Biodesulfurization of hydro-desulfurized diesel in airlift reactor

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This study presents simulation of an indigenously designed airlift reactor (vol. 43.746 dm$^3$) to lower down sulfur content of hydrodesulfurized diesel from 500 ppm (mg/dm$^3$) to ultra-low level using *Rhodococcus* sp. as microbial biocatalyst. A detailed modeling using TSM (tanks in series model) is proposed to demonstrate efficacy of airlift reactor for biodesulfurization.

Keywords: Airlift reactor, Biodesulfurization, Modeling, Simulation

Introduction

Hydrodesulfurization$^{1,2}$ is carried using hydrogen in presence of cobalt, nickel and molybdenum as catalyst at moderate temperature ($>$ 400°C) and high pressure (4-10 MPa). But it is very difficult to remove polyaromatic sulfur compounds (alkylated di-benzothiophene, naphthothiophenes etc.). To reduce sulfur to an ultra low level [10 ppm (mg/dm$^3$) or below] to meet global specifications, microbial biodesulfurization can be used to transform sulfur compounds efficiently$^{3,4}$. An experimental and modeling study on biodesulfurization of hydrotreated diesel in a trickle bed reactor was performed using bacterial strain, *Rhodococcus* sp$^5$. This study presents a rigorous phenomenological simulation study for biodesulfurization in airlift reactor (ALR).

Modeling of Biodesulfurization in Airlift Reactor (ALR)

ALR is modified version of bubble column used now-a-days by several chemical and biochemical industries. From mixing point of view, ALR can be sub-divided into four main sections: i) Bottom where gas distributor is placed and medium is recycled from downcomer; ii) Riser where gas liquid flow upwards; iii) Disengaging section at top of assembly where some portion of gas is separated from gas - liquid mixture; and (iv) Downcomer section where gas-liquid flow downwards. Each section having separate mixing characteristics need to be modeled separately. From two major modeling approaches$^{6,7}$ available, tanks in series model (TSM) is more realistic and advantageous compared to axial dispersion model (ADM). Present study also considered TSM for modeling of desulfurization of diesel in ALR.

A modification of TSM can be done considering back mixing parameter, $m$, as ratio of back flow rate to net forward liquid flow rate. Flow in ALR is considered as flow through a series of equal sized well-mixed stirred tanks. Bottom section ($i = 1$) is treated as well-mixed stage. Riser and top sections ($i = 2, 3, ..., A$) are tanks-in-series with back flow. As flow in downcomer ($i = A + 1, A + 2, ..., B$) is relatively well defined, back flow in downcomer is neglected (Fig. 1). At top section, most of the gas bubbles disengage and a small quantity is only entrained by liquid recirculation through downcomer. So flow through downcomer is almost single phase. Hence $m$ is neglected in this section. Riser, including top and bottom sections, is divided into $A$ number of hypothetical well mixed stages. Consequently, mixing in downcomer is represented by ($B - A$) stages without backflow. Stages in riser are numbered upwards and that of downcomer are numbered downwards. At bottom section, fresh gas feed and recycled flow from downcomer are mixed well. Oxygen concentration in gas phase is assumed to be uniform$^8$. Value of equilibrium dissolved oxygen concentration ($O^*$, 0.00451 mg/dm$^3$ at $t = 0$), was considered to be constant throughout airlift bioreactor. Maximum solubility of oxygen in diesel was obtained experimentally. Temperature was kept constant and hence no energy balance was taken into account. As concentration of microbes or reactants were negligibly small in reactor assembly, effect of enthalpy change, during desulfurization reaction was almost insignificant.

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Material Balances in Different Sections of ALR

TSM with back flow provides simultaneous 1st order ordinary differential equations, which are material balances of microorganisms, substrate (organo-sulfur compounds) and dissolved oxygen for hypothetical well-mixed tanks or stages (Fig. 1). Unsteady state material balances of components were solved simultaneously using MATLAB for all four sections of ALR.

Kinetic Model

Following assumptions were made: i) Feed is sterile; ii) Internal mass transfer resistance is negligible and hence effectiveness factor is unity; iii) Organosulfur compounds are only growth limiting substrates; iv) Microbial growth follows Monod type kinetics; and v) Microbial reaction occurs only at outer surface of bio-film.

