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Catalysis Today 64 (2001) 333–345

CATALYSIS TODAY

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Effect of diluent size on the performance of a micro-scale fixed bed multiphase reactor in up flow and down flow modes of operation

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Abstract

The comparative behaviors of a micro-scale fixed bed multiphase reactor in up flow and down flow modes of operation were studied for hydrodesulfurization of atmospheric gas oil over a commercial catalyst. The experiments for the two modes of operation were conducted for a wide range of diluent size and other process variables such as liquid hourly space velocity and hydrogen/gas oil ratio. The results showed that the down flow mode of operation using 0.19 mm size of diluent could be used for generating reliable and meaningful data. On the other hand, the use of up flow mode of operation is restricted only for higher space velocities even while using 0.19 mm size of diluent. The results also indicated that the performance of the up flow mode of operation was poor at higher hydrogen/gas oil ratio. This change in performance is pronounced when higher size of diluent was used with the catalyst. In contrary, the hydrogen/gas oil ratio had minimum effect on the performance of the reactor for down flow mode of operation.

Keywords: Dilution technique; Up flow; Down flow; Micro-reactor; Gas oil; Hydrodesulfurization

1. Introduction

The commercial hydrodesulfurization (HDS) processes are mostly carried out by passing hydrogen and liquid hydrocarbon feed through a trickle bed reactor containing solid catalyst. HDS of various petroleum products are gaining importance day by day for meeting stringent environmental regulations. Because of increasing commercial importance, the research activities on the development of better catalyst and technology for efficient HDS processes are also increasing at a faster rate.

The development of an improved catalyst involves the performance evaluation of different promising catalyst formulations. It is desired that these performance evaluations should be carried out in systems involving lower cost and producing data that can predict the performance of the commercial reactor. Because of the involvement of lower cost and safer operations, small-scale trickle bed reactors are preferred for catalyst evaluation studies [1,2]. But due to the difference in catalyst quantity, reactor diameter and reactor length between small-scale and commercial trickle bed reactors, the data generated in the former cannot reliably predict the performance of the latter. The inability of the small-scale reactor to predict the performance of the commercial reactor is mainly due to poor wetting of catalyst and higher backmixing of liquid in these small-scale reactors. The details of these problems

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0920-5861/01/$ – see front matter
PII: S0920-5861(00)00536-8

are discussed in literature by number of researchers [2–7].

One option for overcoming these problems to test commercial catalyst in small-scale down flow trickle bed reactors is to dilute the catalyst bed with an appropriate size of non-porous inert diluent. Researchers have established that bench-scale as well as micro-scale trickle bed reactor could be used for generating reliable data [2,4,8–10], if the catalyst bed is diluted with an appropriate size of diluent. For example, Sie [2] has reported that the use of 0.2 and 0.8 mm size of diluent with the catalyst in micro-reactor and bench-scale reactor, respectively, could produce identical results, irrespective of the difference in scale. He has also reported that a bench-scale reactor having a diluted catalyst bed could predict the performance of a commercial reactor operating under comparable process conditions.

The other option, which is also recommended by some researchers for generating reliable data, is to operate the fixed bed reactor in up flow mode of gas and liquid [11]. For example, De Wind et al. [11] have informed that reliable results could be obtained in the up flow operation of a bench-scale reactor containing 75 ml of catalyst and equal volume of 0.5 mm carborandum.

Though both these options are used by different groups of scientists, there exist contradictions regarding the superiority between these two methods. In the recent past, some work has been carried out in this direction for elucidating the difference between these two modes of operation [12–14]. For example, Wild et al. [12] have compared the hydrodynamic characteristics of cocurrent up flow and down flow fixed bed reactors. Khadilkar et al. [13] have also conducted the comparative study between the performances of these two modes of operation in a laboratory fixed bed reactor using hydrogenation of alpha-methyl styrene as a test reaction. They have concluded that the superiority of any mode of operation depends on whether the reaction is liquid limited or gas limited. The up flow mode of operation gave better performance for a liquid limited reaction whereas a gas limited reaction would produce better results in a down flow reactor. The subject has also been reviewed by Dudukovic et al. [14].

Few reports are also available on the comparative study between the performance of up flow and down flow modes of operation of diluted fixed bed reactors [11,15–17]. De Wind et al. [11] have carried out experimental studies to compare the performances of up flow and down flow modes of operation with and without using diluent. They have claimed that up flow mode of operation shows better performance when the catalyst bed was diluted with 0.5 mm size of diluent. However, their experiments were conducted in a bench-scale reactor using 75 ml of catalyst. Wu et al. [15] have also conducted a comparative study between these two modes of operation in a diluted fixed bed reactor and using hydrogenation of alpha methyl styrene as the test reaction. They have reported that diluent plays an important role and the use of a suitable size of diluent can neutralize the difference between these two modes of operation. They have shown that diluting the catalyst bed with 0.2 mm of silicon carbide could produce similar results in both up flow and down flow modes of operation. Their experiments were conducted in a reactor having diameter of 22 mm and a catalyst bed length of 275 mm. Myrstad et al. [17] have also observed equal performances of the two modes of operation using 0.5–0.71 mm size of diluent. In their study, they had used 75 and 400 ml of catalyst volume, respectively, for up flow and down flow modes of operation.

