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Full Length Article

# Hydrocarbon hydrodesulfurization in vertical, inclined and oscillating trickle beds – Hydrodynamics & reactor performance for offshore petroleum marine applications

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## HIGHLIGHTS

- 3-D unsteady-state modeling of flow dynamics and hydrodesulfurization performance.
- Vertical, inclined & oscillating trickle beds.
- Two-phase downflow deviates largely from axial symmetry at high reactor inclination.
- Inclined & oscillating trickle bed catalytically underperforms vertical bed.
- Oscillating trickle bed reflects in oscillatory reaction performances.

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## ABSTRACT

Two-phase flow dynamics and hydrodesulfurization (HDS) performance were numerically analyzed for vertical, inclined, and oscillating trickle beds with a prospect of assessing the potential of implementing HDS operations on marine floating platforms. An unsteady-state three-dimensional model based on the macroscopic volume-averaged mass, momentum, energy and species balance equations coupled with simultaneous diffusion and chemical reaction within sulfide CoMo/alumina catalyst was developed for the purpose of comparative analyses using $H_2$/dibenzothiophene/*n*-hexadecane model system. Angular uniform and sinusoidal oscillatory motion of the reactor between two angled symmetrical positions and between vertical and an inclined position was considered. As in the case of cold-flow passive conditions, in chemical reaction environment two-phase downflow deviates considerably from axial symmetry at higher reactor inclinations with noticeable liquid accumulation in the bottommost reactor cross-sectional area on the tilting side. Also, externally-induced reactor periodic oscillation generates complex reverse secondary flow in radial and circumferential directions and oscillatory patterns of flow field with the amplitude and propagation frequency affected by the type (uniform or sinusoidal), amplitude and period of angular motion of reactor. Inclined, symmetric and asymmetric oscillating trickle-bed reactors underperform the vertical configuration and the decline of symmetric oscillating trickle-bed reactor hydrodesulfurization performance is lower under uniform oscillatory motion conditions. Oscillating trickle-bed reactors generate an oscillatory hydrodesulfurization performance which is affected by the parameters of angular motion of reactor. The inhibiting effect induced by $H_2S$ on the hydrogenolysis is considerable at higher packed bed inclinations and in symmetric oscillating trickle-bed reactors.



## 1. Introduction

The refining industry is continually amended to meet the global trend for more stringent clean fuel specifications, the growing demand for transportation fuels and the shift towards diesel fuel [1]. Catalytic hydrotreating, which is an established refinery process for enhancing the quality of refinery streams by selective removal of sulfur, nitrogen and oxygen heteroatoms via hydrodenitrogenation, hydrodeoxygenation and hydrodesulfurization reactions, has become an increasingly important process in recent years. Hydrotreating processes are operated at different reaction conditions (temperature, hydrogen-to-oil ratio, hydrogen partial pressure, and space velocity), over a variety of catalysts (NiMo, CoMo, etc.), reactor configurations and reaction systems. Because hydrotreating reactions are irreversible under the industrial

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**Nomenclature**

| | |
|---|---|
| $a$ | gas-liquid interfacial area, $m^2/m^3$ |
| $c_{p,\kappa}$ | specific heat capacity of κ-phase ($\kappa = g, \ell$), J/kg K |
| $C_j$ | concentration of species $j$, $kmol/m^3$ |
| $d_p$ | particle diameter, m |
| $D_j$ | molecular diffusivity coefficient of species $j$, $m^2/s$ |
| $D_{j,p}^{eff}$ | effective diffusivity of species $j$ inside catalyst particle, $m^2/s$ |
| $D_{kj}$ | Knudsen diffusion coefficient of species $j$, $m^2/s$ |
| $D_{\ell(g)}$ | liquid and gas dispersion coefficients, $m^2/s$ |
| $f_e$ | fraction of the external catalyst particle surface covered by liquid |
| $f_{\text{int},\kappa,z(r,\theta)}$ | interaction force exerted on $\kappa$-phase, $N/m^3$ |
| $g$ | gravitational acceleration, $m/s^2$ |
| $H$ | reactor height, m |
| $k_\ell a$ | volumetric liquid-side mass transfer coefficient, $s^{-1}$ |
| $k_s$ | liquid-solid mass transfer coefficient, m/s |
| $k'K'_{H_2}$ | rate constant for the hydrogenation times the equilibrium constant for the hydrogen adsorption, $s^{-1}$ |
| $K_{DBT}$ | adsorption constant of DBT for hydrogenolysis, $m^3/kmol$ |
| $K'_{DBT}$ | adsorption constant of DBT for hydrogenation, $m^3/kmol$ |
| $K_{H_2}$ | adsorption constant of $H_2$ for hydrogenolysis, $m^3/kmol$ |
| $K_{H_2S}$ | adsorption constant of $H_2S$ for hydrogenolysis, $m^3/kmol$ |
| $P$ | reactor pressure, Pa |
| $P_j$ | partial pressure of species $j$, Pa |
| $r$ | reactor radial coordinate, radial position within catalyst, m |
| $r_{hn}$ | reaction rate of hydrogenation reaction, $kmol/kg_{cat}s$ |
| $r_{hs}$ | reaction rate of hydrogenolysis reaction, $kmol/kg_{cat}s$ |
| $r_p$ | radius of the catalyst particle, m |
| $R$ | reactor radius, m |
| $R$ | ideal-gas constant |
| $t$ | time, s |
| $T$ | temperature, K |
| $T_a$ | period of angular motion |
| $u_\kappa$ | interstitial velocity of $\kappa$-fluid, m/s |
| $z$ | axial coordinate, m |

