

Performance Evaluation of Hydroprocessing Catalysts—A Review of Experimental Techniques

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The selection of an appropriate reactor for hydroprocessing catalysis research primarily depends on the type of information to be generated, the reliability and reproducibility of the information required, and the cost involved to generate such information. In this article, the various reactors and approaches that have been used at different stages of hydroprocessing catalysis research and process development are reviewed. With the development of the dilution technique, substantial progress has taken place in reducing the size of reactor used for hydroprocessing process development studies. This has decreased the cost of catalyst evaluation as well as increased the operating safety. However, the selection of an appropriate size of diluent is very important. Studies comparing the differences in the behavior between up-flow and down-flow modes of operation of a fixed bed reactor are analyzed. An attempt has been made to provide guidelines for selecting the appropriate reactor and methodology to evaluate hydroprocessing catalysts. Reactors that are commonly used for the kinetic studies of hydroprocessing reactions are also reviewed in this article.

Introduction

The reaction of any petroleum fraction with hydrogen in the presence of a catalyst is commonly known as hydroprocessing. Depending on the purpose it is serving, a hydroprocessing process can be broadly classified as hydrotreating or hydrocracking. Hydrotreating processes remove the undesirable impurities such as sulfur, nitrogen, unsaturated molecules and metals. The fragmentation of heavy molecules into desirable ones is carried out during hydrocracking. Both these processes have been widely used by petroleum refiners in the past and will also find spectacular growth soon. The increasing importance of hydroprocessing has spurred research interest to develop more efficient catalysts and processes for commercial applications.

The development of better catalysts and processes involves different stages of research. These include exploratory screening of catalyst formulations, optimizing the process conditions over the most promising catalyst as identified from screening tests, studying deactivation and regeneration, and evaluating reaction kinetics for design of the commercial reactor.^{1–3} In some cases, experiments are also carried out to study the performance of an established catalyst for the processing of a new or alternative feedstock. Therefore, the choice of a proper experimental apparatus is of utmost importance in order to obtain reliable data at a minimum cost.

It is useful to provide a brief look at the applications for which the catalysts need to be developed, i.e., the commercial processes and reactors in which these cata-

lysts are used. Most of the commercial hydroprocessing reactions are carried out at high pressure (20–200 atm) and temperature (320–440 °C) in trickle bed reactors in which the liquid hydrocarbons and gaseous hydrogen are passed in a cocurrent downward flow through a fixed bed of solid catalysts.⁴ A typical schematic diagram of a hydroprocessing trickle bed reactor is shown in Figure 1. Depending on the capacity of the plant, the reactor may vary from 1 to 6 m in diameter.⁵ Hydroprocessing reactions are generally exothermic in nature. The reactor may contain several (2 to 6) beds of catalysts separated by quench zones. Cold hydrogen gas is introduced and mixed with the partially reacted fluids. Each quench zone contains a distribution tray to provide uniform distribution of liquid to the next catalyst bed. The number of catalyst beds in a reactor and their respective lengths are determined from the temperature rise profiles. A hydrotreating reactor generally has two beds and the maximum bed length may reach 12 m. On the other hand, a typical hydrocracking reactor may have 4–6 catalyst beds and the maximum length of each bed may be up to 6 m.⁶ The catalysts are generally in the shape of cylindrical or mutilobe extrudates having particle diameter in the range of 1 to 2 mm.

In any hydroprocessing reaction, the transport of molecules from the gas phase to the active surface of the catalyst faces resistances from bulk gas to gas–liquid interface, from gas–liquid interface to bulk liquid,

(2) Richardson, J. T. *Principles of Catalyst Development*; Plenum Press: New York, 1989.

(3) Forni, L. *Catal. Today* **1997**, 34, 353.

(4) Topsoe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysts*; Springer: Berlin, 1996.

(5) Speight, J. G. *The Desulfurization of Heavy Oils and Residua*; Marcel Dekker: New York, 2000.

(6) Scherzer, J.; Gruia, A. J. *Hydrocracking Science and Technology*; Marcel Dekker: New York, 1996.

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(1) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.

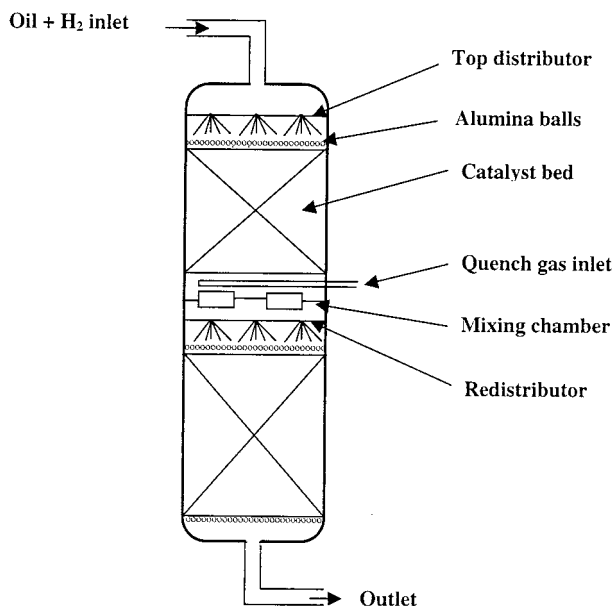


Figure 1. Schematic diagram of a hydroprocessing trickle bed reactor.

from bulk liquid to external catalyst surface, and finally diffusional resistances within the pores of the catalyst pellet. The contacting efficiency of the liquid around the catalyst particle also plays an important role on the overall rate of reaction. In addition, the axial dispersion of liquid may be present in some cases and can reduce the overall rate of reaction.

Almost complete wetting of catalyst is achieved in commercial trickle bed reactors because of very high liquid flow rates and the presence of liquid distributors and redistributors in these reactors. The flow pattern of liquid in these reactors is nearly plug type because of very high liquid flow rates and a high ratio of catalyst bed height to catalyst particle diameter.

The traditional approach to generate data for catalyst and process development is to use smaller versions of commercial reactors. These are generally known as small-scale trickle bed reactors. However, these have various limitations. Because of the presence of a liquid phase, the problems in these small trickle bed reactors are more complex as compared to those present in other small-scale fixed bed catalytic reactors handling only vapor phases. The problems encountered in these small-scale trickle bed reactors will be addressed in detail in a later section.

The various approaches that have been used by different researchers to overcome these limitations for generating reliable and meaningful data in these small-scale reactors are reviewed in this article. Guidelines are provided for the selection of appropriate reactor and methodology for this purpose. For ease of understanding, the discussion is divided in three sections, viz., (a) reactors for screening of exploratory catalyst formulations, (b) reactors for process development and optimization studies, and (c) reactors for kinetic studies.

Reactors for Screening of Exploratory Catalyst Formulations

The pathway to develop an optimum catalyst starts with screening of prepared catalysts by chemical and

physical characterization and evaluation of catalytic properties.⁷ If the desired results are not achieved, then samples with modified properties are prepared and the screening procedure is repeated until a promising catalyst is found. This involves testing of various formulations having differences in composition, support materials as well as in preparation methods.

Some general points at this stage of research are to be noted. The catalysts are made in small quantities and to avoid the complexity of preparing shaped catalysts, it is common to test catalysts in the form of powder or fine particles. This also helps to compare the intrinsic reaction rates of various catalyst formulations. Since the number of catalysts samples to be tested are many, the testing method needs to be simple and fast.⁸ However, this should not compromise with the reliability and meaningfulness of the data generated. Because of the small amount of catalyst available, slurry reactors using batch autoclave or fixed bed continuous microreactors are typically used for this stage of initial catalyst screening.

Batch Autoclaves. High-pressure batch autoclaves having reactor volumes in the range of 50–100 mL have been used extensively by researchers for screening of hydroprocessing catalysts.^{9–19} Catalysts are generally used in the form of crushed particles. Sufficient agitation is required to keep the catalyst suspended in the liquid. The autoclave is pressurized using high-pressure hydrogen. The reaction pressure is controlled at the desired level during the course of reaction by adding gaseous hydrogen to compensate its consumption. Alternatively, the reaction can be carried out by passing hydrogen continuously through the slurry. The reaction time is generally counted from the moment when the temperature of the reactor reaches the prescribed level.