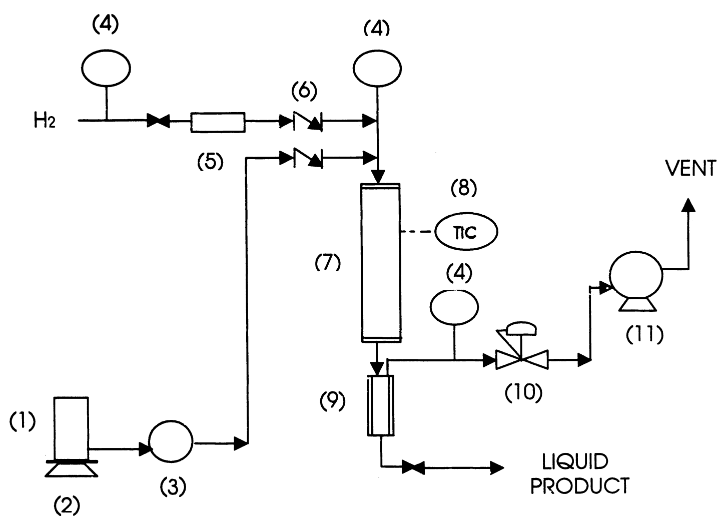
Thus it is evident from the above discussion that most of these comparative studies have been conducted in bench-scale units using 50–100 ml of catalyst. On the other hand, recently there is a great deal of interest in the use of micro-reactors for catalyst and process development activities [1,2]. But, information about the comparative performances of down flow and up flow modes of operation of a micro-reactor using 5–10 ml of catalyst is not available in literature. Because of the smaller amount of catalyst and liquid flow rate in these micro-reactors, the down flow mode of operation have significant wall effect, liquid maldistribution and liquid backmixing. Similarly, the up flow mode of operation of these micro-reactors though provides much better contact between liquid and catalyst, but suffer from significant axial dispersion of liquid. The relative significance of these phenomena in the two modes of operation and their influence on the performance of a catalyst decide the superiority between these two modes of operation. The results obtained from the comparative studies of these two modes of operation in a bench-scale reactor using higher amount of catalyst (~100 ml) are not directly applicable (as will also be evident from Section 3) to such micro-reactors. Thus, there is a need for a systematic study in this direction.

The knowledge about the comparative behaviors of up flow and down flow modes of operation in a fixed bed micro-reactor using different sizes of diluent will be helpful in selecting the proper diluent size and mode of operation for testing small amount (about 5–10 ml) of catalyst and thereby providing a low cost option for generating meaningful data for scale up and scale down activities. Hence the present work has been carried out to study the effect of diluent size and other process variables on the performance of a fixed bed micro-reactor containing as low as 5 ml of commercial catalyst in its up flow and down flow modes of operation. Also, the proper mode of operation and appropriate size of diluent for such a micro-reactor were determined in this study. Keeping in mind the importance of gas–liquid–solid multiphase reactor in the hydroprocessing of petroleum products, HDS of gas oil was selected as a test reaction for the study.

2. Experimental setup and procedure

Fig. 1 shows a simplified schematic diagram of the experimental setup used in this study. All the experiments were carried out at 35 bar in a continuous flow of liquid hydrocarbon and hydrogen. Liquid feed was fed to the reactor through a metering pump. High purity (99.99 vol.%) hydrogen was used for the reaction, the flow of which was measured and controlled through a mass flow controller. The reactor was a stainless tube with an internal diameter of 13 mm and length of 300 mm. The temperature of the catalyst bed was controlled by a temperature controller. The pressure of the system was maintained at 35 bar with the help of a back pressure regulator. Provisions were also made to run the reactor for both up flow and down flow modes, whenever required.

The liquid feedstock used in this study was straight run atmospheric gas oil having sulfur content of 1.47 wt.%. Trilobe shaped commercial Co–Mo based alumina catalyst with a diameter of 1.5 mm and a length/diameter ratio in the range 3–4 was used for the study. A catalyst volume of 5 ml and an equal volume of inert, non-porous silicon carbide of appropriate size as diluent were used in each experiment.



(1) liquid feed tank; (2) weighing balance; (3) liquid feed pump; (4) pressure indicator (5) mass flow controller for hydrogen; (6) check valve; (7) reactor and furnace assembly; (8) temperature indicator and controller (9) high pressure gas-liquid separator; (10) back pressure regulator; (11) gas flow meter.

Fig. 1. Simplified schematic diagram of the experimental setup.

The catalyst and the diluent were loaded in the reactor as per the procedure proposed by Al-Dahhan et al. [18] and is briefly outlined below. Initially, 2.5 ml of the catalyst was loaded in the reactor. The reactor was then vibrated mildly. After this, 2.5 ml of selected size of silicon carbide was loaded. The reactor was vibrated again mildly allowing the diluent to settle in the void of the catalyst bed. The above procedure was then repeated to load the remaining 2.5 ml of catalyst and equal amount of diluent. The height of the diluted catalyst bed was dependent on the size of diluent used. For example, when 1.1 mm size diluent was used, the bed height was 75 mm. But it decreased to 40 mm for diluent size of 0.16 mm. Suitable sizes of silicon carbide were also used at the top and bottom of the reactor for supporting the catalyst bed and distributing the incoming and outgoing streams.

After the reactor was loaded with the catalyst and diluent, hydrogen was passed at the rate of 2500 ml/h. The temperature of the catalyst bed was increased from ambient to 175°C within 7 h. The reactor was then pressurized to 35 bar. The catalyst was then sulfided by following the procedure as suggested by the catalyst manufacturer and is described below. Initially, atmospheric gas oil containing desired concentration of dimethyl disulfide was passed at a higher rate (30 ml/h) for 3 h to fully wet the catalyst. After this initial period of soaking the catalyst bed, the flow rate of the atmospheric gas oil containing dimethyl disulfide was reduced to 15 ml/h. This flow rate was then maintained for a period of 24 h. During this period, the temperature was raised from 175 to 340°C using a predetermined temperature program. After this, the temperature of the reactor was maintained at 340°C and the gas oil was fed at the required rate. All the experiments in this study were carried out at a constant temperature of 340°C. After steady state was reached, the product samples were collected and analyzed for their sulfur contents at regular intervals of time using X-ray fluorescence equipment.

