Biodesulfurization of hydrodesulfurized diesel in a trickle bed reactor—
Experiments and modeling

M Mukhopadhyaya, R Chowdhury* and P Bhattacharya
Chemical Engineering Department, Jadavpur University, Kolkata 700 032

Received 20 May 2005; revised 10 February 2006; accepted 10 March 2006

Hydrodesulfurized diesel [sulfur content, 200-540 ppm (mg/dm$^3$)] has been used for bio-desulfurization using Rhodococcus sp. Biomass concentration with the progress of time has been determined using dry cell weight method. Batch studies have been conducted with a two phase medium [non-aqueous to aqueous phase ratio, 10:90 to 100:0 (i.e. 0-100% diesel)]. Sulfur concentration has been determined using a Universal Oil Products (UOP) standard method (UOP 357-80). Microbial strains have been observed to follow classical Monod type growth kinetics under the present range of substrate concentration. A systematic and programmed analysis was made to determine following intrinsic kinetic parameters: maximum growth rate ($\mu_{max}$), 0.096 h$^{-1}$; and half saturation constant ($K_s$), 71 mg/dm$^3$. Biodesulfurization of hydrodesulfurized diesel has been conducted in a trickle bed reactor (diam, 0.066 m; height, 0.6 m) under continuous mode. Pith balls have been used as the immobilization matrix for the microorganisms with a constant bed porosity of 0.6. Flow rate of inlet diesel has been varied (0.25-0.5 dm$^3$/h). Sulfur conversion up to 99% has been achieved. A mechanistic mathematical model, developed for the trickle bed bioreactor, can explain the reality satisfactorily.

Keywords: Bio-desulfurization, Diesel, Intrinsic kinetic parameters, Monod model, Trickle bed reactor

IPC Code: C10L1/10

Introduction

Sulfur is the most undesirable element present in petroleum and thus desulfurization of diesel fuel is growing worldwide into a process critical to petroleum refinery profitability. Worldwide awareness led countries in the major developed regions to legislate almost sulfur free highway diesel fuel for 2007. In the conventional hydrodesulfurization process, using available range of catalysts (CoMo, NiMo etc.) thermo chemically difficult to remove polyaromatic sulfur compounds like alkylated di-benzothiophene, naphthothiophenes etc. exist unconverted and hence, removal of sulfur to an ultra low level [10-50 ppm (mg/dm$^3$)] as required by the new US and European norms, is not possible. Microbial biocatalysts have been identified that can biotransform sulfur compounds, which are very difficult to be removed by conventional hydrodesulfurization. In this regard, most attention is given on Kodama 4S pathway of Rhodococcus Sp., which can remove sulfur from substituted and unsubstituted di-benzothiophene. A few pioneering works have been reported on the bio-desulfurization of model organosulfur compounds$^2$-$^4$. However, behaviour of pure model organosulfur compounds towards biodesulfurization is expected to be different from that of natural organosulfur compounds occurring in diesel$^{12,13}$. Conventional way$^{14}$ of lowering the sulfur level from 100 to ultra low level of 10 ppm (mg/dm$^3$) would be to add a second stage to the existing hydro-treating unit. Therefore, under the present investigation bio-desulfurization of diesel itself has been carried out to assess the actual behaviour of a real system. A deterministic mathematical model, based on mechanistic approach, has been developed to simulate the system behaviour.

Theory

Mathematical model of the system has been developed on following assumptions (Fig. 1): 1) Feed is sterile; 2) Internal mass transfer resistance is negligible and hence effectiveness factor $\eta$ is unity; 3) Organo-sulfur compounds are the only growth limiting substrates; 4) Microbial reaction occurs only at the outer surface of the bio-film; 5) Microbial growth follows the Monod kinetics; 6) Bio-film thickness (Lf) remains constant and it is a stagnant phase; 7) Newly grown microorganisms remain in the liquid phase and are not attached to the packing materials; 8) Immobilization matrixes, namely pith
balls are perfect spheres (radius $R$); 9) Some of the spheres, $n$, are always in contact with one spherical particle and it leads to loss in biofilm surface area ($A_L$) and volume ($V_L$) per unit sphere in contact; and 10) Bed porosity ($\varepsilon$) remains constant throughout the operation.