The catalyst can also be kept in a spinning basket located inside the autoclave. Such an arrangement has been used by Dong et al.²⁰ for studying the deactivation of hydrotreating catalysts. They used 40–60 mesh of crushed commercial CoMo catalyst in a spinning basket of an autoclave reactor. As an alternative similar to this,

- (7) Kochloefl, K. *Chem. Eng. Technol.* **2001**, *24*, 3.
- (8) Le Page, J. F.; Cosyns, J.; Courty, P.; Freund, E.; Franck, J. P.; Jacquuin, Y.; Juguin, B.; Marcilly, C.; Martino, G.; Miquel, J.; Montarnal, R.; Sugier, A.; Van Landeghem, H. *Applied Heterogeneous Catalysis: Design, Manufacture, Use of Solid Catalysts*; Technip Publications: Paris, 1987.
- (9) Sakanishi, K.; Ando, M.; Abe, S.; Mochida, I. *Sekiyu Gakkaishi* **1991**, *34*, 553.
- (10) Ma, X.; Sakanishi, K.; Mochida, I. *Ind. Eng. Chem. Res.* **1994**, *33*, 218.
- (11) Lecrenay, E.; Sakanishi, K.; Mochida, I. *Catal. Today* **1997**, *39*, 13.
- (12) Isoda, T.; Nagao, S.; Korai, Y.; Mochida, I. *Sekiyu Gakkaishi* **1998**, *41*, 22.
- (13) Iwata, Y.; Araki, Y.; Honna, K.; Miki, Y.; Sato, K.; Shimada, H. *Catal. Today* **2001**, *65*, 335.
- (14) Sakanishi, K.; Nagamatsu, T.; Mochida, I.; Whitehurst, D. D. *J. Mol. Catal. A: Chem.* **2000**, *155*, 101.
- (15) Kameda, K.; Wada, T.; Murata, S.; Nomura, M. *Energy Fuels* **1998**, *12*, 298.
- (16) Farag, H.; Whitehurst, D. D.; Mochida, I. *Ind. Eng. Chem. Res.* **1998**, *37*, 3533.
- (17) Reinhoudt, H. R.; Troost, R.; van Schalkwijk, S.; van Langeveld, A. D.; Sie, S. T.; van Veen, J. A. R.; Moulijn, J. A. *Fuel Process. Technol.* **1999**, *61*, 117.
- (18) Lamure-Meille, V.; Schulz, E.; Lemaire, M.; Vrinat, M. *Appl. Catal. A: General* **1995**, *131*, 143.
- (19) Reinhoudt, H. R.; Troost, R.; van Langeveld, A. D.; Sie, S. T.; van Veen, J. A. R.; Moulijn, J. A. *Fuel Process. Technol.* **1999**, *61*, 133.
- (20) Dong, D.; Jeong, S.; Massoth, F. E. *Catal. Today* **1997**, *37*, 267.

the catalyst can be kept in a static basket inside the autoclave where only the liquid is agitated.

It becomes difficult to achieve a steady state under constant operating conditions in a batch autoclave with catalyst that requires a long time to reach at the steady state.⁸ Although there are some other drawbacks of a batch autoclave in generating reliable kinetic data (which will be discussed in the Kinetics section), these reactors are efficient, cheap, and easy to operate for the purpose of initial catalyst screening using small amounts of materials.

Continuous Fixed Bed Microreactors. Microreactors operated in a continuous mode have been used quite extensively by various researchers for carrying out initial catalyst screening.^{21–24} A number of studies have been conducted at atmospheric pressure, however the discussion in the present article will be limited to only those studies carried out at higher pressure and temperature corresponding to the operating conditions of a commercial plant.

The full wetting of catalyst in these microreactors depends on the flow rate of the liquid hydrocarbon as well as on the size of the catalyst particle. Since the catalyst is in the form of fine particles, maldistribution of liquid is generally not a problem in these reactors. Letourneur et al.²¹ used a micro-scale down-flow trickle bed reactor of 2 mL volume for hydrodesulfurization (HDS) of some model compounds. The catalyst used by them had a particle size of $<80\ \mu\text{m}$. Navaro et al.^{22–24} carried out HDS studies in a microreactor using 0.3 g of catalyst having particle size in the range of 0.25–0.3 mm.

The length of the catalyst bed can be increased by adding suitable sizes of diluent in the bed and therefore the axial back mixing of liquid can be reduced. Reinholdt et al.^{17,19} tested catalyst in a micro-scale trickle bed reactor using about 2 g of catalyst having particle sizes 180–250 μm . They had diluted the catalyst bed with an equal amount of inert SiC particles of 100 μm size.

Van Looij et al.²⁵ used larger amounts of catalyst (about 20 mL) for their hydroprocessing studies in a trickle bed reactor. The catalyst used in their experiments had particle sizes of 180–600 μm . The catalyst bed was diluted using equal amounts of inert SiC. Sambhi et al.²⁶ used a much greater amount of catalyst (about 38 mL) and larger size of catalyst particles. They used a 1:1 mixture of Kiselguhr (inert) and catalyst having particle sizes of 8–16 mesh.

The sizes of the catalyst and the diluent depend on the length of the catalyst bed and internal diameter of the reactor. Sie²⁷ has given guidelines for selecting the

sizes of the catalyst and the diluent for various sizes of trickle bed reactors to ensure complete wetting of catalyst as well as to have negligible axial dispersion of liquid. This will also be discussed in detail in the subsequent section.

The use of up-flow mode of operation of gas and liquid has also been practiced to achieve complete wetting of catalyst. Letourneur et al.²⁸ have illustrated the application of an up-flow microreactor to evaluate the performance of HDS catalyst. Their reactor had an i.d. of 6 mm. The catalyst had particle sizes of 80–125 μm . About 0.1–2 mL of catalyst located between two layers of inert alumina was used.

The use of higher liquid hourly space velocity (LHSV) also provides beneficial effect in both up-flow and down-flow modes of operation. Higher LHSV improves catalyst wetting in down-flow mode whereas it reduces axial dispersion of liquid in both up-flow and down-flow modes of operation.²⁹ However, operating at higher LHSV reduces the conversion level. Since these experiments are used for preliminary screening of catalysts, lower conversion may not be a problem and hence the advantages obtained at higher space velocities should be exploited. The role of axial dispersion is also less important if the conversion is lower. The screening of catalyst at lower conversion levels is recommended from another point of view. This helps to discriminate among various catalysts having high activities.³⁰ However, if understanding selectivity or product patterns (which may be important for hydrocracking) is one of the objectives, then reactions should preferably be carried out at higher conversion. This is important because selectivity toward various products usually depends on the conversion level.

In summary, if preliminary catalyst screening is planned to be conducted at lower conversion using higher LHSV, the use of up-flow mode may be a better choice as it ensures full wetting of catalyst as well as negligible axial dispersion of liquid.

Reactors for Process Development and Optimization Studies

The best catalyst selected through previous screening tests is formed into a shape (cylindrical or multilobe) and undergoes further experimentation for process development and optimization. Some additional experiments are needed at this stage to select the proper size and shape of the catalyst and also to determine the effect of other ingredients such as binders and additives used in forming.³ Two points are very important in selecting an appropriate reactor at this stage of research. First, the catalysts need to be tested in their commercially applied size and shape. Second, the objective at this stage of research is to predict the full performance of the catalyst for a commercial operation rather than simple preliminary screening.

The typical values of catalyst bed length, reactor diameter, and approximate amount of catalyst used in commercial, pilot plant, bench-scale and micro-scale

(21) In *Hydrotreatment and Hydrocracking of Oil Fractions*, Letourneur, D., Vrinat, M., Bacaud, R., Froment, G. F., Delmon, B., Grange, P., Eds.; Elsevier: Amsterdam, 1997.

(22) Navaro, R.; Pawelec, B.; Fierro, J. L. G.; Vasudevan, P. T. *Appl. Catal. A: General* **1996**, *148*, 23.