3. Results and discussion

The present investigation was carried out with a view to study the effect of diluent size and other process variables such as liquid hourly space velocity (LHSV) and hydrogen/gas oil volumetric ratio on the performance of a micro-reactor when the same is operated in up flow and down flow modes. No appreciable deactivation was observed during the experimental period. The catalyst activity was expressed in terms of apparent rate constant of the HDS reaction. The apparent rate constant was calculated from Eq. (1). Various authors [11,19,20] have established that the value of n is close to 1.5–1.7 for HDS of atmospheric gas oil. In the present study, the value of n is assumed to be 1.65. Similar value for n has been used by De Wind et al. [11] for HDS of gas oil over a commercial hydrotreating catalyst,

$$k = \frac{1}{n-1}\left[\frac{1}{S_{\mathrm{p}}^{n-1}} - \frac{1}{S_{\mathrm{f}}^{n-1}}\right]\mathrm{LHSV} \qquad (1)$$

where k is the apparent rate constant for hydrodesulfurization of atmospheric gas oil, h^{-1} (wt.%)$^{-0.65}$; n the order of hydrodesulfurisation reaction; S_p the sulfur in product, wt.%; S_f the sulfur in feed, wt.%; LHSV the liquid hourly space velocity, h^{-1}.

3.1. Effect of diluent size

The diluent size has a significant effect on the performance of a small-scale multiphase reactor. A change in the size of average particle diameter of the diluent brings change in the hydrodynamic characteristics of a reactor, which in turn influences the catalyst performance. It was established in our earlier studies [4] that a micro-scale trickle bed reactor using 5 ml of commercial catalyst diluted with equal volume of 0.19 mm of silicon carbide could predict the performance of a bench-scale unit containing 100 ml of catalyst. It was found in this study that the value of apparent rate constant for the HDS of atmospheric gas oil over a commercial catalyst at 340°C and a hydrogen/gas oil ratio of 500 l/l was about 6.4–6.6 h^{-1} (wt.%)$^{-0.65}$ for both micro-reactor and bench-scale reactor. Therefore, the down flow operation of a micro-reactor as described above was taken as reference for comparing the performances of the up flow mode of operation using different sizes of diluent and different levels of other process variables.

In order to study the effect of diluent size in a detailed and systematic way, the experiments were conducted at three levels of LHSV of 1.0, 3.0 and 7.0 h^{-1}.

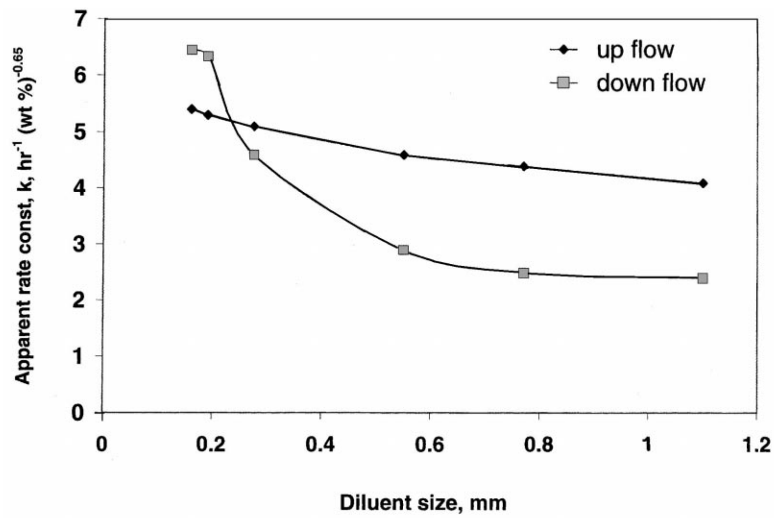


Fig. 2. Effect of diluent size on apparent rate constant of HDS for up flow and down flow modes of operation at an LHSV of $1.0\,h^{-1}$, temperature of 340°C and hydrogen/gas oil ratio of 500 l/l.

At each space velocity, the experiments were conducted for six different sizes of diluent (0.16–1.1 mm) while keeping temperature and the hydrogen/gas oil ratio constant at 340°C and 500 l/l, respectively, for all these sets of experiments. The results are shown in Figs. 2–4, respectively, for LHSV of 1.0, 3.0 and $7.0\,h^{-1}$.

The Figs. 2–4 indicate that the catalyst performance was dependent on the mode of operation of the reactor, the diluent size and the space velocity of gas oil. For example, when the reactor was operated in down flow mode at low flow rate of gas oil, corresponding to an LHSV of $1.0\,h^{-1}$, the apparent rate constant increased slowly with decrease in diluent size up to 0.55 mm