*Greek letters*

| | |
|---|---|
| $\alpha$ | angle of packed-bed column inclination with respect to the horizontal plane |
| $\alpha_{\max}$ | amplitude of the angular motion |
| $\varepsilon$ | packed bed porosity, – |
| $\varepsilon_\kappa$ | $\kappa$-phase holdup, – |
| $\varepsilon_b$ | porosity in the bulk region of the packed bed, – |
| $\varepsilon_p$ | catalyst particle porosity |
| $\Delta H_r$ | reaction enthalpy, kJ/kmol |
| $\eta_i$ | effectiveness factor of reaction $i$ ($i = hs,\ hn$) |
| $\lambda_{r,\theta}^{eff}$ | radial (circumferential) effective thermal conductivity, J/ms K |
| $\mu_\kappa$ | $\kappa$-phase dynamic viscosity, kg/ms |
| $\mu_\kappa^{eff}$ | $\kappa$-phase effective viscosity (combination of bulk and shear terms), kg/m s |
| $\rho_\kappa$ | $\kappa$-phase density, $kg/m^3$ |
| $\rho_{pb}$ | packed bed density, $kg/m^3$ |
| $\tau$ | tortuosity, – |
| $\sigma_\ell$ | surface tension, N/m |
| $\theta$ | circumferential coordinate, m |

*Subscripts/superscripts*

| | |
|---|---|
| $g$ | gas phase |
| $hn$ | hydrogenation |
| $hs$ | hydrogenolysis reaction |
| $in$ | reactor inlet |
| $\ell$ | liquid phase |
| $p$ | catalyst particle |
| $r$ | radial direction |
| $s$ | solid phase, surface of catalyst particle |
| $z$ | axial direction |

*Abbreviations*

| | |
|---|---|
| *BiPh* | biphenil |
| *CHB* | cyclohexylbenzene |
| *DBT* | dibenzothiophene |

reaction conditions, reaction temperature is constrained by the required reaction rate and the catalyst tolerance to deactivation [2] and typically lies in the range 573–663 K. Catalyst hydrotreating is carried out in two-phase or three-phase reactor systems. Light feeds, such as naphtha and middle distillates, with a boiling point range of 300–500 K, are hydrogenated in two-phase (gas-solid) fixed-bed reactors. Conversely, when distillation range of the feed increases (480–663 K), reactions are often performed in three-phase reactors. Hydroprocessing of heavy oils is generally carried out in trickle-bed reactors [3] and this is the object of our study.

Recently, the offshore petroleum industry, which operates in profound waters and away from coast in one of the world's harshest environments, is increasingly interested on the effect of very complex sea states on the performance of reactors onboard floating production, storage and offloading (FPSO) nonstationary units [4–7]. The offshore environment challenged by wind, marine currents and waves can generate translational and angular ship motions which bring important performance deviations and safety problems on floating/production platforms [4]. Floating trickle-bed reactors for catalytic hydrotreating onboard FPSO units certainly are no exemption to sea vagaries and their consequences on reactor performances. Therefore, the optimal design of offshore hydrotreating trickle beds operated in unstable sea environments challenged by wind and waves needs improved understanding and quantification of the hydrodynamics and transport processes coupled with the kinetics, thermal effects and thermodynamics [4,5]. Additionally, the operation of offshore reactors onboard floating systems necessitates implementation of efficient counteractive actions (extra capacity, liquid distribution) to anticipate any performance deviations regarding the onshore catalytic hydrotreating units [8].

The hydrodynamic behavior of floating packed beds onboard FPSO platforms was reported very sparsely in the literature [6–12]. Hydrodynamic studies in inclined packed beds show noticeable liquid accumulation in the bottommost reactor cross-sectional area on the tilting side at high packed bed inclinations. On the other side, sinusoidal and uniform translation and rotation motions of packed beds induce a worsening of phase maldistribution compared with the static vertical bed. The hydrodynamic experiments were performed with air/kerosene systems in laboratory-scale (column diameter = 5.7 cm and bed height = 160 cm) inclined (until 50°) packed beds [10] and packed beds mounted on an hexapod ship motion simulator subject to sinusoidal translation (sway, heave) and rotation (roll, roll + pitch, yaw) motions at different frequencies [8,12]. Currently, there is no information available in the literature related to the performance of inclined and time periodic off-axis trickle-bed reactors.

Consequently, it is judged appropriate to maintain improving the conceptual knowledge base of trickle-bed reactor hydrodynamics especially the complex hydrodynamics of reactors experiencing ship motion in sea unstable environments. Also, our