(23) Navaro, R.; Pawelec, B.; Fierro, J. L. G.; Vasudevan, P. T.; Cambra, J. F.; Arias, P. L. *Appl. Catal. A: General* **1996**, *137*, 269.

(24) Navaro, R.; Pawelec, B.; Fierro, J. L. G.; Vasudevan, P. T.; Cambra, J. F.; Guemez, M. B.; Arias, P. L. *Fuel Process. Technol.* **1999**, *61*, 73.

(25) van Looij, F.; van der Laan, P.; Stork, W. H. J.; DiCamillo, D. J.; Swain, J. *Appl. Catal. A: General* **1998**, *170*, 1.

(26) Sambhi, I. S.; Khulbe, K. C.; Mann, R. S. *Ind. Eng. Prod. Res. Dev.* **1982**, *21*, 575.

(27) Sie, S. T. *Rev. Inst. Fr. Petrol.* **1991**, *46*, 501.

(28) Letourneur, D.; Bacaud, R.; Vrinat, M.; Schweich, D.; Pitault, I. *Ind. Eng. Chem. Res.* **1998**, *37*, 2662.

(29) Chander, A.; Kundu, A.; Bej, S. K.; Dalai, A. K.; Vohra, D. K. *Fuel* **2000**, *80*, 1043.

(30) Cavalli, L.; Mario, A. D. *Catal. Today* **1997**, *34*, 369.

Table 1. Values of Various Parameters for Typical Commercial, Pilot Plant, Bench-Scale, and Micro-scale Trickle Bed Reactors^a

parameters	commercial reactor	pilot plant reactor	bench-scale reactor	micro-scale reactor
catalyst bed length, cm	2000	800	50	10
diameter, cm	250	4	2	1
catalyst volume, L	100 000	10	0.15	0.008
ratio of reactor diam/ catalyst diam ^b	1667	27	13	7
ratio of catalyst bed length/catalyst diam ^b	13333	5333	333	66
liquid velocity, ^c cm/s	0.55	0.2	0.015	0.003
Reynolds number	30	12	1	0.2

^a Ref 27. ^b Assuming a catalyst particle diameter of 0.15 cm.^c Assuming a LHSV of 1.0 h⁻¹.

units are given in Table 1.²⁷ The diameter of a small-scale (bench- or micro-scale) trickle bed reactor is much smaller than those of a commercial reactor. Hence, the ratio of the reactor diameter to catalyst particle diameter is very low. The ratio of the catalyst bed height to the particle diameter is also low in these reactors. Due to the smaller volume of catalyst used, the liquid flow rate is also lower. The values of these parameters along with the Reynolds number for various sizes of reactors are given in Table 1. Because of the low values of these factors, a number of problems such as incomplete wetting of catalyst and back mixing of liquid are observed in these small-scale reactors.^{27,31–33} Westerterp and Wammes³⁴ have provided a correlation between the wetting efficiency and liquid load. It is observed from their correlation that corresponding to the liquid load and Reynolds number for small-scale trickle bed reactors, the wetting of catalyst is only partial. Similarly, a correlation between Bodenstein number and Reynolds number has been reported for trickle bed reactors by Gierman.³⁵ The Bodenstein number (Bo), a measure of the axial dispersion of liquid, is defined as

$$Bo = (d_p v_l) / D_{ax}$$

where, D_{ax} is the axial diffusivity, d_p is the diameter of the catalyst particle, and v_l is the superficial velocity of the liquid. As per his correlation, axial dispersion of liquid is a significant problem in these small-scale reactors.

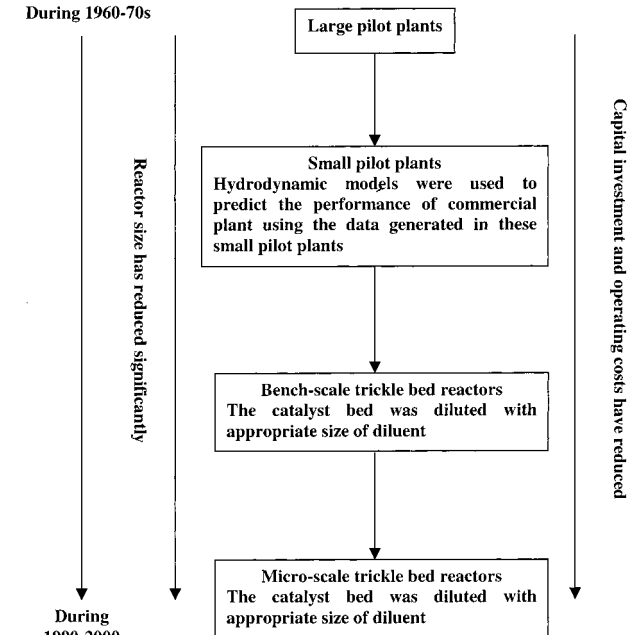
Earlier Approaches. There were basically two approaches which were used in the past for hydroprocessing process development studies using catalyst in the commercially applied size and shape. The first one, which was followed 30 to 40 years ago in various industrial research and development centers, was to test the commercial catalyst in large pilot plants.³⁶ Le Nobel and Choufour³⁷ reported that a pilot plant having a catalyst volume of 0.02 m³ and a bed length of 4 m could

During 1960-70s

Reactor size has reduced significantly

During 1990-2000

Capital investment and operating costs have reduced

**Figure 2.** Advances in hydroprocessing catalyst testing methodology.

represent the performance of a commercial unit. However, such pilot plants involved huge capital investment as well as high operating costs.^{38,39} Besides this, safety was also a big concern for these pilot plants.

The second approach was to use a smaller pilot plant and simulate the data generated in these units applying a suitable hydrodynamic model to predict the performance of a commercial unit.^{40,41} The hydrodynamic model involved parameters for taking care of incomplete wetting of catalyst, external mass transfer resistance, and nonideal flow pattern of liquid.

Recent Advances. The advances that have taken place in reducing the size of reactors used for hydroprocessing process development studies are shown in Figure 2. The figure clearly indicates that during last three decades there has been significant reduction in the size of reactors used for process development studies. This in turn has caused substantial decrease in cost and increase in safety. With progress in the understanding of catalyst bed dilution using inert particles, much advancement has taken place to use smaller size trickle bed reactors for predicting the performance of commercial reactors.

The theories of dilution techniques have been explained in detail by various researchers.^{27,32,38,42} The selection of the proper size of diluent is very important. The physical situation of a catalyst bed in a small-scale reactor when diluted with a larger and a smaller size

(31) Bej, S. K.; Dabral, R. P.; Gupta, P. C.; Mittal, K. K.; Sen, G. S.; Kapoor, V. K.; Dalai, A. K. *Energy Fuels* **2000**, *14*, 701.

(32) Sie, S. T.; Krishna, R. *Rev. Chem. Eng.* **1998**, *14* (3), 203.

(33) Al-Dahhan, M. P.; Wu, Y.; Dudukovic, M. P. *Ind. Eng. Chem. Res.* **1995**, *34*, 741.

(34) Westerterp, K. R.; Wammes, W. J. A. *Three-Phase Trickle Bed Reactors*. In *Ullmann's Encyclopedia of Industrial Chemistry, Volume B4, Principles of Chemical Reaction Engineering and Plant Design*, 5th ed.; Elvers, B., Hawkins, S., Schulz, G., Eds.; VCH Publications: New York, 1992.

(35) Gierman, H. *Appl. Catal.* **1988**, *43*, 277.

(36) Sie, S. T.; Krishna, R. *Rev. Chem. Eng.* **1998**, *14* (1), 47.

(37) Le Nobel, J. W.; Choufour, J. H. *Development in Treating Processes for the Petroleum Industry. Proc. 5th World Petroleum Congress Sect. III*; 5th WPC Inc.: New York, 1959.

(38) Sie, S. T. *AIChE J.* **1996**, *42*, 3498.

(39) In *Deactivation and Testing of Hydrocarbon Processing Catalysts*; Sie, S. T., Conner, P. O., Takatsuka, T., Woolery, G. L., Eds.; ACS Symposium Series, **1996**, *634*, 6.

(40) Henry, H. C.; Gilbert, J. B. *Ind. Eng. Chem. Process. Des. Dev.* **1973**, *12* (3), 328.

