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The mixing aspects of NiMo and CoMo hydrotreating catalysts in ebullated-bed reactors

Ezra K.T. Kam[a,*], Mohammad H. Al-Mashan[b], Homoud Al-Azmi[b]

[a]*Petroleum Technology Department, Kuwait Institute for Scientific Research, Kuwait City, Kuwait*
[b]*Kuwait National Petroleum Company, Shuaiba Refinery, Ahmadi, Kuwait*

Abstract

Recently, the Shuaiba Refinery of Kuwait National Petroleum Company (KNPC) conducted a test run using mixed NiMo/CoMo catalysts in one of the H–Oil reactors to verify the specifications of a CoMo catalyst. However, reduced unit performance and unstable operation were experienced. This led to the unit shut-down and process time loss. To search the causes for the different reactor behaviours, a research work was undertaken in the Petroleum Technology Department at Kuwait Institute for Scientific Research (KISR). It had found that the hydrodynamics of the mixed NiMo/CoMo and CoMo catalysts in a cold flow ebullated-bed reactor (EBR) were very different than NiMo catalyst alone. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: H–Oil unit; Mixing; Hydrotreating catalyst; Ebullated-bed; Catalyst carry-over

1. Introduction

Owing to the diminishing availability of preferred feedstocks and the inability to project long-term market requirements forecasting, the economic advantage to any refining operation is to choose flexible refining processes [1]. The H–Oil process is one of these hydrotreating processes which is capable to maximize the throughput of heavy feedstocks to produce environmental-friendly lighter products. The unit is designed to operate at high severity to produce maximum distillates and minimum fuel oils. The H–Oil installation [2] in Shuaiba Refinery, KNPC has been in operation since 1968 and is one of the three surviving first generation H–Oil units in the world. It is a very important operation in Shuaiba Refinery since it is the only unit which can process the crude vacuum tower bottoms continuously without major operation problems.

The heart of the H–Oil unit is the EBR. The reactions involve hydrotreating and hydrocracking vacuum residues in the reactor in which heavy oil feed stock, hydrogen and extrudate catalyst particles are brought together in constant motion and contact. The feed is constituted of a mixture of very large hydrocarbon molecules, metals, sulphur and many other undesirable materials. Catalysts are suspended in the heavy oil and are ebullated by a constant flow of liquid and gas from the bottom of the reactor. The mixture of the gas (make-up and recycle hydrogen) and liquid (feed and recycle oils) reactants enters the reactor plenum chamber and is well mixed through the specially designed gas/liquid mixer, spargers and catalyst support grid plate. A homogeneous environment

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[*] Corresponding author.

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is created to hydrotreat and hydrocrack the heavy feedstocks. Operating in this ebullated state results in low pressure drop and temperature spread in the EBR. The liquid recycle rate can be adjusted by varying the ebullation pump speed. Fresh catalysts can be added and spent catalysts withdrawn without disturbing the process operation while the catalyst activity and selectivity are maintained. The catalyst replacement rate can be adjusted to suit feed properties, or product slate and quality requirements. Lighter products are further separated and taken to a separation train. The unconverted heavy oils are recirculated back to the reactor with a small amount of diluent to improve the fluidity, overall conversion [3]. Catalysts may have been changed several times following the recommendations of the licenser in the 30 years operation. However, only a single catalyst type has been used. No attempt has never been made to use mixed catalysts.

2. Problems from mixed NiMo and CoMo catalysts

In April 1994, the two H–Oil trains in Shuaiba Refinery were back on stream after repairing all the damages from the Gulf War. During the start-up, both fresh and spent NiMo catalysts were used in the H–Oil unit. However, as a step to implement the waste-minimization drive in the refinery, as well as to verify the specifications of a CoMo catalyst, a mixture of NiMo and CoMo fresh catalysts was added to Train A H–Oil unit during the daily catalyst addition. Although the amount of CoMo catalyst was restricted to a predetermined ratio with NiMo, different reactor performance was observed. The catalyst addition rate, hydrogen consumption, catalyst spread temperature and exotherms were higher. The catalyst bed level in the EBR was unstable and conversion was lower. Foaming occurred in the preflash vessel (07V102). Moreover, considerable amount of catalyst particles and fines were found in the downstream flow circuits. Lower efficiencies in the process equipment such as the hydrogen gas preheater (07E101), ebullation pump (07P102) and recycle hydrogen compressor (07C101) were noted. Table 1 shows some H–Oil process data in the period using mixed catalysts.