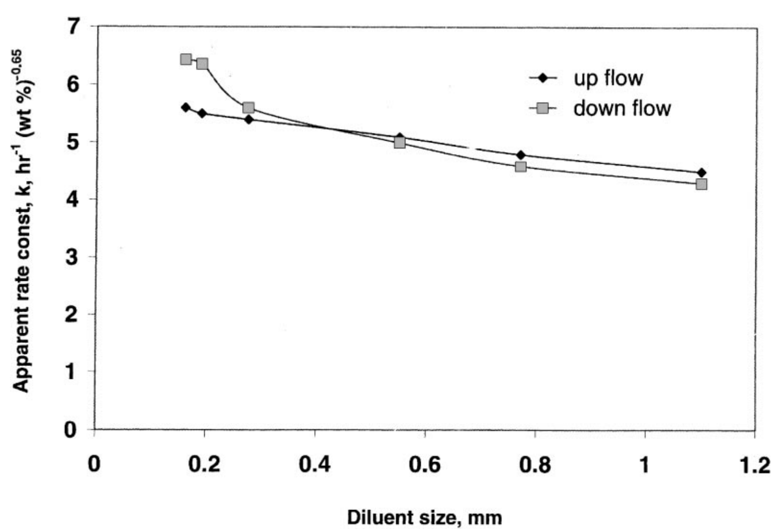


Fig. 3. Effect of diluent size on apparent rate constant of HDS for up flow and down flow modes of operation at an LHSV of $3.0\,h^{-1}$, temperature of 340°C and hydrogen/gas oil ratio of 500 l/l.

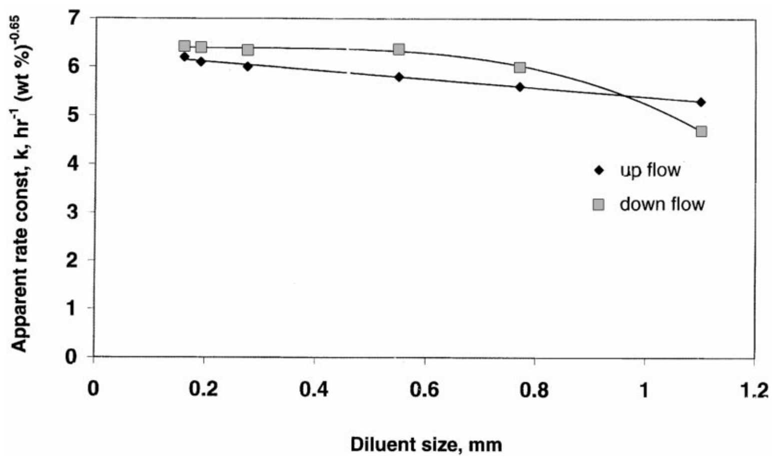


Fig. 4. Effect of diluent size on apparent rate constant of HDS for up flow and down flow modes of operation at an LHSV of 7.0 h^{-1}, temperature of 340°C and hydrogen/gas oil ratio of 500 l/l.

(see Fig. 2). Its value increased steadily up to a diluent size of 0.19 mm and then levels off with further decrease in diluent size. The superior performance of the down flow mode of operations representing the actual activity of the catalyst was noticed using diluent size of 0.19 mm and lower. The improvement in performance due to decrease in diluent size was because of the increased wetting of catalyst particles. It has been reported in literature [21] that as the hydroprocessing reactions are carried out at high pressure and in the presence of a high volumetric ratio of hydrogen/gas oil, the dissolved hydrogen in the gas oil is sufficient for removing sulfur present in gas oil. Therefore, the HDS of gas oil is a liquid limited reaction. For a liquid limited reaction, as the wetting of catalyst particle increases, the performance of the trickle bed reactor also increases [13].

The sharp increase in the performance of the catalyst for a diluent size of 0.19 mm could be attributed to the sharp increase in the liquid hold up of the catalyst bed due to the small size of diluent, which filled up the voids of the catalyst bed. The increased liquid hold up helped to achieve higher wetting of catalyst particles. The details of the liquid hold up studies using water as liquid phase and air as gaseous phase for different sizes of diluent has been discussed elsewhere [4].

In order to understand the increase in catalyst wetting with decrease in diluent size, an attempt has been made to calculate the wetting of catalyst particles in this micro-flow trickle bed reactor. Researchers have proposed different [22–24] correlation for calculating the wetting efficiency of catalyst in trickle bed reactors. The wetting efficiency of the catalyst particles for the present study has been calculated by correlation proposed by Al-Dahhan and Dudukovic [22] based on the values of modified Reynolds number for liquid, modified Galileo number and pressure drop per unit length of the catalyst bed. Their correlation though could prove the increase in wetting efficiency with decrease in diluent size (like wetting efficiency of 0.11 for 1.1 mm particle and 0.17 for 0.19 mm particle) but was unable to explain the complete wetting of catalyst for a diluent size of 0.19 mm and lower. This is perhaps due to the extremely low flow rate of liquid and lower values of liquid Reynolds number, Re_L(e.g., liquid superficial flow of 0.08 ml/min and Re_L of 3.2×10^{-4}) for the present study as compared to those values (e.g., liquid superficial flow rate of 0.42 ml/min and Re_L of about 10) based on which the correlation of Al-Dahhan and Dndukovic [22] were proposed and verified.

Similarly, the wetting efficiency for the present micro-reactor has been calculated using the correlation of El-Hiswani et al. [24] based on the values of liquid Reynolds number and Galileo number. Though, it showed comparatively higher wetting efficiency (0.48 for 0.19 mm size of diluent and 0.43 for 1.1 mm size of diluent) but still could not explain almost complete wetting of catalyst for a diluent size of 0.19 mm.

On the other hand, El-Hiswani et al. [24] has proposed a correlation (Eq. (2)) based on the values of dynamic liquid saturation. The wetting efficiency, η_{CE}, is given by

$$\eta_{\mathrm{CE}} = \omega_{\mathrm{d}}^{0.224} \tag{2}$$

where ω_{d} is the dynamic liquid saturation, liquid volume/void volume.

