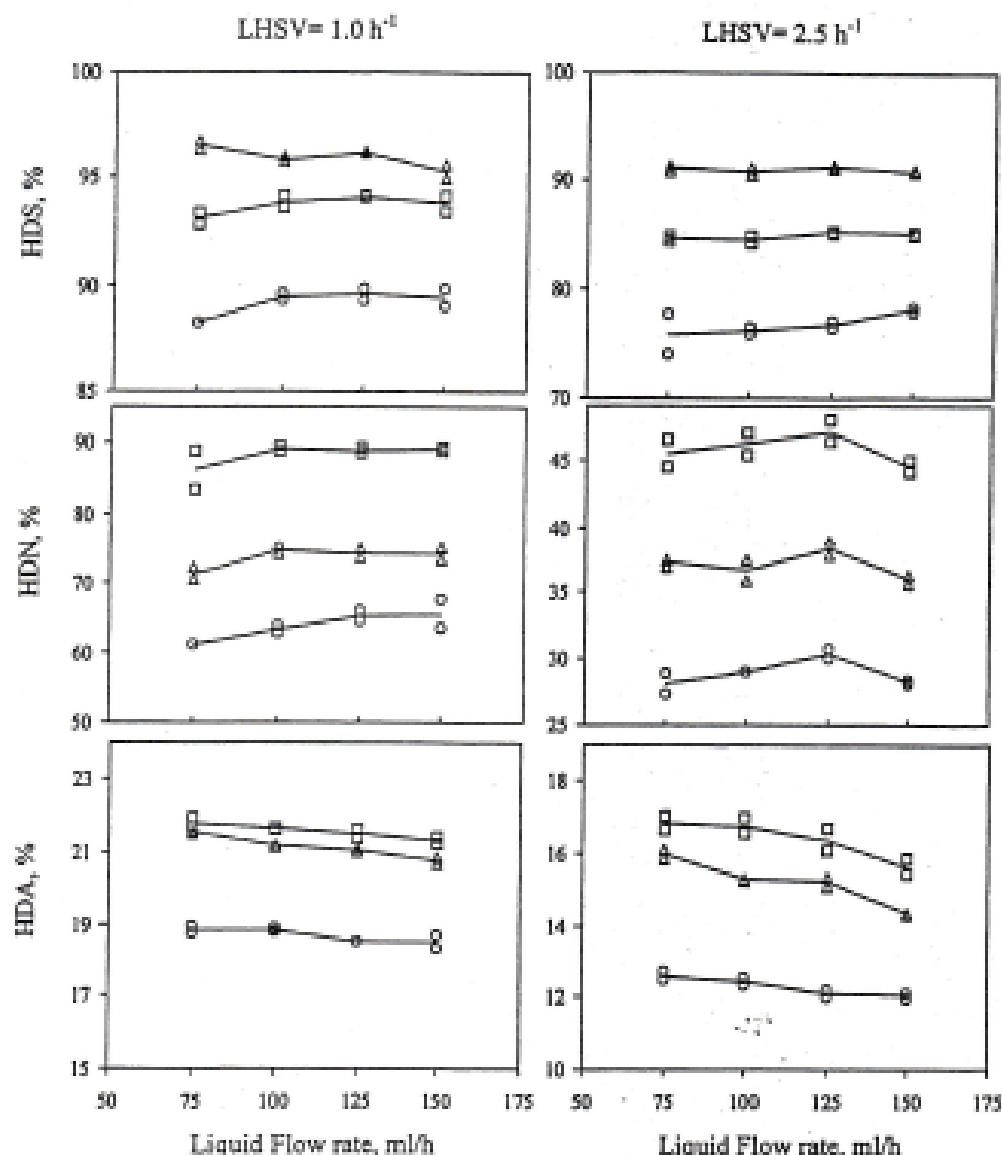


Figure 8. Mass transfer gradients at constant LHSV. (○) 613 K, (△) 633 K, (□) 653 K.

The diluent used in the present study was silicon carbide, which has smaller particle diameter than the commercial NiMo catalyst. This is one important reason for having very small external mass transfer gradients in our pilot plant experiments.

To compare the behavior of the pilot reactor using or not catalyst bed dilution, we carried out a series of experiments without inert in the catalytic bed. Unfortunately the feedstock used for these tests was different to that employed with bed dilution. The new feed was a little more heavier than the previous one: specific gravity 20/4 °C of 0.8733, 1.704 wt % sulfur, 0.59 wt % nitrogen, and 44.5 wt % aromatics. Results obtained in experiments without catalyst bed dilution are not totally comparable with those obtained with bed dilution.

Despite this, some general observations can be made for comparison purposes.

In principle, as was shown in Figure 2, diluted and nondiluted beds have slightly different reactor temperature profiles. The former presents less deviations from the desired value than the latter, which confirms that the use of catalyst bed dilution improves reactor temperature homogeneity.