The modification in the reactor performance cannot be explained from the reaction kinetics alone since the bed expansion and heat and mass transfer characteristics also change the chemical compositions and physical properties of the ebullation media, which result different hydrodynamic behaviours [4–7]. Table 2 shows the physical properties of the catalyst characterizations for both catalysts obtained from the manufacturer and confirmed by two international catalyst testing facilities. No obvious difference are observed apart from their colours. Before attempting the more complex reaction kinetics, it is advantageous to look into the mixing and hydrodynamic aspects of the combined CoMo/NiMo catalysts. However, it is impossible to observe any irregularities in transport phenomena or hydrodynamic aspects in the commer-

Table 1
H–Oil process conditions using mixed catalysts

Day	Oil feed	Diluent feed	Catalyst addition rate	Catalyst average temperature	Conversion (%)
1	Base	Base	Base[a]	Base	56
2	0.96	1	0.138	0.991	53
3	0.96	1	0.184	0.991	42
4	0.96	1	0.129	0.991	42
5	0.96	1	0.129	0.997	42
6	0.96	1	0.138	0.991	49
7	0.96	1	0.138	0.997	49
8	0.96	0.667	0.129	1.001	52
9	1	0.667	0.115	1.001	50
10	1.04	1	0.119	1.003	49
11	1.04	1	0.119	1.003	49
12	1.04	1	0.119	1.009	49

[a] The base for catalyst loading during start-up is 50% fresh +50% spent catalysts.

Table 2
Physical properties of NiMo and CoMo catalysts

Physical property	NiMo	CoMo
Colour	Green	Blue
Mean particle length (mm)	5.2	4.7
Fine content (<40 mesh) (wt%)	0.03	0.03
Particle diameter (mm)	0.97	1.038
Bulk density (compacted) (lb/ft^3)	34.8	35.3
Average crush strength (lb/mm)	2.1	1.9
Attrition loss (wt%)	0.9	0.9
Surface area (m^2/gm)	310.0	289.0
Pore volume (H_2O adsorption) (cm^3/gm)	0.81	0.81
Average oil penetration (% dia.)	88.0	91.0

cial unit. They have to be investigated in a transparent cold-flow EBR.

3. Hydrodynamic study in a cold-flow EBR

Studies of mixing and stratification of solid particles in multiphase reactors have been reported for different size and density particles [6,8,9]. In this study, attempt is made to study the mixing aspects of two hydrotreating catalysts with similar physical properties in a cold-flow EBR. Some observations on catalyst mixing exhibiting different behaviours than that in a normal ebullated-bed operation are noted. However, only the results relevant to the phenomena experienced in the refinery's mixed catalyst operation will be reported with some qualitative explanations.

3.1. The cold-flow EBR

Briefly, the reactor consists several short and tall glass columns and metal spools with all internal diameter at 0.15 m, which accumulated a total height of 4.5 m. The size of piping network for liquid flow is 0.0375 m and that of the gas flow is 0.0125 m. Two pumps and a compressor are used for liquid and gas feeds transportation, and liquid ebullation. Air, H–Oil hydrotreating catalysts and heavy kerosene are used as gas, solid and liquid phase materials. A schematic of