This correlation was also used to calculate the wetting efficiencies of the micro-scale trickle bed used in the present investigation. It was found that this correlation could explain both the increasing trend of wetting with decreasing diluent size as well as almost complete wetting (about 0.96) of catalyst for a diluent size of 0.19 mm and lower. The values of dynamic liquid saturation for the micro-scale trickle bed reactor used was taken from our earlier work [4]. Thus catalyst wetting efficiency for the entire range of diluent used in the present study can be calculated using the correlation of El-Hiswani (Eq. (2)). The performance of the reactor can then be calculated from the known values of wetting efficiency and kinetic parameters for the catalyst being tested using different models as proposed by earlier researchers [25,26].

Besides these, Sie [1,2] has used the criterion of wetting number (*W*) for checking even and uniform irrigation of catalyst by liquid in a micro-scale trickle bed reactor. We have also used this criterion for calculating the wetting number for our reactor for different sizes of diluent. The calculation shows that for diluent size of 1.1 mm, the catalyst particles are not properly irrigated whereas almost complete wetting is achieved for a diluent size of 0.19 mm and lower.

Besides increasing the catalyst wetting, the decrease in diluent size also helped in approaching plug flow behavior of the liquid. For understanding the effect of diluent size on the plug flow behavior of liquid, the values of Peclet number (*Pe*) were calculated for different sizes of diluent using the procedure as proposed by earlier researchers [2,6]. Based on their correlation and assumptions, it was found that the value of *Pe* corresponding to negligible axial backmixing of liquid for about 70% conversion in a micro-scale trickle bed reactor should be above 15. It was found that the values of *Pe* for a liquid flow rate of 5 ml/h (corresponding to LHSV of 1.0 h^{-1}) and for a diluent size of 1.1 mm was only 3 and thus could not satisfy the criterion of negligible axial dispersion. Whereas, the value of *Pe* increased with decrease in diluent size and reached close to about 15 for a diluent size of 0.19 mm and hence could meet the condition of plug flow behavior of liquid. Thus, the use of 0.19 mm and lower size of diluent increased wetting of catalyst as well as brought plug flow behavior of liquid in the down flow mode of operation and hence superior performance of the reactor was noticed.

When the reactor was operated in the up flow mode with an LHSV of 1.0 h^{-1}, a decrease in diluent size increased the values of the apparent rate constant at a slower rate (see Fig. 2). Since the reaction is liquid limited one, as discussed earlier, comparatively lesser availability of hydrogen in the up flow mode would not affect the performance of the reactor. In the up flow mode, the wetting of catalyst is almost complete. But the performance of the reactor at this mode of operation is lower at larger size of diluent (about 1.1 mm) possibly because of the presence of significant axial backmixing of liquid. But as the diluent size was decreased, the axial dispersion reduces and the performance of the reactor improved. The reduction of axial dispersion with the decrease in diluent size in the up flow mode of operation has been observed in our earlier study [16]. In contrast to the down flow mode of operation, the presence of axial backmixing could not be completely eliminated in up flow mode of operation even for a diluent size of 0.16 mm. Hence, the up flow mode of operation gave slightly inferior performance for an LHSV of 1.0 h^{-1} even for a diluent size of 0.16 mm. When the testing of catalyst was carried out using a diluent size of 0.25 mm and above, apparently better performance of the up flow mode compared to that of down flow mode was observed. Because, at this size of diluent, as discussed above, the wetting of catalyst in the down flow mode was not complete. However, the up flow mode of operation also could not represent the real performance of the commercial catalyst (i.e. corresponding to an apparent rate constant of about 6.4–6.6 h^{-1} $(\mathrm{wt.\%})^{-0.65}$) because of the presence of significant amount of axial backmixing of liquid for a diluent size of 0.25 mm and higher.

The effect of diluent size on the apparent rate constant for both the modes of operation at slightly higher flow rate of gas oil, corresponding to an LHSV of 3.0 h^{-1}, is shown in Fig. 3. The performances of the two modes of operation were almost equal and also showed similar trend of improvement up to a particle size of about 0.25 mm. Since the flow rate was higher, the liquid–catalyst contact in the down flow mode was better as compared to the earlier case (corresponding to LHSV of $1.0\,h^{-1}$) but still could not achieve complete wetting of catalyst for diluent size of 0.25 and higher. Thus the difference between the two modes of operation in this range of diluent reduced as compared to the case of LHSV of $1.0\,h^{-1}$. However, both the modes of operation could not show the real performance of the catalyst up to a diluent size of about 0.25 mm because the down flow mode of operation could not provide complete wetting of catalyst whereas the up flow mode of operation could not completely eliminate axial backmixing of liquid. But when the diluent size was decreased to 0.19 mm and lower, complete wetting of catalyst as well as almost plug flow of liquid was achieved in the down flow mode. On the other hand, the reduction of diluent size though decreased axial dispersion to some extent but could not eliminate it completely in the up flow mode of operation. Thus in this range of diluent size (0.19 mm and lower), the down flow mode of operation showed a better performance as compared to that with up flow mode.

The change in apparent rate constant with the change in diluent size for two modes of operation corresponding to an LHSV of $7.0\,h^{-1}$ is shown in Fig. 4. This figure indicated that the performance of the down flow mode of operation was slightly superior to that of up flow mode of operation for the diluent size less than 0.9 mm. As the flow rate of gas oil was higher, almost complete wetting of catalyst and plug flow behavior of liquid was achieved even for diluent size of up to 0.9 mm. But the up flow mode of operation had some axial backmixing of liquid. On the other hand, for a diluent size of higher than 0.9 mm, the wetting of catalyst in the down flow mode was not complete and hence it showed inferior performance as compared to that of up flow mode of operation.