(41) Skala, D. U.; Saban, M. D.; Orlovic, A. V.; Meyn, V. W.; Severin, D. K.; Rahimian, I. G. H.; Marjanovic, M. V. *Ind. Eng. Chem. Res.* **1991**, *30*, 2059.

(42) Al-Dahhan, M. H.; Dudukovic, M. P. *AIChE J.* **1996**, *42* (9), 2594.

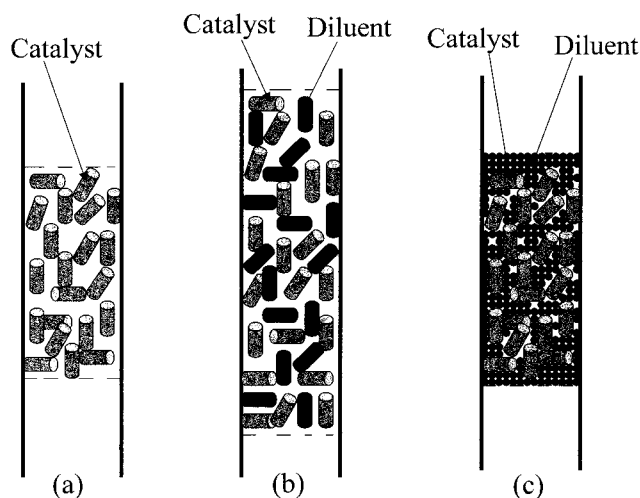


Figure 3. Overview of catalyst bed in a micro-scale reactor using (a) only commercial size catalyst, (b) equal volumes of commercial size catalyst and coarser size diluent, and (c) equal volumes of commercial size catalyst and fine diluents.

of inert particles is shown in Figure 3. Equal volumes of diluent and catalyst were used for this comparison. For the case of an undiluted bed (case (a), Figure 3), only commercial size catalyst is packed in a small-scale reactor. The wall effect is very significant and causes channeling of liquid in this case. Because of the high void space inside the catalyst bed, the liquid holdup in the catalyst bed is also very low. As a whole, there is incomplete wetting of catalyst and only partial utilization is achieved in this case. Besides this, an appreciable amount of axial back mixing is present in the undiluted catalyst bed. When a larger size of diluent is used, it cannot enter the void space between the catalyst particles (case (b), Figure 3). Thus it does not increase liquid holdup and hence only partial utilization of catalyst is obtained in this case also. However, the addition of diluent increases the bed height which in turn reduces liquid axial dispersion to some extent. When the diluent size is smaller, it can enter the narrow void space between the catalyst particles and can increase the liquid holdup of the bed (case (c), Figure 3). Thus almost complete wetting of catalyst is achieved by using a fine size of diluent. The use of fine size of diluent also reduces the axial dispersion in a significant way.

In essence, diluting catalyst bed with appropriate size of inert particles increases liquid holdup, improves catalyst wetting, and reduces liquid back mixing. The selection of diluent size depends on several factors such as length and i.d. of the reactor, size, shape and amount of catalyst, and the flow rate of reactants. Therefore, there was lots of research interest to determine the appropriate size of diluent for various sizes of small-scale reactors in order to overcome their limitations.

Bench-Scale and Micro-scale Down-Flow Trickle Bed Reactors Using Diluted Catalyst Bed. A number of researchers have demonstrated that the use of diluent having particle size in the range of 0.2–0.5 mm in the catalyst bed of a bench-scale trickle bed reactor using commercial catalyst can practically remove all of its shortcomings.^{27,43–46} Myrstad et al.⁴⁷ compared the performance of a trickle bed reactor containing 400 mL of commercial catalyst with those of a commercial

reactor. They diluted the catalyst bed of the laboratory reactor with an equal amount of 500–710 μm size SiC. They observed that data obtained from the laboratory trickle bed reactor fall close to those obtained from a commercial reactor. Sie³² compared the results of hydrodenitrogenation (HDN) of vacuum gas oil in a commercial reactor to that of a bench-scale reactor having a diluted catalyst bed. Both the reactors showed almost similar performance in nitrogen removal.

It is made now possible with further advancement in understanding of the dilution technique to use even micro-scale trickle bed reactors for producing reliable and meaningful data using as low as 5–10 mL of commercial catalyst.^{27,31,32} However, very few studies are available providing information on the size of diluent to be used in the catalyst bed of a microreactor. Results of studies comparing the performances of microreactors to those of larger size (bench-scale or commercial) reactors are presented in Table 2.

Sie²⁷ reported that the performances of a bench-scale and a micro-flow reactor both containing commercial catalyst and beds diluted with 0.2 mm SiC particles show identical performance toward the HDS of heavy gas oil. Bej et al.³¹ studied the effect of diluent size on the performance of a micro-scale trickle bed reactor for the HDS of atmospheric gas oil. They confirmed that the use of diluent having particle size in the range of 0.16–0.19 mm in a micro-scale trickle bed reactor containing as low as 5 mL of commercial catalyst could produce results which were comparable to those obtained from a bench-scale reactor containing 100 mL of catalyst and using 0.19 mm size diluent. In this case, both reactors were operated under a LHSV of 1.0 h^{-1} . It was also observed that decreasing the diluent size from 0.19 to 0.16 mm did not improve the performance of the microreactor further. They also reported that the use of a higher size of diluent (0.25 mm size) in a microreactor could also produce reliable results; however, in that case the reactor needed to be operated at a very high space velocity (corresponding to a LHSV of about 6 h^{-1}). Unfortunately, mostly all commercial hydroprocessing operations are carried out at much lower LHSV.

Sie and Krishna³² compared the results of a micro-flow trickle bed reactor containing 9.35 mL of commercial catalyst to that of a commercial reactor containing 122 m^3 of catalyst for the HDS of heavy gas oil. The catalyst bed in the micro-scale reactor was diluted with an appropriate size of diluent. The catalyst used in both the cases was 1.2 mm trilobe extrudates. Both the systems gave almost the same conversion toward HDS. Bej et al.^{48,49} have used microreactors with diluted catalyst beds to test the activity of commercial Ni–Mo

(43) De Bruijn, A. In *Proceedings of the 6th International Symposium on Catalysis*; Bond, G. C., Wells, P. B., Tomkins, F. C., Eds.; The Chemistry Society Publishers: 1976; p 951.

(44) Koros, R. M. *Proc. 4th Symp. Chem. Reaction Eng., Heidelberg* **1976**, p 372.

(45) van Klinken, J.; van Dongen, R. H. *Chem. Eng. Sci.* **1980**, *35*, 59.

(46) Carruthers, J. D.; DiCamillo, D. J. *Appl. Catal.* **1988**, *43*, 253.

(47) In *Hydrotreatment and Hydrocracking of Oil Fractions*; Myrstad, R., Rosvoll, J. S., Grande, K., Blekkan, E. A., Froment, G. F., Delmon, B., Grange, P., Eds.; Elsevier: Amsterdam, 1997.

(48) Bej, S. K.; Dalai, A. K.; Adjaye, J. *Energy Fuels* **2001**, *15* (2), 377.

(49) Bej, S. K.; Dalai, A. K.; Adjaye, J. *Energy Fuels*, **2001**, *15* (5), 1103.

Table 2. Studies Comparing the Performances of Micro-scale Trickle Bed Reactors with Larger Size Reactors

researchers	details of the micro-scale trickle bed reactor	comparison has been made with the following:	results of comparison
De Vries (see cross ref. in ref 27)	micro-scale trickle bed reactor using commercial catalyst and the bed diluted with 0.2 mm of diluent	bench-scale trickle bed reactor using commercial catalyst and the bed diluted with 0.2 mm of diluent	performances of micro-scale reactor and bench-scale reactor were identical
Sie and Krishna ³²	micro-scale trickle bed reactor using 9.35 mL of commercial catalyst and the bed diluted with appropriate size of diluent	commercial reactor containing 122 m ³ of commercial catalyst	performances of micro-scale reactor was equal to that of the commercial reactor
Bej et al. ³¹	micro-scale trickle bed reactor having 13 mm i.d. and using 5 mL of commercial catalyst; the bed was diluted with 0.19 mm of diluent	bench-scale trickle bed reactor having 25 mm i.d. and using 100 mL of commercial catalyst; the bed was diluted with 0.19 mm of diluent	performances of micro-scale reactor and bench-scale reactor were comparable

catalyst for the hydrotreatment of oil sands derived heavy gas oil.