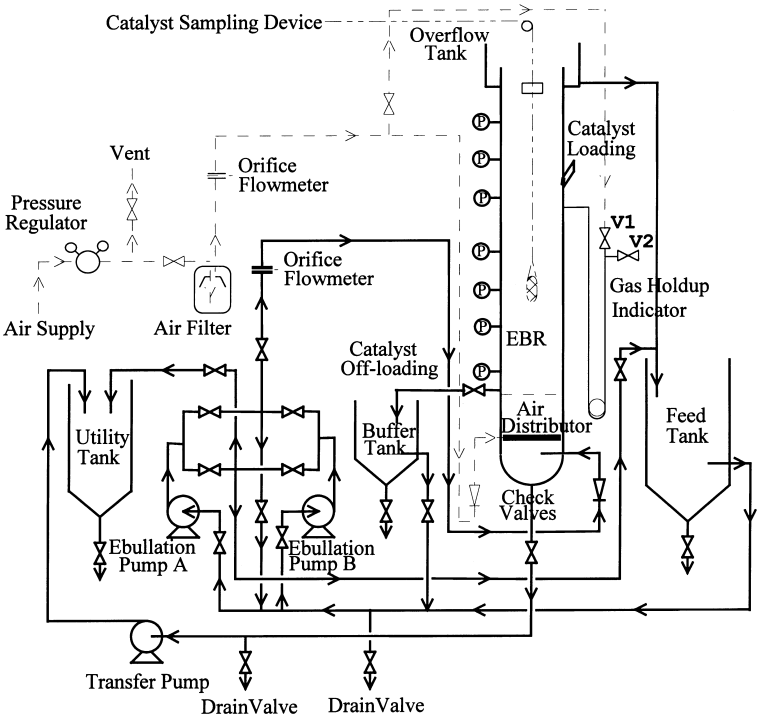

Fig. 1. A schematic flow diagram of the cold-flow ebullated-bed reactor.

the cold-flow EBR [10] is shown in Fig. 1. There were two special features in the experimental set-up, namely, the catalyst sampling device and the gas holdup indicator. The former one was used to obtain catalyst samples at any reactor depth during ebullation for catalyst stratification determination. The gas holdup indicator was a closed end manometer using the same liquid medium to estimate the gas holdup. The liquid levels in the manometer were calibrated with known volumes of liquid in the reactor. The initial manometer level had to be set to a fixed height determined from the calibration and this could be done by manipulating V1, the compressed air intake valve and V2, the air release valve as shown in Fig. 1. Hence the gas holdup could be read directly after stopping both the gas and liquid feeds simultaneously.

Table 3
Process parameter ranges

Parameters	Range
Gas superficial flow rate U_g (m/s)	0–0.135
Liquid superficial flow rate U_l (m/s)	0.02–0.08
Catalyst loading W (kg)	5
NiMo/CoMo (wt%)	0–100

Table 4
Properties of heavy kerosene

Property	Value
Boiling point (K)	510
Density (kg/m^3) at 298 K	815
Viscosity (Pa s) at 298 K	1.986

3.2. Process parameters

In this study, the pressure and temperature were kept in ambient conditions. The main process parameters to be manipulated were liquid and gas flow rates, and one level of catalyst loading at 5 kg. However, the proportion between NiMo and CoMo catalysts varied. The loaded catalyst gave a static bed height, H_0 of 0.5 m. The ranges of process parameters are shown in Table 3. Their effects on bed expansion, pressure, phase holdups and axial catalyst distribution of the solid mixture were the subjects in this investigation. Table 4 shows some properties of the heavy kerosene.

4. Results and discussion

The dynamic pressure profiles for CoMo catalyst at U_l between 0.0235 to 0.0705 m/s and U_g=0.0227 m/s are shown in Fig. 2. All the profiles follow the same characteristics but with slight difference at the interface between the dense phase and free-board region. The pressure increases as U_l. The thick solid line