Experimental Section

Internal loop ALR (Fig. 2) was constructed of an inner diameter (0.18 m) borosilicate glass column (ht, 2 m). Draft tube (inner diam, 0.1 m; ht, 1.5 m) was made up of borosilicate glass (thickness, 0.002 m). Therefore, cross-sectional area of draft tube acting as riser is $7.854 \times 10^{-3}$ m$^2$. Draft tube was placed at 0.15 m above the bottom of reactor. Gas sparger (diam, 0.06 m) at the bottom contains perforations (diam, 1 mm) with a triangular pitch (7 mm). A series of experiments were performed by varying flow rate of gas monitored through calibrated rotameter with help of precisely controlled valve (0.1 - 0.7 l/s). Superficial gas velocity obtained was 0.025 - 0.09 m/s. Air and diesel were used as gas and liquid phases. Static liquid (ht, 1.72 m) was from bottom of airlift assembly. Individual gas hold ups of riser and downcomer sections were measured by standard procedure using U-tube manometer filled with iodine mixed (for color) carbon-tetra-chloride as manometric fluid (density, 1.58 g / cm$^3$). Liquid circulation velocity in airlift system was measured by using a deep fried almond seed tracer (0.02 m × 0.01 m × 0.001 m; density, 1030 kg / m$^3$) by using stop watch to measure time taken to travel between two marked points at 1 m distance apart. Several readings were taken for a single set and data obtained were tested statistically to judge accurate circulation velocity. Details of experimentation procedure are reported. Overall mass transfer coefficients ($k_\text{d}$) of riser and downcomer sections were measured separately using hand-held dissolved oxygen-meter DO – 110 (Eutech Make, Singapore). Obtained data were in good agreement with experimentally observed $k_\text{d}$ values for petroleum fractions reported earlier. Design parameters and operating conditions are as follows: Overall volume of ALR assembly ($V_{\text{ALR}}$), 43.746 dm$^3$; Volume of riser ($V_r$), 11.781 dm$^3$; Volume of downcomer ($V_d$), 25.905 dm$^3$; Volume of bottom section ($V_b$), 3.817 dm$^3$; Volume of top section ($V_t$), 1.7804 dm$^3$; Volumetric flow rate of gas ($Q_g$), 1.524 × 10$^{-3}$ m$^3$/s; Hold up of riser ($\varepsilon_r$), 0.06; Hold up of downcomer ($\varepsilon_d$), 0.034; Volumetric oxygen transfer coefficient of riser ($k_\text{r}$), 0.017 s$^{-1}$; Volumetric oxygen transfer coefficient of downcomer ($k_\text{d}$), 0.012 s$^{-1}$; Velocity of liquid in riser ($V_{lr}$), 0.32 m/s; and Velocity of liquid in downcomer ($V_{ld}$), 0.27 m/s.

Results and Discussion

Determination of Model Parameters

Growth kinetics of *Rhodococcus* sp. and associated parameters ($\mu_{\text{max}}$, $K_s$ and $Y$) were as reported. Other parameters ($\delta$ and $\phi$) that depend on dimension and type of reactor were fitted for present ALR system using previously obtained experimental data ($\delta$, 0.001; $\phi$, 0.000814 h$^{-1}$).
Estimation of Number of Stages for Riser and Downcomer

Downcomer operates as a plug flow reactor. Without any significant back-mixing ($m = 0$). Now relationship between ADM and TSM is given as

$$\frac{1}{Pe} = \frac{m + \left(\frac{1}{2}\right)}{B} \quad \text{...(1)}$$

where, $Pe$ is Peclet number and $B$ denotes number of stages present in ALR. Now, if $m = 0$, equivalent number of tanks ($B$) is given by $Pe / 2$.

Peclet number is a dimensionless quantity defined as

$$Pe = \frac{V_{ld} h_D}{D_{ax,d}} \quad \text{...(2)}$$

where, $h_D = \frac{h_L}{1 - \varepsilon}$ is height of dispersion and $D_{ax,d}$ is axial dispersion coefficient ($0.025 \text{ m}^2/\text{s}$).

Values $A = 12$ and $B = 10$ were obtained using above procedure. So riser and downcomer sections were sub-divided into 12 and 10 equal parts respectively. Bottom, riser and top sections are completely mixed and hence value of $m$ was considered to be 1 for each of them.