Thus, it is clear that either a bench-scale or a micro-scale reactor having diluted catalyst bed is a proven tool for generating reliable and meaningful data for scale-up and scale-down activities of commercial reactors. Unfortunately, there are a number of publications in which hydroprocessing studies have been conducted using small-scale trickle bed reactors but without giving proper emphasis to the selection of appropriate size of diluent. Sie²⁷ has provided very useful guidelines for selecting the appropriate size of diluent for testing commercial catalysts in small trickle bed reactors.

The successful utilization of the dilution technique in testing commercial catalyst in micro-scale trickle bed reactors has led to a gradual replacement of the traditionally used costly pilot plants by cheap and simple microreactors.³⁸ Sie has reported that during the period 1970 to 1987, the number of pilot plants in one of the Shell R&D centers has been reduced significantly. During this period, the number of micro-flow reactors in that R&D center has increased dramatically.³⁸

Bench-Scale and Micro-scale Up-Flow Fixed Bed Reactors Using Diluted Catalyst Bed. The second approach, which has also been recommended by researchers⁵⁰ for process development studies is to run the fixed bed reactor containing commercial catalyst (with or without diluent) in the up-flow mode of gas and liquid, i.e., flowing from bottom to top. These reactors are typically known as submerged fixed bed or flooded fixed bed reactors. Though this mode of operation ensures complete wetting of catalyst, it suffers from other disadvantages.²⁹ The up-flow mode of operation may not portray the commercial trickle bed reactor in terms of continuous and dispersed phases. Moreover, the up-flow mode suffers from the drawbacks of nonideal flow of liquid and formation of stagnant zones inside the catalyst bed. The full wetting of catalyst in these reactors is obtained because of increased liquid holdup, which may alter the relative rates of homogeneous and heterogeneous reactions.⁴² In addition, the availability of hydrogen in hydrotreating processes is possibly reduced in the up-flow mode of operation.

There exist contradictions regarding the superiority between the up-flow and down-flow modes of operation

though both these modes of operation are used by various researchers. In the recent past, some work has been carried out in this direction for elucidating the differences between these two modes of operation. The results of these studies are summarized in Table 3.

Mystrad et al.⁴⁷ found an equal performance for both the modes of operation using 0.5–0.71 mm size of diluent. However, the length and diameter of the catalyst bed were not the same for both the modes of operation. The down-flow trickle bed reactor had an i.d. of 37.5 mm with a catalyst volume of 400 mL. On the other hand, the up-flow reactor had an i.d. of 19.3 mm with a catalyst volume of 75 mL.

Carruthers and DiCamillo⁴⁶ conducted a comparative study on the performances between these two modes of operation. They used a reactor of 24 mm i.d. and a catalyst volume of 100 mL. The catalyst bed was diluted with an equal amount of 20–60 mesh inert having average particle size of 0.5 mm. Excluding the behavior during initial few days, the performances of the two modes of operation were the same for the rest of the test period.

De Wind et al.⁵⁰ studied the performances of a bench-scale reactor in its up-flow and down-flow modes of operation. The reactor used in their study contained 75 mL of commercial catalyst and an equal amount of 0.5 mm size of diluent. They claimed that the up-flow mode of operation showed better performance.

Chander et al.²⁹ showed through a residence time distribution study carried out in a bench-scale reactor that substantial differences in the behavior between these two modes of operation existed when a larger size of diluent (1.1 mm size) was used. The differences between the two modes of operation were reduced slightly at higher liquid flow rate even when the larger size of diluent was used. However, the use of a smaller size (0.3 mm size) of particle could neutralize all the differences between the two modes of operation.

Wu et al.⁵¹ also compared the performance of up-flow and down-flow modes of operation of a diluted fixed bed reactor for the hydrogenation of α -methyl styrene. They found that the size of diluent played an important role and the differences between these two modes of operation could be reduced by the use of a suitable size of diluent.

(50) de Wind, M.; Plantenga, F. L.; Heinerma, J. J. L.; Homan Free, H. W. *Appl. Catal.* **1988**, *43*, 239.

(51) Wu, Y.; Khadilkar, M. R.; Al-Dahhan, M. H.; Dudukovic, M. P. *Ind. Eng. Chem. Res.* **1996**, *35*, 397.

Table 3. Studies Comparing the Performances of Up-flow and Down-flow Modes of Operation of Fixed Bed Hydroprocessing Catalytic Reactors

researchers	details of reactor, catalyst and diluent used during:		major findings
	down-flow mode	up-flow mode	
De Wind et al. ⁵⁰	(i) Reactor of 21 mm i.d. (ii) 75 mL of commercial size catalyst (iii) 75 mL of 0.5 mm size diluent	(i) Reactor of 21 mm i.d. (ii) 75 mL of commercial size catalyst (iii) 75 mL of 0.5 mm size diluent	Up-flow mode of operation showed better performance.
Carruthers and DiCamillo ⁴⁶	(i) Reactor of 24 mm i.d. (ii) 100 mL of commercial size catalyst (iii) 100 mL of 20–60 mesh (0.5 mm average size) diluent	(i) Reactor of 24 mm i.d. (ii) 100 mL of commercial size catalyst (iii) 100 mL of 20–60 mesh diluent	Performances of up-flow and down-flow modes of operation were almost equal.
Myrstad et al. ⁴⁷	(i) Reactor of 37.5 mm i.d. (ii) 400 mL of commercial size catalyst (iii) 400 mL of 500–710 μ m size diluent	(i) Reactor of 19.3 mm of i.d. (ii) 75 mL of commercial size catalyst (iii) 75 mL of 500–710 μ m size diluent	Equal performance for both the modes of operation was observed.
Bej et al. ⁵³	(i) Reactor of 13 mm i.d. (ii) 5 mL of commercial size catalyst (iii) 5 mL of diluent (iv) Diluent size was varied from 0.16 to 1.1 mm	(i) Reactor of 13 mm i.d. (ii) 5 mL of commercial size catalyst (iii) 5 mL of diluent (iv) Diluent size was varied from 0.16 to 1.1 mm	Up-flow mode showed better performance when larger size of diluent was used. Down-flow mode showed better performance when smaller size of diluent was used.
Lopez et al. ⁵²	(i) Reactor of 14.3 mm i.d (ii) 14.5 mL of commercial size catalyst (iii) 14.5 mL of 1.4–2.3 mm size of diluent	(i) Reactor of 14.3 mm i.d (ii) 14.5 mL of commercial size catalyst (iii) 14.5 mL of 1.4–2.3 mm size diluent	Up-flow mode of operation showed better performance.

Castaneda-Lopez et al.⁵² conducted a comparative study between the up-flow and down-flow modes of operation. They used a reactor having an internal diameter of 14.3 mm and a catalyst volume of 14.5 mL. The catalyst particle had a diameter of 2.3 mm. The catalyst bed was diluted with inert alumina having particle diameter in the range of 1.4–2.3 mm. They reported that up-flow mode of operation gave superior performance as compared to that of down-flow mode. However, the size of diluent used was larger as compared to that recommended for overcoming the shortcomings of a small-scale trickle bed reactor having similar catalyst volume. Nevertheless, the study provided important information that the up-flow mode of operation showed apparently better performance using a larger size of diluent. Had a lower size of diluent been used the situation might be different.

A detailed comparative study varying the size of diluent in both the modes of operation was done by Bej et al.⁵³ They studied the effect of diluent size and LHSV on the comparative behavior of a micro-scale fixed bed reactor using as low as 5 mL of commercial catalyst in its up-flow and down-flow modes of operation.⁵³ The up-flow mode of operation using larger size of diluent (0.77 mm) in combination with lower space velocities of liquid showed better performance than that of the down-flow mode of operation. However, the use of smaller size of diluent (0.19 mm) gave better reactor performance in down-flow mode of operation. The data

generated in the second case using smaller size (0.19 mm) of diluent in down-flow mode of operation could predict the performance of a bench-scale reactor and thus represented the true activity of the catalyst. They also observed that the differences in the performance between the up-flow and down-flow mode of operation decreased at higher space velocities when smaller size of diluent was used.