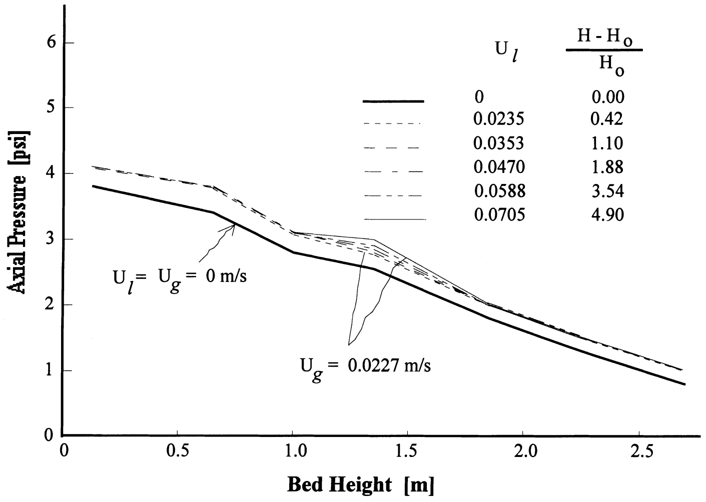

Fig. 2. Axial pressure profiles of ebullated CoMo catalyst bed.

shows the static pressure profile where U_l and $U_g = 0$. Similar trends are found for the mixed NiMo and CoMo as well as NiMo catalysts but at a slightly higher magnitude.

As mentioned before, the gas holdup, ϵ_g was obtained from the gas holdup indicator. The solid holdup, ϵ_s was calculated by the following expression:

$$\epsilon_s = \frac{W}{\rho_s A H}, \tag{1}$$

where W is the catalyst loading, A the cross-section area of the column and H is the height of bed expansion. The results were then compared with a number of empirical correlations from which the modified Begovich and Watson correlation of ϵ_{BW} [11] appeared to fit very well. The correlation is expressed as

$$\epsilon_s = 1 - \epsilon_{BW} = 1 - \Phi_s 3.93 U_l^{0.271} U_g^{0.041} \times (\rho_s - \rho_l)^{-0.316} d_e^{-0.268} \mu_l^{0.055} D_c^{-0.033}, \tag{2}$$

where Φ_s is the shape factor, d_e the effective particle diameter and D_c is the column diameter. Hence the liquid holdup, ϵ_l was calculated by

$$\epsilon_l = 1 - \epsilon_g - \epsilon_s. \tag{3}$$

From the above determination, the gas holdup from CoMo catalyst was higher than the mixed CoMo/NiMo catalysts which in turn was more than NiMo catalyst. Hence the pressure profiles from CoMo were lower than the others. The additional gas in the expanded bed could explain the foaming formation and higher catalyst average temperature in the H–Oil reactor. More hydrogen gas should enhance mass transfer for the exothermic hydrocracking and hydrotreating reactions to produce more lighter products and hence the higher temperature. On the other hand, the extra bubbles of light hydrocarbons produced from the hydrocracking reactions could facilitate the foam formation, which could carry away smaller catalyst particles and fines. Subsequently, the readings from the catalyst level detectors of the H–Oil EBR were disturbed [12,13]. Furthermore, the carry-over catalysts and fines proceeded onto the downstream pipework and equipment which surfaces would be fouled and hence reduced in efficiencies.

The effect of U_l and U_g on bed expansion is shown in Fig. 3. The effect of U_l was more than that of U_g. Catalyst carry-over occurred when U_l reaches 0.0705 m/s even with U_g=0. A slight bed contraction is observed when air was introduced into the ebullated-bed at U_g lower than 0.076 m/s. Such behaviour was also observed by other workers [14,15]. However, when U_g increased thereafter, bed expansion proceeded. Similar effects were found in the mixed NiMo/CoMo catalyst. In the case of NiMo catalyst, the bed expansion was comparatively lower than that