Applying the model assumptions, the differential mass balance equations for biomass and organo-sulfur compounds within a differential element (Fig. 1) of thickness may be written as,

$$\frac{dC_A}{dZ} = \frac{1}{FA} \frac{\mu_{max} C_B C_A}{(Ks + C_B)} A_L a_f (1 - \varepsilon) \quad \ldots(1)$$

$$\frac{dC_B}{dZ} = -\frac{1}{FA} \frac{\mu_{max} C_B C_A}{(Ks + C_B)} A_L a_f (1 - \varepsilon) \quad \ldots(2)$$

where, $a_f$ is specific area considering the loss due contact area and volume of spheres associated with each packing material (assumption 9). Thus $a_f$ may be calculated as follows,

$$a_f = \frac{4 \pi (R + L_f)^2 - nAL}{4 \frac{1}{3} \pi (R^3)} \quad \ldots(3)$$

and $A_L = 2 \pi (R + L_f) L_f \quad \ldots(4)$

where, $F_A$ = volumetric flow rate, dm$^3$/h; $C_A$ = concentration of biomass, mg/dm$^3$; $C_B$ = concentration of substrate, mg/dm$^3$; $Z$ = Axial position in the reactor, m; $A$=cross-sectional area of the reactor, m$^2$.

Growth kinetic parameters, for desulfurization of diesel are as follows: saturation constant ($Ks$), 71 mg/dm$^3$; yield coefficient ($Y$), 0.2 g biomass consumed/g of substrate consumed; and maximum specific growth rate ($\mu_{max}$), 0.096h$^{-1}$. Eqs (1) to (4) have solved by 4th order Runge-Kutta technique with the following initial conditions:

$$Z = 0 \text{ and } \begin{bmatrix} C_A = 0 \\ C_B = C_{B,0} \end{bmatrix}.$$

**Materials and Methods**

**Materials**

Beef extract and peptone for bacteriology (E. Merck, Mumbai); NaCl GR (Ranbaxy, Mumbai); methanol GR, acetone GR, dithiozone GR, purified NaOH pelletes, mercuric oxide red purified, HCl GR, and nickel aluminum alloy powder for the production of Raney Nickel (E. Merck, Mumbai); benzo thiophene for synthesis (Lancaster, England); acetic acid glacial GR and isopropyl alcohol GR (Process chemical industries, Kolkata); and N$_2$ (Prakash traders, Kolkata) were used. *Rhodococcus Sp.* (pure culture) was purchased from NCIM, Pune (no. 2891). Hydrodesulfurized diesel samples [initial BP, 140°C; final BP, 370°C; sulfur content, 330-500 mg/dm$^3$, aromatic content (27.16%, w/w)] were purchased from IOC (Indian Oil Corporation), Kolkata.

Composition of the medium for growing microorganisms was as follows: Beef extract, 10; NaCl, 5; and peptone, 10g/dm$^3$.

**Analytical Methods**

Biomass concentration in the reaction broth was determined by Dry Weight Method, in which the broth was centrifuged at the rate of 10,000 rpm for 15 min at -15°C. The bacterial mass was then transferred to a pre-weighed aluminium cup and dried at 50°C overnight. The exact weight of bacterial mass was
determined by subtracting the weight of dry cup from that of the cup containing dry bacterial mass. Nickel Reduction Method (UOP357-80) has been followed to determine the concentration of sulfur in diesel samples. Batch type experiments were conducted in Erlenmeyer flasks. Ratio of aqueous medium to diesel oil was maintained in the range of 90:10 to 0:100. The overall sulfur concentration was varied from 200 to 540 mg/dm$^3$. The kinetic parameters ($\mu_{\text{max}}$, $K_s$ and $Y$) have been determined using these data.