Figure 8 shows a comparison between HDS obtained with and without catalyst bed dilution. It can be seen that bed dilution presents higher HDS conversions than nondiluted bed. This is due to the reduction in external concentration gradients obtained with catalyst bed dilution, because the use of small particle size diluent lodged among the catalyst particles helps in narrowing

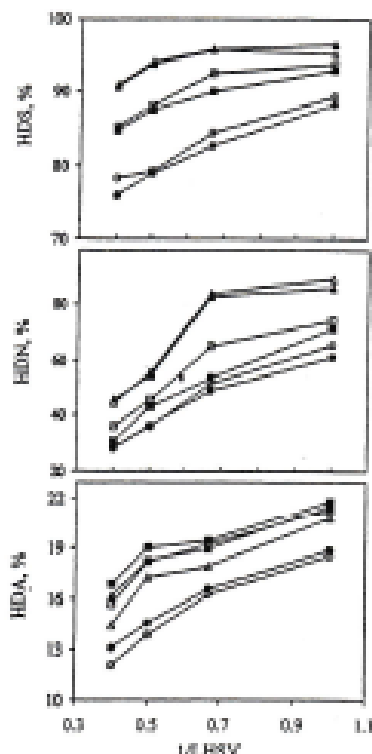


Figure 7. Mass transfer gradients at variable LHSV, (○) 613 K, (△) 633 K, (□) 653 K, (○, △, and □) maximum amount of catalyst, (●, ▲, and ■) minimum amount of catalyst.

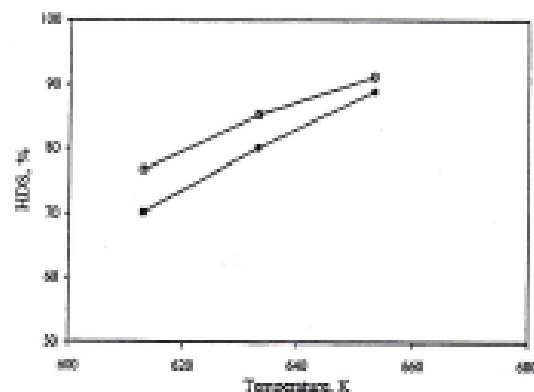


Figure 8. Comparison of HDS between diluted (○) and nondiluted (■) catalyst beds at 2.5 h⁻¹ LHSV.

the liquid flow channels, and axial dispersion is reduced to the extent where plug flow can be established, improving catalyst wetting and contact efficiency.

Importance of the Results. As we have mentioned in initial sections, the main goal of our present work is to describe a systematic study for conducting experiments in a TBR reactor in order to define the best operating conditions to ensure ideality during HDT reactions. To do this we have used both catalyst and feedstock recovered from commercial HDT unit. On the basis of experimental results, the following recommendations can be stated:

•It was confirmed that homogeneity of reactor temperature can be improved with the use of dilution of catalyst bed with an inert material, since temperature differences inside the pilot reactor were ± 2 K for diluted bed and ± 6 K for undiluted bed (Figure 2). The diluent size should be smaller than that of the catalyst. In our case we have employed silicon carbide with an average spherical particle size of 1.4 mm.

•Determination of flow regime is very important in the case of hydrotreating reactions. At pilot scale, gas oil HDS can take place in gas phase or in liquid–gas phase depending mainly on reaction conditions, type and properties of feed, and type and size of reactor. A remarkable difference can exist between catalyst activities of both systems,¹⁶ and criteria for neglecting back-mixing and other effects can also vary.⁷ Therefore, it is necessary to define first the flow regime which can be done by using commercial process simulators.

•It was demonstrated that the use of traditional empirical criterion based on L/d , ratio for verifying the presence of back-mixing in trickle-bed systems is not totally appropriate, since it does not distinguish between gas and liquid phases. Mears criterion¹⁴ is more suitable, since it can be applied for both phases. However, values of Peclet numbers used in this criterion vary depending on the correlation employed. It is highly recommended to utilize the correlation which gives the smallest Peclet number to have the highest back-mixing.

•Typical tests used for verifying the presence of mass transfer gradients indicate that our experiments are conducted without external diffusional gradients. It is crucial to conduct this type of evaluations and to define suitable range of liquid flow rates.

•The effect of catalyst bed dilution was also demonstrated since undiluted catalyst bed yielded less conversion than the diluted one. It means that when the catalyst is employed in commercial size for HDS experiments the use of inert material as diluent is mandatory.

Finally, it should be emphasized that for HDS experiments we have used the catalyst with commercial size and shape and most of the literature works employ crushed catalysts. However, when the latter are tested their properties are affected by the crushing and sieving operations, and the data obtained may not be representative for industrial practice, since it can affect not only the apparent activity of catalyst, but also the selectivity and deactivation behaviors.⁵

Conclusions

An experimental study was carried out in a trickle-bed pilot reactor using catalyst and feedstock recovered from a commercial HDT plant. Various recommendations are highlighted in order to define the best operating conditions to ensure ideality during hydrotreating reactions.

It was confirmed that the HDT pilot reactor operates in trickle-bed flow regime. Axial dispersion was very low in phase gas, while axial dispersion in liquid phase was

high. This latter deviation from ideal plug flow behavior was reduced by using catalyst bed dilution.

Sulfur, nitrogen, and aromatics conversions obtained when experiments were conducted at constant and variable space velocities indicate that external mass gradients are very low at the operating conditions used in the present study.

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