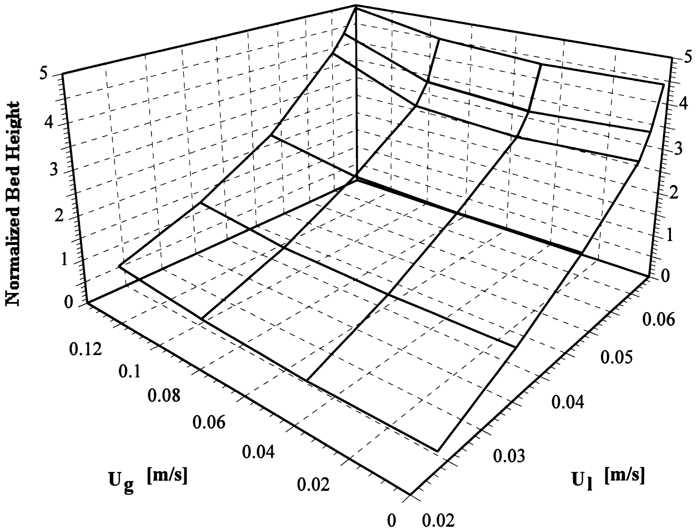

Fig. 3. Effect of U_l and U_g on CoMo catalyst bed expansion.

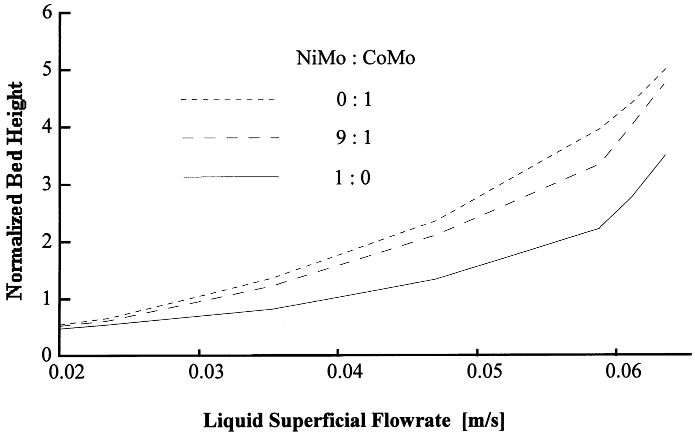

Fig. 4. Comparison of normalized bed height for the three catalyst mixtures.

of the mixed and CoMo catalysts, Fig. 4. No catalyst carry-over until U_l reached 0.0819 m/s. A comparison of the normalized bed expansion of the NiMo, CoMo and mixed NiMo/CoMo catalysts at U_l ranging between 0.0235 and 0.06345 m/s and at U_g=0.1363 m/s is shown in Fig. 4. The expended CoMo catalyst bed was considerably higher than that of the NiMo catalyst. Even the bed levels of the mixed catalyst, which consisted only 10% of CoMo, were also well above the NiMo values. This was due to the mean particle length of the two catalysts. CoMo (4.7 mm) was smaller than NiMo (5.2 mm). Thus CoMo had a slightly higher bulk density since smaller particles could be packed more compactly, as shown in Table 2.

One interesting observation in the axial solid distribution of NiMo and CoMo catalysts in the expanded bed was that their mixing was not homogeneous and the ratio was different than the original NiMo/CoMo