It is thus clear that recent studies have made advances in understanding the differences between up-flow and down-flow modes of operation. Wetting of catalyst and back mixing of liquid are the two important issues involved in deciding the superiority between these two modes of operation. The importance of the degree of catalyst wetting and liquid back mixing in the up-flow or down-flow mode is dependent on the size of diluent, the length of the catalyst bed, and the level of space velocity used. The relative importance of these parameters for these two modes of operation in bench-scale and micro-scale reactors, as revealed from earlier studies,^{29,31,53} are given in Table 4. The overall performances in these two modes of operation are also summarized in the table.

Both incomplete wetting of catalyst and liquid axial back mixing reduce the performance in down-flow mode of operation if a larger size of diluent is used. Whereas in the up-flow mode, the catalyst gets fully wetted even if diluent size is larger. However, the larger size of diluent increases liquid axial back mixing in up-flow mode. But the decrease in performance in the down-flow mode by the combined effect of incomplete catalyst wetting and non ideal liquid flow is more than the decrease in performance in the up-flow mode of operation due to liquid axial back mixing. As a result, the

(52) Castaneda-Lopez, L. C.; Martinez, F. A.; Juarez, J. A.; Maity, S. K.; Segundo, E. R.; Guerra, M. N. M. *Energy Fuels* **2001**, 15 (5), 1139.

(53) Bej, S. K.; Dalai, A. K.; Maity, S. K. *Catal. Today* **2001**, 64 (3–4), 333.

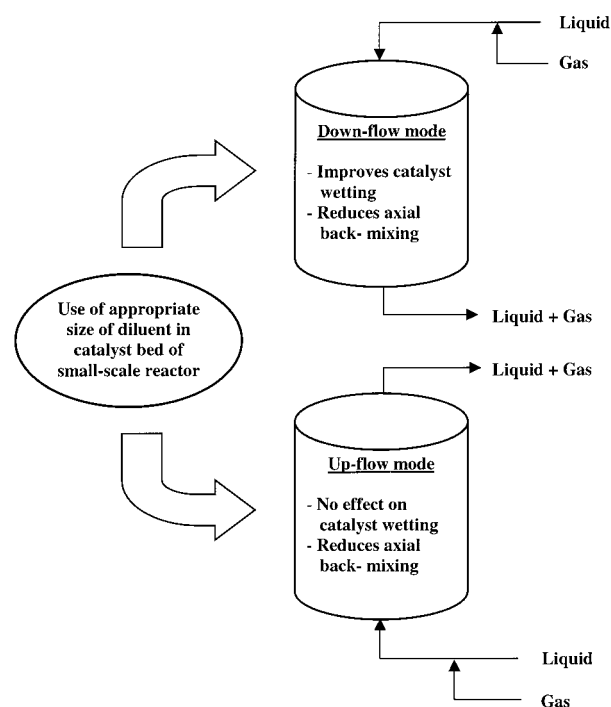
Table 4. Relative Importance of Catalyst Wetting and Liquid Axial Back Mixing in Up-Flow and Down-Flow Modes of Operation When Larger and Smaller Size of Diluent is Used in Bench-Scale and Micro-Scale Trickle Bed Reactors

	When larger size (>0.8 mm) of diluent is used in:				When smaller size (<0.2 mm) of diluent is used in:			
	bench-scale reactor		micro-scale reactor		bench-scale reactor		micro-scale reactor	
	up-flow	down-flow	up-flow	down-flow	up-flow	down-flow	up-flow	down-flow
catalyst wetting	complete	partial	complete	partial	complete	complete	complete	complete
presence of liquid axial back mixing	high	low	very high	high	very low	very low	low	very low
relative performance	superior to down-flow	inferior to up-flow	superior to down-flow	inferior to up-flow	close to down-flow	close to up-flow	slightly inferior to down-flow	slightly superior to down-flow
Is the performance close to the commercial unit?	no	no	no	no	yes	yes	no	yes

performance in the down-flow mode of operation is always better when the experiments are carried out using a larger size of diluent or without diluent. The data generated in the up-flow mode, though apparently shows higher activity, may not represent the true activity of the catalyst as these are not generated in the complete absence of liquid back mixing.

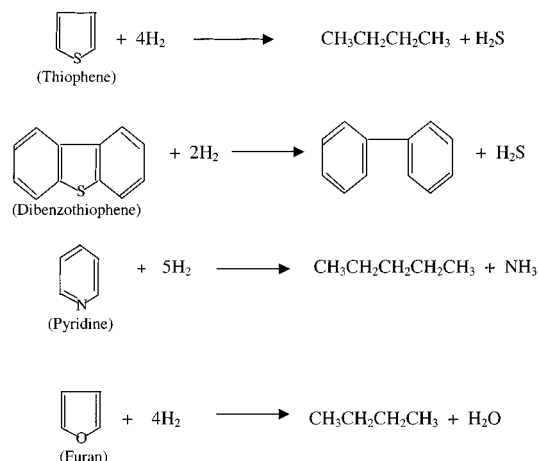
The situation using a smaller size of diluent in both modes of operation is now analyzed here. The down-flow mode of operation using smaller size of diluent can achieve full wetting of catalyst as well as an almost plug flow pattern of liquid (even at a lower LHSV) and the data generated in this way represent the true activity of the catalyst. In the up-flow mode of operation, the catalyst will definitely achieve full wetting when a smaller size of diluent is used. However, the complete removal of liquid axial back mixing in the up-flow mode will depend on the length of the catalyst bed as well as on the level of LHSV. Thus one may expect plug flow pattern of liquid in a bench-scale reactor in the up-flow mode using smaller size of diluent. Equal performances in these two modes of operation using a smaller size of diluent have been observed in bench-scale reactors.^{46,51} On the other hand, in a micro-scale reactor where the catalyst bed height is comparatively lower, complete absence of liquid back mixing in the up-flow mode is observed only at higher LHSV. Therefore, the performance in up-flow mode of operation becomes equal to that of down-flow mode in a micro-scale fixed bed reactor at a higher level of LHSV.⁵³ At a lower level of LHSV, the up-flow mode shows slightly inferior performance due to the presence of a small amount of liquid back mixing.⁵³

In summary, the effect of diluent in up-flow and down-flow mode is shown in Figure 4. The appropriate size of diluent improves catalyst wetting and reduces axial back mixing of liquid in down-flow mode. For the up-flow mode, the diluent reduces axial dispersion but has no effect on catalyst wetting. It may be added here that until further advancement to resolve the differences between the up-flow and down-flow modes, the trickle bed reactor using down-flow mode of operation and using an appropriate size of diluent in the catalyst bed should be preferred for the process development studies of hydroprocessing reactions.

**Figure 4.** Effect of appropriate size of diluent on the performance of a fixed bed multiphase reactor when operated in up-flow or down-flow mode.

Reactors for Kinetic Studies

The molecules containing sulfur, nitrogen, and oxygen are broken down during hydroprocessing and the heteroatom is released as H_2S , NH_3 , and H_2O , respectively. Reactions involving the HDS, HDN, and hydrodeoxygenation (HDO) of some typical model compounds are shown in Table 5. In some cases, the product of the reaction may act as an inhibitor for the reaction. For example, several workers have reported large inhibiting effects of H_2S on the HDS reaction.^{54–58} Various types of kinetic models such as the simple power law model, the different forms of Langmuir-Hinshelwood-Hougen-Watson (LHHW) model, detailed mechanistic models, and lumped parameter models have been used to describe the rate of these reactions. A detailed discussion about this is available in the literature^{54,59,60} and is outside the scope of this review. However, a typical

Table 5. Typical Reactions for the Removal of Various Hetero-atoms

LHHW model for the rate of hydrogenolysis of dibenzothiophene is given below:⁶¹

$$r_{\text{HDS}} = k \frac{K_{\text{DBT}} p_{\text{DBT}}}{(1 + K_{\text{DBT}} p_{\text{DBT}} + K_{\text{H}_2\text{S}} p_{\text{H}_2\text{S}})^2} \frac{K_{\text{H}_2} p_{\text{H}_2}}{(1 + K_{\text{H}_2} p_{\text{H}_2})}$$

where k is the rate constant, K is the equilibrium constant, p is the partial pressure, and the subscript DBT is dibenzothiophene.