3.2. Effect of liquid hourly space velocity

The effect of LHSV on the performance of the catalyst was carried out for three levels of diluent size of 0.77, 0.25 and 0.19 mm. The LHSV was varied from 1.0 to $7.0\,h^{-1}$ while keeping temperature and hydrogen/gas oil ratio constant at 340°C and 500 l/l, respectively. The results are plotted in Figs. 5–7. The results showed that for a diluent size of 0.77 mm, the apparent rate constant increased with the increase in space velocity for both the modes of operation (see Fig. 5). In the down flow mode of operation, the apparent rate constant increased from 2.5 to $6.1\,h^{-1}$ $(wt.\%)^{-0.65}$ when LHSV was increased from 1.0 to $7.0\,h^{-1}$. Since the diluent size was higher, the down flow mode was

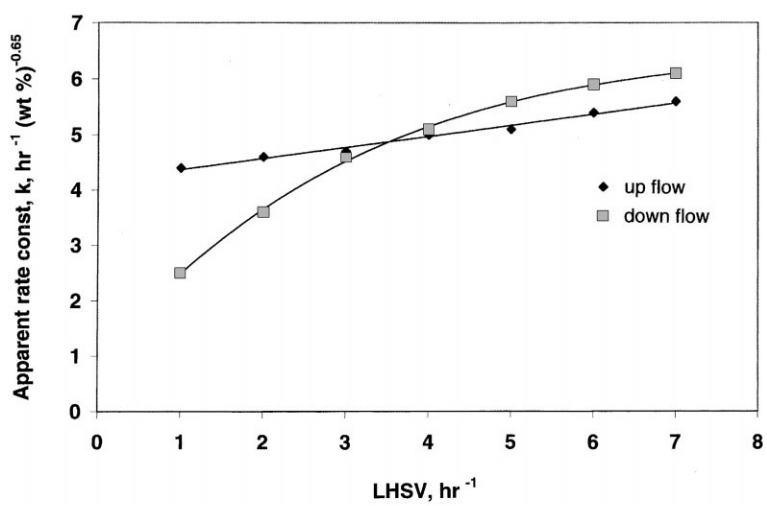


Fig. 5. Effect of LHSV on apparent rate constant of HDS for up flow and down flow modes of operation for a diluent size of 0.77 mm at a temperature of 340°C and a hydrogen/gas oil ratio of 500 l/l.

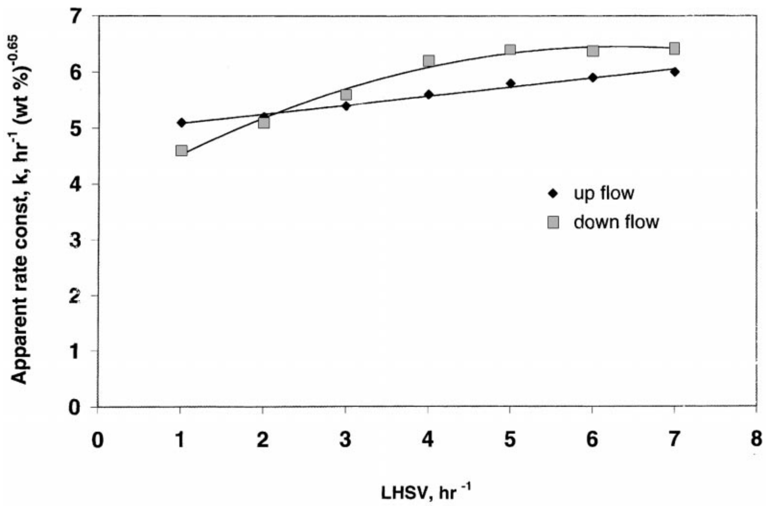


Fig. 6. Effect of LHSV on apparent rate constant of HDS for up flow and down flow modes of operation for a diluent size of 0.25 mm at a temperature of 340°C and a hydrogen/gas oil ratio of 500 l/l.

suffering from both incomplete wetting of catalyst as well as non-ideal flow of liquid at lower levels of space velocities. But as the LHSV is increased, the liquid flow rate is also increased. The increase in liquid flow rate increased liquid hold up which in turn increased the wetting of catalyst. Higher wetting of catalyst was achieved for this size of diluent (0.77 mm) for flow rates corresponding to LHSV of about $7.0\,h^{-1}$. This higher flow rate of gas oil also reduced the axial backmixing of liquid. The figure also showed that for up flow mode of operation, the value of apparent rate constant increased at a slower rate with increase in LHSV due to reduction in axial backmixing at higher liquid flow rate (i.e. due to higher LHSV). Therefore, the use of both down flow and up flow mode of operation could not produce reliable results when they were

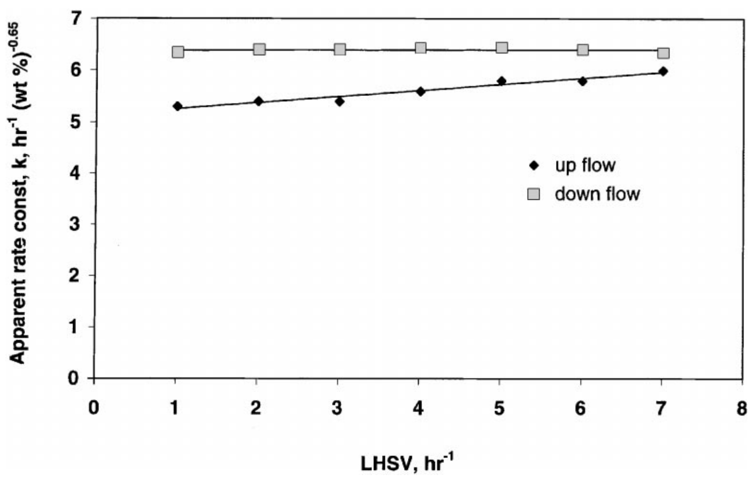


Fig. 7. Effect of LHSV on apparent rate constant of HDS for up flow and down flow modes of operation for a diluent size of 0.19 mm at a temperature of 340°C and a hydrogen/gas oil ratio of 500 l/l.

operated at lower space velocities (corresponding to LHSV of 1–4 h^{-1}). The up flow mode of operation apparently showed superior performance as compared to that with the down flow mode of operation at low space velocities and still suffered from the drawbacks of liquid backmixing.