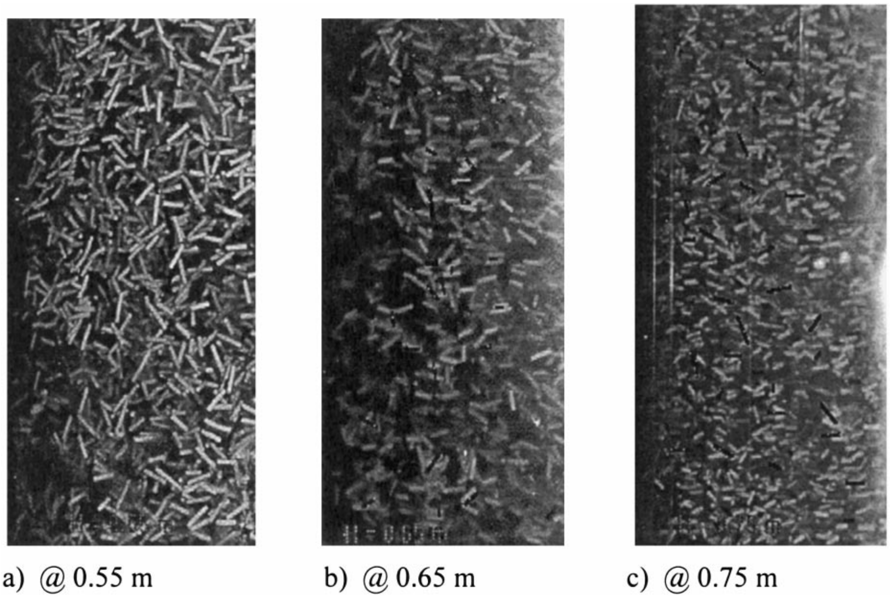
a) @ 0.55 m b) @ 0.65 m c) @ 0.75 m

Fig. 5. Snap shots of catalyst distribution at three bed heights.

Table 5
Comparison of CoMo concentration in NiMo at three bed heights

Axial position from grid (m)	NiMo catalyst (%)	CoMo catalyst (%)	Mean particle length (mm)
0.55	91.4	8.6	5.4
0.65	90.9	9.1	5.1
0.75	87.2	12.8	4.6

mixing ratio from 9 to 1. More CoMo catalyst particles in the upper part than the lower region of the reactor was found. Three snap shots were taken from three positions at 0.55, 0.65 and 0.75 m from the grid as shown in Fig. 5(a)–(c), respectively. The superficial velocities of the liquid and gas were 0.0235 and 0.1363 m/s, respectively. Apparently, the concentration of CoMo catalyst increased as the bed height. This was confirmed by analysing the solid samples taken from the reactor using the catalyst sampling device as shown in Fig. 1. Table 5 shows the wt% of catalyst particles from each sample. However, the mean particle lengths reduced and CoMo catalyst concentration increased as the bed height increased.

5. Concluding remarks

The physical appearance of both NiMo and CoMo catalysts is very similar apart from their colours. This is confirmed by the catalyst characterization analyses on their physical properties. Even their hydrotreating activity indexes, supplied by both the manufacturer and international testing facilities, are very close. However, when they are tested in a cold flow ebullated-bed reactor, difference in hydrodynamics is reviewed. The CoMo catalyst which has a slightly smaller mean particle length but slightly larger diameter than NiMo, exhibits lower axial pressure profiles, higher gas holdup and bed expansion. This seems to be a good catalyst for the H–Oil hydrotreater using ebullated-bed technology. However, the reactor performance was found to be not matching its specifications from the test run in a commercial H–Oil unit. And some process problems were also experienced.

Since the test run in the commercial unit has lasted less than 10 days, catalyst attrition will not be very pronounced [7]. However, the attrition effect has been scheduled in the our next phase of the research work in the cold-flow EBR. It is no doubt that the catalyst attrition will add an extra dimension to the hydrodynamic behaviours and H–Oil unit operation problems.

Some final thoughts on the catalyst testing procedures in the commercial environment in which fixed beds and continuous flow stirred tank reactors (CFSTR) are generally used. Do the test results really represent the true situation in fluidized-bed reactors or EBR? Are the existing catalyst characterization procedures adequate to analyse the physical properties of catalysts which are used in fluidized-bed reactors or EBR? Should hydrodynamic behaviour analyses be included in catalyst characterization procedures for such catalysts?

6. Nomenclature

A	column cross-section area (m^2)
d_e	effective particle diameter (m)
D_c	column diameter (m)
H, H_0	expanded and static bed heights (m)
U_l, U_g	superficial liquid and gas velocities (m/s)
W	catalyst loading (kg)

Greek Symbols

ϵ_{BW}	Begovich and Watson correlation [11]
ϵ_g, ϵ_l, ϵ_s	gas, liquid and solid holdups
Φ_s	shape factor
ρ_l,ρ_s	liquid and solid densities (kg/m^3)
μ_l	liquid viscosity (Pa s)

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