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Modeling on scale-up of an ebullated-bed reactor for the hydroprocessing of vacuum residuum

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ABSTRACT

An ebullated reactor for heavy vacuum residuum (VR) hydroprocessing under a high hydrogen pressure of 15 MPa and a high temperature of 425 °C was simulated using a two-bubble class model. To account for the influence of the strong back-mixing of the liquid phase and the non-uniform distribution of the catalyst on the performance of the reactor, axial dispersions for the two phases are incorporated into the plug flow model. Based on the bench-scale experiments conducted in a reactor of 0.036 m ID and 2.0 m in height, scaling up of the reactor to an annual processing capacity of 1.0 million t of VR was proposed. To determine the optimal reactor dimension, a reactor of 3 m ID and 36.86 m in height and one with 4.5 m ID and 16.38 m in height are compared. It shows although the two reactors give very similar conversions as a CSTR reactor, the 3 m ID reactor shows a higher gas–liquid mass transfer coefficient and a larger slurry circulation velocity than the 4.5 m ID one, which suggests the 3 m ID reactor is a better choice in the scale up.

1. Introduction

Ebullated bed process has been proven as one of the most efficient way of handling petroleum bottoms and other heavy hydrocarbons for hydrodesulfurization, hydrodemetallization, and Conradson carbon reduction since the 1960s. In recent years, the use of ebullated-bed reactors (EBR) has renewed importance due to the sharply increase of heavy feedstocks delivered to refineries and eventually to the hydrocracking process. These heavier feeds are difficult to be handled with conventional technologies, due to the high contents of sulfur, nitrogen, metals (nickel and vanadium), and asphaltenes, which have much negative impact on catalyst activity and stability. Over the years, a variety of EBR methods for upgrading of residuum have been suggested, e.g., EBR in series with interstage gas/liquid separation has been implemented to concentrate the liquid phase entering to the following reactor, while in some cases the feed to the second stage is blended with an aromatic solvent and/or residuum, sometimes the unconverted residuum may be blended with gasoil to improve the conversion of VR [1].

At present, H-Oil and LC-Fining are the two major EBR technologies for VR hydroprocessing [1,2]. The catalyst used in these ebullated-beds is typically a 0.8 mm in diameter extrudate with nickel-molybdenum or cobalt-molybdenum as the active metals. The catalyst is maintained in fluidized state through the upward lift of liquid reactants and hydrogen. The height of the ebullated catalyst bed is mainly controlled by the flow rate of recycled liquid adjusted by the speed of the ebullating pump, which is used to control the flow of ebullating liquid from the internal vapor/liquid separator inside the reactor. In addition, a recycle cup which comprises a conduit riser with inner helical members that impart a tangential velocity component to the fluid is designed to achieve a maximum separation of liquid and gas in order to minimize the amount of gas recycled back to the reactor.

Different from the H-Oil and LC-Fining reactor design, the reactor described in this paper is not installed with an ebullating pump due to smaller catalyst being used. The catalyst is a spherical pellet with an average diameter of 0.4 mm and a density of 926 kg/m^3, which makes the catalyst more easily fluidize than the 0.8 mm extrudate used in the H-Oil and LC-Fining processes. To facilitate the separation of the catalyst within the reactor, a three-phase disengaging zone is designed at the top of the reactor. The three-phase disengaging zone is an expanded section above the cylindrical column, where two draft tubes of different diameters and heights are installed, so that three zones are formed for the disengagement of the gas and solid phases. In the central zone confined by the inner

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Symbols

A	model parameter, defined in Eq. (21)
a_g	specific gas–liquid surface area, m^{-1}
c	concentration, mol m^{-3}
D_{al}	axial dispersion coefficient of the liquid, $m^2\ s^{-1}$
D_t	reactor diameter, m
E	activation energy, kJ mol^{-1}
E_s	dispersion coefficient of the solid phase, $m^2\ s^{-1}$
g	gravitational acceleration, m s^{-2}
H	reactor height, m
H_{H_2}	Henry constant of hydrogen, dimensionless
k_0	pre-exponential factor $(mol\ m^3)^{-n_i}$
k_1	mass transfer coefficient, m s^{-1}
n	reaction order, dimensionless
p	pressure, MPa
R	ideal gas constant, 8.314 J $mol^{-1}\ K^{-1}$
T	temperature, K
V_{10}	centerline velocity of the liquid, m s^{-1}
u	superficial velocity, m s^{-1}
u_p	settling velocity of solid particles, m s^{-1}
u_t	terminal settling velocity of a single particle, m s^{-1}
V	bubble rising velocity, m s^{-1}
V_{10}	center line liquid velocity, m s^{-1}
x	conversion, dimensionless
y	normalized concentration of hydrogen, dimensionless
z	axial position, m