The effect of LHSV for a diluent size of 0.25 mm is shown in Fig. 6. In this case, for down flow mode of operation, the effect of LHSV on apparent rate constant was relatively lower as compared to that with higher size of diluent (0.77 mm). Also, the values of the rate constant almost leveled off at a slightly lower LHSV of 5.0 h^{-1} as compared to earlier case. Thus for LHSV of 5.0 h^{-1} and lower, the catalyst was not properly wetted for 0.25 mm size of diluent. But almost complete wetting of catalyst was achieved for LHSV of about 6.0 h^{-1} and higher. For the up flow mode of operation, the effect of LHSV on the apparent rate constant was low.

The change in apparent rate constant with the change in LHSV for a diluent size of 0.19 mm is shown in Fig. 7. In this case, the performance of the catalyst in the down flow mode of operation was independent of space velocity. Thus, almost complete wetting of catalyst and plug flow behavior of liquid was achieved for 0.19 mm size of diluent even for lower LHSV of 1.0 h^{-1}. The values of the rate constant were higher for this mode of operation as opposed to the up flow mode. The apparent rate constant for up flow mode of operation increased to some extent with LHSV. Thus, even the use of small size of diluent could not overcome the limitations of a micro-reactor in its up flow mode of operation. This might be due to the presence of significant axial backmixing in such small reactors, which was reduced with increase in space velocity of gas oil. This mode of operation can be used only at very high LHSV (about 6.0 h^{-1} and above) to produce meaningful data even when the reactor is packed with catalyst and 0.19 mm size of diluent.

Thus it is evident from the present study that almost complete wetting of catalyst as well as minimum deviation from plug flow behavior of liquid can also be achieved in a up flow micro-reactor but the experiments need to be conducted at very higher values of LHSV. The use of higher LHSV though could scale down the commercial reactor in terms of hydrodynamic characteristics but the conversion in such a case would be lower because of shorter residence time. The situation will be comparable to that what happens in the topmost part of the catalyst bed of the commercial reactor. Though it is possible to describe the conversion of an integral reactor, however, this will require a substantial experimental effort and may therefore be impractical in most cases [2].

On the other hand, the present study also reveals that full wetting of catalyst and almost plug flow of liquid can be achieved in the down flow mode of operation even at a very low LHSV of 1.0 h^{-1} by diluting the catalyst bed with diluent size of 0.19 mm and lower. The use of lower space velocity is of importance since it represents the contact time of real commercial trickle bed reactor used for the HDS of gas oil. The data generated in this way during testing of newer catalyst as well as alternative feedstock for an established process can be directly compared to those, which would be obtained in the commercial reactor. Therefore, it is better to follow this methodology of using diluent size of 0.19 mm and lower in a micro-scale trickle bed reactor where scaling done would work by comparing it to real conditions.

So far as scale up is concerned, the data generated in this way (using a micro-scale trickle bed reactor and 0.19 mm of diluent in the catalyst bed) avoids number of complications. Generally, fluid hydrodynamics and reaction kinetics are very much interrelated in a trickle bed reactor and hence their effects on conversion are inseparable [2]. Thus, a suitable model incorporating different aspects such as axial dispersion of liquid, liquid–catalyst wetting efficiency, reaction kinetics and intraparticle diffusion is used for scale up of trickle bed reactors [25–27]. But in the present study, the hydrodynamics and kinetics were decoupled by the use of an appropriate size of diluent in the micro-scale trickle bed reactor. In such a system, the hydrodynamics of the reactor is mainly controlled by the small size of diluent [2]. Also, the flow of liquid closely approached plug type and the wetting of catalyst was almost complete. In addition, as the catalyst was tested in the form as used in commercial operation, lots of modeling could be avoided to account for the intraparticle diffusional resistance [3]. Thus the data generated in such a system could be used directly using a very simple model.

Though it was reported in earlier literature that smaller size of diluent could eliminate all the drawbacks such as wall effect, incomplete catalyst wetting and liquid backmixing present in small-scale trickle bed reactor, but information regarding the effect of diluent size on these phenomena and their relative significance on the comparative performance of a micro-scale fixed bed reactor in its up flow and down flow mode of operation was not available in open literature. The present study focussed light in this direction.

3.3. Effect of hydrogen/gas oil ratio

The hydrogen/gas oil ratio also influences the performances of multiphase hydroprocessing reactors. The effect of hydrogen/gas oil ratio on apparent rate constant for HDS was studied using different sizes of diluent (0.19–0.77 mm) for both up flow and down flow modes at a constant temperature of 340°C and an LHSV of 1.0 h^{-1}. The results for up flow and down flow modes are plotted in Figs. 8 and 9, respectively.