Simulation of Sulfur Removal

Extensive experimentations were conducted with internal loop airlift assembly earlier for estimating all important parameters of system like overall gas hold up ($\varepsilon_g$), individual hold ups for riser ($\varepsilon_r$) and downcomer ($\varepsilon_d$), liquid circulation velocity in riser ($V_{lr}$) and downcomer ($V_{ld}$) as well as overall-mass-transfer coefficients in riser ($k_{l,a}$), and downcomer ($k_{l,a}$), as a function of superficial gas velocity ($U_{gr}$). Theoretical models were also developed for prediction of these parameters with variation of superficial gas velocities. Biodesulfurization process was simulated in internal loop ALR with gas free liquid column (ht, 1.72 m) with constant flow rate of air (5.5 m$^3$/h) maintained. ALR was considered to be operating in a semi-batch mode with hydrodesulfurized diesel fed to ALR in batch mode and with continuous passing of air. All mass balance equations along with kinetic equation were solved simultaneously using stiff equation solver routine of MATLAB. Initial conditions considered for biomass ($X$), organosulfur compounds ($S$) and dissolved oxygen concentrations ($O$) at time $t = 0$, were as follows: $X_0 = 0.001 \text{ mg/dm}^3$, $S_0 = 500 \text{ mg / dm}^3$ (ppm); and $O_0 = 0.00451 \text{ mg/dm}^3$.

Simulated results (Fig. 3) indicate that biomass concentration increases with time and reaches saturation at 120 h. Concentration of organo-sulfur compounds (Fig. 4) diminishes with passage of time, due to microbial action and reached to almost zero level at 120 h, when biomass concentration also got saturated. So, using internal loop airlift assembly with specified design and operating parameters, it is possible to remove almost entire quantity of sulfur compounds present in hydro-treated diesel in 120 h. So airlift bioreactor can be
employed for deep and ultra desulfurization. As only air and water were used, process is green and environment friendly.

Dissolved oxygen quantity in bio-culture decreased with time (Fig. 5), because oxygen was consumed for desulfurization as well as required by microbes for survival and growth. As time increased, oxygen concentration decreases marginally from $4.51 \times 10^{-3}$ mg/dm$^3$ (which is maximum solubility of oxygen in diesel at room temperature) and stabilized at $3.2 \times 10^{-3}$ mg/dm$^3$ at 120 h. So even after desulfurization, fermentation broth was not completely devoid of oxygen.

Simulated results of concentration distributions of different zones of riser and downcomer sections for instantaneous operation were provided (Figs 6–8). Riser section was subdivided into 12 equal parts in accordance with previously calculated number of stages ($A = 12$) from bottom to top as per movement of fluid. Similarly, downcomer was partitioned in 10 equal parts (as previously estimated $B = 10$) from top to bottom. Fig. 6 represented change in biomass concentration for instantaneous operation at 82$^\text{nd}$ h, wherein panel 6a depicted steady rise of biomass concentration from 2 mg/dm$^3$ to almost 20 mg/dm$^3$ due to continuous bubbling of fresh air (source of oxygen) in riser section. Biomass concentration remained almost constant at 22 mg/dm$^3$ in downcomer section (Fig. 6b) as growth is restricted due to decreased dissolved oxygen concentration in liquid medium. Fig. 7a indicated more biodesulfurization reaction occurring in riser section causing reduction of organo-sulfur compound (substrate) from 484.5 to 432 mg/dm$^3$ vis-à-vis almost steady concentration at 425 mg/dm$^3$ in entire downcomer section (Fig. 7b), may be due to unavailability of sufficient dissolved oxygen in downcomer section.

Concentration distribution for dissolved oxygen in different sections or riser and downcomer of ALR during 82$^\text{nd}$ h operation were reported (Fig. 8). Dissolved oxygen was sufficiently high in bottom portion (section 1) of riser (0.0045 mg/dm$^3$) and gradually reduced to 0.004 mg/dm$^3$ on top zone (section 12) (Fig. 8a). Consumption of oxygen for biodesulfurization reaction
(Fig. 7a) caused reduction oxygen concentration. Fig. 8b indicated that dissolved oxygen concentration of liquid medium downcomer section was sufficiently low (0.0039 mg/dm$^3$) and hence further reaction was almost negligible (Fig. 7b). As reaction in downcomer section was insignificant, no appreciable drop in dissolved oxygen concentration was noticed (Fig. 8b).

Conclusions

Modeling and simulation of internal loop ALR was carried out using TSM under unsteady state conditions for biodesulfurization of hydrodesulfurized diesel oil. Reactor showed relatively uniform axial dissolved oxygen concentration varying from small band of $4.51 \times 10^{-3}$ mg/dm$^3$ to $3.2 \times 10^{-3}$ mg/dm$^3$ at 120 h. Internal loop airlift bioreactor can be used quite effectively to reduce organo-sulfur concentration from 500 ppm to almost nil in about 120 h. So designed airlift assembly can efficiently be employed for ultra and deep desulfurization operation in semibatch mode, and an environment friendly product is obtained as per specification of US and European norms. Simulation study with *Rhodococcus* Sp. can be extended with other suitable microbes as well. Experimental studies are essential to accommodate effect of change of initial liquid column height in ALR and mass transfer effects on overall performance of the process.

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References