The analysis of the different types of sulfur compounds present in a real feedstock is difficult. Besides this, the various aromatics and nitrogen compounds present in the real feedstock may also show competitive adsorption effects on the active surface of the catalyst.⁶² The prediction of the rate of HDS for the case of a real feed through a LHHW model is thus very complicated. Therefore, a simple power law model of the type as given below has most frequently been used by various researchers to describe the removal of sulfur compounds from a real feedstock:

$$r_{\text{HDS}} = k c_s^n$$

where k is the reaction rate constant, c_s is the initial concentration of total sulfur in the feed, and n is the order of the reaction. The value of n generally depends on the boiling point of the feedstock and the nature of the sulfur compounds present on it.

Similar power law kinetics have also been used for the hydrodemetallization as well as for the removal of asphaltene and micro-carbon residues from heavier fractions of petroleum.⁶³

The kinetics of a reaction are used to reliably translate laboratory and pilot plant data into the design and

rating of a commercial unit.⁶⁴ The kinetic studies can be carried out under different sets of experimental conditions depending on whether the kinetic data is generated in the presence or absence of internal or external mass transfer limitations. Accordingly, experiments can be conducted in three levels:⁶⁵

(i) Experiments that are carried out using a fine size of catalyst particles and under appropriate conditions to eliminate both internal and external mass transfer limitations. This gives the intrinsic kinetics of the catalyst.

(ii) Experiments that are conducted using commercial size catalyst but eliminating only the external mass transfer resistances. This provides the apparent kinetic model.

(iii) Experiments which are carried out in such a way that neither internal diffusional resistances nor the external mass transfer limitations are eliminated. This gives the extrinsic kinetic model of a reaction.

Although apparent kinetic models are not usually favored for scientific or academic studies, it has frequently been used by the industrial researchers for the scale-up of commercial reactors.^{27,65} This is because it helps to predict the performance of the catalyst in the form in which it will be used in the commercial reactor and thus eliminates lots of modeling studies for incorporating the diffusional effects.⁴² However, such kinetics cannot be extrapolated to a different catalyst shape. Thus, it is advisable to conduct such kinetic studies when the shape of the catalyst has been decided for commercial application.

Sometimes experiments for measuring the relative reactivity of various model compounds present in a real industrial feedstock as well as understanding the mechanistic pathways for the reactions are also required at this stage to generate knowledge for the development of better catalysts.

Batch autoclave, continuously operated trickle bed reactors, and recycle reactors have been generally used for the kinetic studies of hydroprocessing reactions. These are discussed in the following section.

Batch Autoclave. Few researchers have used batch autoclaves for the kinetic studies of hydroprocessing reactions. As discussed earlier (in the catalyst screening section), the catalyst can be used in the form of fine powder or may be kept either in a spinning basket or in a static basket located inside the autoclave. Ideal mixing is easy to achieve in a batch autoclave. The reactor is cheaper than a continuous reactor. Geneste et al.⁶⁶ used an agitated autoclave for the kinetic studies of benzothiophene, methylbenzothiophene, and dibenzothiophene HDS. Krishnamurthy et al.⁶⁷ studied the kinetics of hydrodeoxygenation of dibenzofuran and related compounds in a batch autoclave. Daly⁶⁸ used a Parr Model high-pressure batch reactor for studying the kinetics of benzothiophene HDS. In this study, the

(54) Vrinat, M. L. *Appl. Catal.* **1983**, 6, 137.

(55) van Parijs, I. A.; Hosten, L. H.; Froment, G. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, 25, 431.

(56) van Parijs, I. A.; Hosten, L. H.; Froment, G. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, 25, 437.

(57) Korsten, H.; Hoffmann, U. *AIChE J.* **1996**, 42 (5), 1350.

(58) Papayannakos, N.; Marangozis, J. *Chem. Eng. Sci.* **1984**, 39, 1051.

(59) Kim, H. G.; Curtis, C. W. *Energy Fuels* **1990**, 4, 206.

(60) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, 30, 2021.

(61) Broderick, D. H.; Gates, B. C. *AIChE J.* **1981**, 27, 663.

(62) Frye, C. G.; Mosby, J. F. *Chem. Eng. Prog.* **1967**, 63 (9), 66.

(63) Callejas, M. A.; Martinez, M. T. *Energy Fuels* **1999**, 13, 629.

(64) Berger, R. J.; Hugh Stitt, E.; Marin, G. B.; Kapteijn, F.; Moulijn, J. A. *CATTECH* **2001**, 5 (1), 30.

(65) Bos, A. N. R.; Lefferts, L.; Marin, G. B.; Steijns, M. H. G. M. *Appl. Catal. A: General* **1997**, 160, 185.

(66) Geneste, P.; Amblard, P.; Bonnet, M.; Graffin, P. *J. Catal.* **1980**, 61, 115.

(67) Krishnamurthy, S.; Panvelkar, S.; Shah, Y. T. *AIChE J.* **1981**, 27, 994.

(68) Daly, F. P. *J. Catal.* **1978**, 51, 221.

catalyst was placed in a basket attached to the stirrer shaft.

It becomes difficult to achieve a steady state in a batch autoclave for catalysts which require a longer time to arrive at steady state. Though this does not have significant effect for initial screening of catalyst formulations, this is an important drawback for carrying out kinetic studies. Le Page et al.⁸ have suggested that this problem could possibly be overcome by aging the catalyst beforehand in a reactor operated in a dynamic mode and then carefully transferring the aged catalyst to the batch autoclave. Another difficulty in studying kinetics in a batch reactor is the uncertainty of the reaction conditions. The problem is to bring together reactants, catalyst, and operating conditions of temperature and pressure so that at zero time everything is as desired.⁶⁹ To overcome this, Daly⁶⁸ had increased the pressure after the temperature of the reactor reached very close to the desired level. Krishnamurthy et al.⁶⁷ and Schulz et al.⁷⁰ have followed a slightly different method for overcoming this problem. After loading the catalyst and raising the pressure and temperature, they put the reaction mixture into the batch autoclave at zero reaction time. Taking samples may constitute another problem if the amounts withdrawn influence the results obtained.⁷¹ Separation of the influence of individual factors is difficult, in particular of reaction kinetics and possible deactivation.⁸

Fixed Bed Continuous Reactors. Fixed bed continuous reactors using either catalyst in the form of pellets or crushed particles have widely been used for kinetic studies of hydroprocessing reactions. The catalyst bed is generally diluted with an appropriate size of inert diluents. The selection of the proper size of diluent is very important and has already been discussed in the process development section. One special aspect of diluting the catalyst bed with the appropriate size of diluent is that hydrodynamics are controlled by the diluent while the kinetics are solely dictated by the catalyst pellet.²⁷

These reactors are operated either in a differential mode (keeping conversion <10%) or in an integral mode where a higher level of conversion is targeted. During differential mode of operation, concentration and temperature gradients are small and hence analysis of data is simpler. However, high analytical accuracies are required. On the other hand, substantial gradients of concentration and temperature exist during integral operation and hence interpretation of data is more difficult, especially if a complex kinetic model is used. However, the accuracy requirements for chemical analysis are relaxed.⁷¹

Korsten and Hoffmann⁵⁷ conducted a kinetic modeling study for HDS of vacuum gas oil in a trickle bed reactor using commercial catalyst having an equivalent diameter of 1.72 mm. They used 160 g of catalyst in a reactor having an i.d. of 3 cm. The total height of the catalyst bed containing catalyst particles and a suitable size of diluent was 66.5 cm. They carried out a simulation

study using a LHHW kinetic model and suitable parameters incorporating the effects of incomplete catalyst wetting, external mass transfer resistances, and axial liquid back mixing.