For up flow mode of operation (see Fig. 8), the values of apparent rate constant remained nearly constant up to a hydrogen/gas oil ratio of about 300 l/l for all three sizes of diluent. When the hydrogen/gas oil ratio was increased further, the values of apparent rate constant started decreasing for all the sizes of diluent. Interestingly, the rate of decrease of apparent rate constant with hydrogen/gas oil ratio increased with increasing diluent size. With the increase in hydrogen/gas oil ratio, the flow of hydrogen was increased. The increased flow of hydrogen caused turbulence and stirring and hence mixing in the liquid phase which resulted in higher backmixing of liquid inside the catalyst bed. This backmixing caused deviation of the liquid flow from plug type to mixed type. As the diluent size is increased, the void space in the catalyst bed was increased and as a result of this the backmixing of liquid was more prominent for higher size of diluent and higher hydrogen/gas oil ratio. The increase in axial backmixing with increasing gas/liquid ratio for higher size of diluent have also been reported for bench-scale up flow fixed bed reactor by earlier workers [16,28].

When the reactor was operated in the down flow mode, the effect of hydrogen/gas oil ratio on apparent rate constant were somewhat different (see Fig. 9). In this case, the values of apparent rate constant increased somewhat with variation of hydrogen/gas oil ratio from 200 to 400 l/l, and then remained almost constant with further increase in the values of this ratio. The initial positive dependencies of apparent rate constant on hydrogen/gas oil ratio might be due to the effect of hydrogen partial pressure on HDS reaction. Besides increasing hydrogen partial pressure, the increased hydrogen/gas oil ratio also reduced the concentration of hydrogen sulfide inside the reactor. It is well known that the high concentration of hydrogen sulfide in the catalyst bed inhibits the rate of gas oil

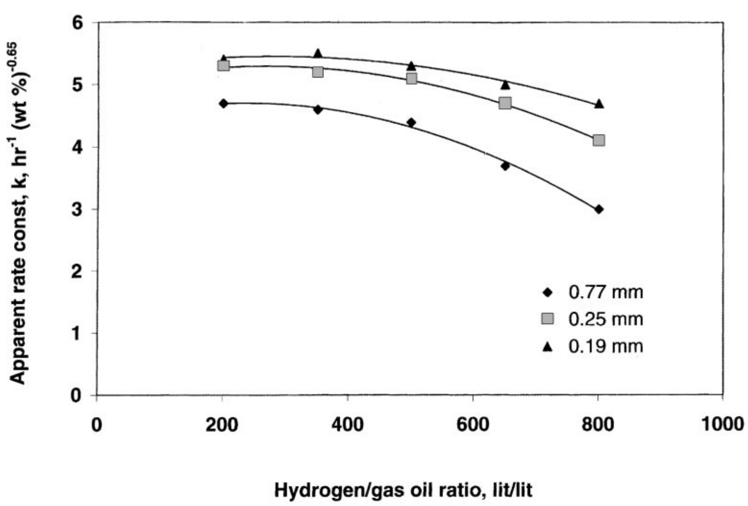


Fig. 8. Effect of hydrogen/gas oil ratio on apparent rate constant of HDS for different sizes of diluent for up flow mode of operation at 340°C and an LHSV of 1.0 h^{-1}.

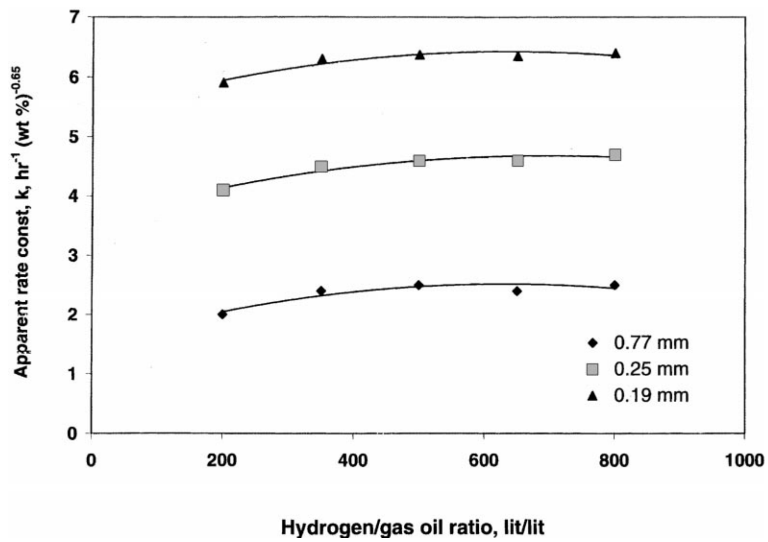


Fig. 9. Effect of hydrogen/gas oil ratio on apparent rate constant of HDS for different sizes of diluent at down flow mode of operation at 340°C and an LHSV of $1.0\,h^{-1}$.

HDS reaction. Thus the reduced concentration of hydrogen sulfide due to the increased hydrogen/gas oil ratio helped to have higher values of apparent rate constant. Korsten and Hoffmann [29] have also reported the increase in sulfur conversion by increasing the hydrogen/oil ratio. It is obvious from the data in Fig. 9 that smaller diluent could increase the reaction rate significantly.

4. Conclusions

The performances of a micro-scale multiphase fixed bed reactor in its up flow and down flow modes of operation was dependent on the size of diluent used along with the catalyst, level of space velocities of gas oil and the hydrogen/gas oil ratio. Up flow mode of operation using higher size of diluent (0.77 mm) in combination with lower space velocities of gas oil showed comparatively better performance than that with down flow mode of operation. However, use of small size of diluent (0.19 mm) gave better reactor performance with down flow mode of operation. The data generated in such case could represent the true activity of the catalyst. The differences between the performances in these two modes of operation at higher space velocities when smaller (0.19 mm) size of diluent was used. The reactor performance for up flow mode of operation was dependent on hydrogen/gas oil ratio whereas for down flow mode, it was almost independent on this ratio.

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