Greek letters

α	stoichiometric coefficient with respect to H_2, dimensionless
ε_s	solid holdup in the liquid–solid slurry, dimensionless
ε_{ms}	average solid holdup in the liquid–solid slurry, dimensionless
ψ_1	average liquid holdup in the slurry
μ	viscosity, Pa s
ρ	density, kg m^{-3}
σ	surface tension, N m^{-1}
ξ_{cat}	the dimensionless settled bed height

sub and superscripts

*	at equilibrium
g	gas phase
i	component index (S, N, CCR, Ni, V)
l	liquid phase
lb	large bubble
s	solid phase
sb	small bubble
tran	bubbling to churn turbulent flow transition literature cited

draft tube, all the three phases are flowing upward, where the gas phase is disengaged in the upward free space region; In the circular zone between the two draft tubes, only liquid and catalyst phases are present and the two phases are allowed to flow downwards; In the wall zone between the wall and the outer draft tube, the liquid product free of catalyst powder is allowed to leave the reactor.

It should be noted that, the reactor is different from the conventional bubble column slurry bed, since the slurry was observed to fluctuate violently due to the extra driving force for slurry circulation induced by the draft tubes installed at the top of the reactor.

2. The ebullated-bed reactor model

Since there is a strong internal liquid circulation in the ebullated bed, the reactor performance is much similar to a continuously stirred tank reactor (CSTR). However, it is recommended to use the axial dispersion model (ADM) in view of its great flexibility in accounting for the back-mixing effect to any degree [3,4]. In this work, the results of CSTR and ADM will be compared.

It should be noted that, although it may be reasonable not to consider catalyst distribution if the catalyst size is less than 0.1 mm [5]. In the present EBR, the catalyst size is 0.4 mm, the distribution of catalyst may not be uniform from the bottom to the top of the reactor. To get a quantitative description of the axial solid concentration distribution in this reactor, the so-called sedimentation–dispersion model [6–9] is applied in this work. In this model, the concept of the widely used axial dispersion model is applied to the solid phase, i.e., the solid phase is treated as a pseudo-homogeneous one. From the net motion of solid particles due to the difference between sedimentation and convection fluxes characterized by the solid settling velocity and the dispersive transport which is assumed to obey the Fick's law, the solid dispersion coefficient could be evaluated.

Under the assumption that the liquid–solid mass transfer resistance can be neglected, six mass conservation equations in the liquid phase are established for hydrogen (H_2), sulfur (S), nitrogen (N), Conradson carbon residuum (CCR), nickel (Ni), and vanadium (V).

2.1. The CSTR model

The CSTR model assumes an infinitely large liquid-phase circulation velocity, which leads to uniform distributions of the three phases. Consequently, the following mass conservation equations for hydrogen and VR impurities can be established, which are coupled and should be solved together:

(1) For hydrogen

$$u_1 C^*_{H_2,1}(1-y_{H_2,1}) = [(k_1a_g)_{large} + (k_1a_g)_{small}]\left(\frac{c_{H_2,g}}{H_{H_2}} - c^*_{H_2,1} y H_{2,1}\right) - \sum_{i=1}^{5} \alpha_{VR,i}\cdot(1-\varepsilon_g)\varepsilon_{ms}\cdot\rho_s\cdot k_{0,i}\exp\left(-\frac{E_i}{RT}\right)(c^*_{H_2,1}y_{H_2,1}) \times [c^0_{VR,i}(1-x_i)]^{n_i} \quad (1)$$

(2) For the five VR impurities

$$u_1 c^0_{VR,i}(1-x_i) = (1-\varepsilon_g)\varepsilon_{ms}\cdot\rho_s\cdot k_{0,i}\exp\left(-\frac{E_i}{RT}\right)(c^*_{H_2,1}y_{H_2,1}) \times [c^0_{VR,i}(1-x_i)]^{n_i} \quad (2)$$

where, i = S, N, CCR, Ni, and V.

2.2. The axial dispersion model

The axial dispersion model in this paper is characterized by the following points:

(1) The gas-phase is described by the two-bubble class model which is composed of small bubbles and large bubbles. The large bubbles are traversing the column in plug flow, while the small bubbles are entrained in the liquid phase and have the back-mixing characteristics of the liquid.
(2) The concentration distribution of VR in the axial direction is described by the axial dispersion model.