Miller and Hineman⁷² studied the kinetics of quinoline HDN in a trickle bed reactor having length and i.d. of 80 and 1.0 cm, respectively. The catalyst used for the study was of 14/20-mesh size. Tsamatsoulis and Papayannakos⁷³ investigated the intrinsic HDS kinetics of vacuum gas oil in a trickle bed reactor with backmixing effects. They used a reactor having an i.d. of 2.5 cm and a catalyst of about 100 g. The catalyst particles had sizes in the range of 0.34–0.4 mm. Yui and Sanford⁷⁴ studied the kinetics of mild hydrocracking of bitumen-derived coker and hydrocracker heavy gas oil in a trickle bed reactor having an i.d. of 1.7 cm and a catalyst volume of 120 mL. The catalyst was a commercial one but diluted with 50% volume of 45 mesh silicon carbide. Satterfield and Yang⁷⁵ and Yang and Satterfield⁷⁶ used a trickle bed reactor having an internal diameter of 0.52 cm for studying the kinetics of quinoline HDN. The catalyst particle had an average diameter of 0.2 cm. The catalyst was diluted with inert silicon carbide of the same size. Kwak et al.⁷⁷ carried out the kinetic studies for bitumen and bitumen-derived liquids in a fixed bed reactor using the up-flow mode of gas and liquid. Vradman et al.⁷⁸ studied the kinetics for the deep desulfurization of model compounds in a small trickle bed reactor. In their studies, they have used 5 mL of catalyst mixed with 10 mL of 0.2 mm silicon carbide in a 2.2 cm i.d. reactor.

Continuous Stirred Tank Reactor (CSTR). Recycle reactor systems, which approximate CSTR behavior by employing either external or internal recirculation are probably the most useful for obtaining catalytic kinetic data for hydroprocessing reactions.⁷⁹ These reactors are generally typified by Berty and Carberry type reactors. CSTRs are referred to as gradientless reactors as they suppress the internal gradient of heat and mass. Because the reactor is well mixed, the reactor is effectively at the exit concentration. Data generated in a gradientless reactor provides advantages in easy and meaningful kinetic analysis and interpretation. Different types of these gradientless CSTRs have been discussed in detail by various authors.^{69,80}

For hydroprocessing reactions, mechanical pumps, and the need to cool and reheat the recycle stream plague external circulation. Gradientless reactors having internal cycle have found widespread applications in hydroprocessing kinetic studies. Two versions of these reactors have generally been used and are shown in Figure 5. The first version is the spinning basket reactor (Figure 5a) in which the catalyst is kept in a basket located inside the reactor and the basket is rotated by

(72) Miller, J. T.; Hineman, M. F. *J. Catal.* **1984**, 85, 117.

(73) Tsamatsoulis, D.; Papayannakos, N. *Chem. Eng. Sci.* **1998**, 53, 3449.

(74) Yui, S. M.; Sanford, E. C. *Ind. Eng. Chem. Res.* **1989**, 28, 1278.

(75) Satterfield, C. N.; Yang, S. H. *Ind. Eng. Chem. Process Des. Dev.* **1984**, 23, 11.

(76) Yang, S. H.; Satterfield, C. N. *Ind. Eng. Chem. Process Des. Dev.* **1984**, 23, 20.

(77) Kwak, S.; Longstaff, D. C.; Deo, M. D.; Hanson, F. V. *Fuel* **1994**, 73 (9), 1533.

(78) Vradman, L.; Landau, M. V.; Herskowitz, M. *Catal. Today* **1999**, 48, 41.

(79) Mahoney, J. A.; Robinson, K. A.; Myers, E. C. *Chemtech* **1978**, 8, 758.

(69) Berty, J. M. *Experiments in Catalytic Reaction Engineering*; Elsevier: Amsterdam, 1999.

(70) Schulz, H.; Bohringer, W.; Ousmanov, F.; Waller, P. *Fuel Process. Technol.* **1999**, 61, 5.

(71) Schouten, E. P. S.; Borman, P. C.; Westerterp, K. R. *Chem. Eng. Process.* **1996**, 35, 43.

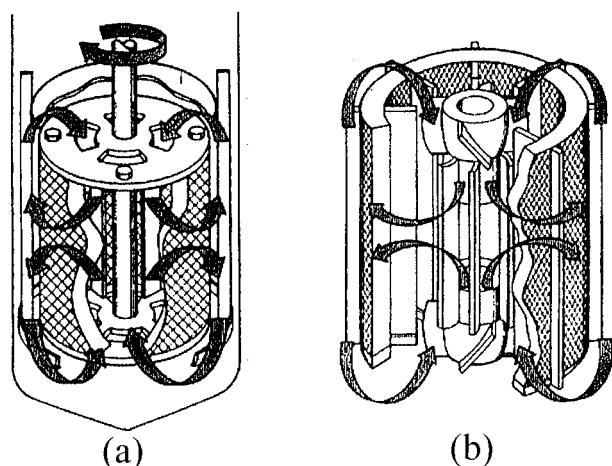


Figure 5. Schematic diagrams of internal circulation CSTRs when (a) the catalyst is kept in a rotating basket, and (b) the catalyst is kept in a static basket.

suitable means. This is known as the Mahoney-Robinson reactor. Mahoney et al.⁷⁹ used such a spinning basket CSTR for studying the HDS kinetics of dibenzothiophene.

The second version (Figure 5b) is the one in which the catalyst is held in a static basket inside the reactor and a suitable stirrer agitates the liquid. One such reactor, most popularly known as the Robinson-Mahoney reactor, was used by Vanrysselberghe and Froment⁸¹ for the HDS of dibenzothiophene. They used crushed catalyst having particle size in the range of 710–800 μm for obtaining intrinsic kinetic rates. Gray et al.⁸² also used a Robinson-Mahoney reactor for studying the deactivation kinetics of bitumen-derived

residue hydroprocessing. A similar reactor was used by them for studying the kinetics of bitumen hydrocracking.^{83–85} Callejas and Martinez also used a similar type CSTR having a static basket of crushed catalyst (particle size between 53 and 530 μm) for finding the intrinsic kinetics of removing asphaltene, sulfur, nitrogen, Ni, and V from a Maya residue.^{86,87}

In summary, the CSTR should be preferred in the kinetic studies of hydroprocessing reactions because of the ease in analysis of data generated in these reactors, especially if an elaborate kinetic model development is the objective.

Conclusions

The initial catalyst screening experiments can be conducted either in a batch autoclave or in a continuously operated fixed bed microreactor. However, the process development and optimization studies should be carried out in bench-scale or micro-scale trickle bed reactors with catalyst bed diluted with inert particles. The selection of diluent size is very important and depends on several factors such as length and i.d. of the reactor, size, shape and amount of catalyst, and the flow rate of reactants. Contradictions exist in the behavior of up-flow and down modes of operation of a fixed bed hydroprocessing reactor. The differences in the two modes of operation can be reduced by selecting the proper size of reactor and using an appropriate size of diluent and LHSV. The Gradientless CSTR is preferred for kinetic studies, especially when a complicated kinetic model is handled.

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(80) Chaudhari, R. V.; Shah, Y. T.; Foster, N. R. *Catal. Rev.-Sci. Eng.* **1986**, 28 (4), 431.

(81) Vanrysselberghe, V.; Froment, G. F. *Ind. Eng. Chem. Res.* **1996**, 35, 3311.

(82) Gray, M. R.; Zhao, Y.; McKnight, C. M.; Komar, D. A.; Carruthers, J. D. *Energy Fuels* **1999**, 13, 1037.

(83) Gray, M. R.; Ayasse, A. R.; Chan, E. W.; Veljkovic, M. *Energy Fuels* **1995**, 9, 500.

(84) Nagaishi, H.; Chan, E. W.; Sanford, E. C.; Gray, M. R. *Energy Fuels* **1997**, 11, 402.

(85) Ayasse, A. R.; Nagaishi, H.; Chan, E. W.; Gray, M. R. *Fuel* **1997**, 76 (11), 1025.

(86) Callejas, M. A.; Martinez, M. T. *Energy Fuels* **2000**, 14, 1304.

(87) Callejas, M. A.; Martinez, M. T. *Energy Fuels* **2000**, 14, 1309.