**Operation of the Trickle Bed Bioreactor**

The trickle bed reactor (diam, 0.066 m; height, 0.6 m; bed porosity, 0.6) was initially packed with pith balls (diam, 0.012 m). Bacterial medium containing *Rhodococcus Sp.* was circulated through the packed bed until the bio-film thickness on the sphere became 0.00001 m. Diesels having different organo-sulfur concentration (200, 330, 430 and 540 mg/dm$^3$) were fed into the trickle bed reactor at 0.25-0.5 dm$^3$/h in downward direction. The reactor was continuously sparged with air at 480 dm$^3$/h in upward direction. The substrate loading in the reactor was initially $1.46 \times 10^{-4}$ kg/m$^3$/h for initial substrate concentration of 200 mg/dm$^3$ at 0.25 dm$^3$/h and was varied up to $7.84 \times 10^{-3}$ kg/m$^3$/h for 540 mg/dm$^3$ of initial substrate concentration in diesel at 0.5 dm$^3$/h. Outlet stream coming out of the bio-reactor was analyzed for biomass and organosulfur compounds using Dry Weight method and Nickel method (UOP357-80) respectively.

**Results and Discussion**

Simulated values of biomass concentration in the liquid phase at the minimum feed rate (0.25 dm$^3$/h) of diesel have been plotted against axial length of the reactor with initial sulfur concentration as a parameter (Fig. 2). The experimental data have been superimposed on the same plot. Biomass concentration increases with the axial length of the trickle bed reactor. On the other hand, the maximum achievable concentration of biomass at the reactor exit increases with the increase in the sulfur concentration in the feed diesel. The simulated data follow the same trend. Similar plots have been made for substrate concentration (Fig. 3). The figure reveals that the model is able to explain the real trend properly. Simulated concentration profile of biomass was plotted against axial length of the reactor at different flow rates (Fig. 4). The corresponding experimental values are found to justify the simulated results.
Simulated and experimental profiles of substrate concentration against axial length of the reactor indicate that the experimental trend is well explained by the simulated results (Fig. 5).

Simulated data for the concentration of sulfur (Fig. 4) and biomass (Fig. 5) have been plotted against reactor height for the sulfur concentration in feed diesel of 200 mg/dm$^3$ with inlet flow rate of diesel as parameter. The flow rate of diesel was varied (0.25-0.5 dm$^3$/h). The corresponding experimental results have also been plotted on the same graph. Close analysis (Fig. 4) reveals that the value of sulfur concentration in the reactor exit stream increases i.e. the ultimate sulfur conversion decreases with the increase in the flow rate. At the lowest inlet diesel flow rate (0.25 dm$^3$/h), sulfur removal efficiency of 99.46 percent has been predicted by the mathematical model, whereas the corresponding experimental value is 99 percent. Similarly, the simulated and experimental values of sulfur removal efficiency corresponding to the feed rate of 0.5 dm$^3$/h are 80 percent and 77.8 percent respectively. In the same way, maximum exit concentration of biomass has been achieved for the lowest feed rate of diesel. This is, however, expected as the increase in flow rate implies the decrease in reactor residence time causing drop in the ultimate conversion of the reactant. In both cases, the simulated trend can explain the experimental ones. However, in all figures, small deviation of the simulated data from the experimental ones has been observed. This may be due to the idealistic assumptions like constancy of porosity, absence of mass transfer resistance etc. in the model.

Conclusions

*Rhodococcus Sp.* (NCIM 2891) have shown high activity to reduce sulfur level in diesel. The initial sulfur concentration was varied in the range of 200-540 mg/dm$^3$. A trickle bed reactor was studied with the liquid flow rate and inlet sulfur concentration as parameters. A mathematical model that describes the biodesulfurization of diesel in a trickle bed reactor has been proposed. The simulated values are able to explain the experimental observation satisfactorily. However, it is felt that there is a scope of refinement of the model by the incorporation of more realistic characteristics like variation of porosity, presence of mass transfer resistance etc. prevailing in the actual system.

Acknowledgements

M Mukhopadhyay acknowledges CSIR, New Delhi for financial support as SRF.

References


