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Two phase mathematical model for a bio-trickling reactor for the production of ultra low sulfur diesel (ULSD) from deeply hydrodesulfurized diesel

M. Mukhopadhyaya, R. Chowdhury *, P. Bhattacharya

Chemical Engineering Department, Jadavpur University, Kolkata 700032, India

Abstract

A trickle bed reactor (TBR) having a diameter of 0.066 m and a height of 0.6 m has been used for the bio-desulfurization of hydrotreated diesel fraction having sulfur concentration in the range of 200–540 ppm. *Rhodococcus* sp. (NCIM 2891, Pune) has been used to degrade the residual organo-sulfur compounds present in deeply hydrodesulfurized diesel. The microorganisms have been immobilized on the packing material prior to desulfurization within the trickle bed reactor. The volumetric flow rate and hence, the substrate loading rate have been used as the parameters. Sulfur reduction within the range of 84–95% has been achieved. To avoid the excess accumulation of the biomass within the reactor, backwashing technique is incorporated. For such desulfurization, batch studies have been conducted in Erlenmeyer flasks maintaining the concentration of diesel in the range of 0–100% in a diesel supplemented sulfur-free aqueous medium. The concentration of biomass with time has been monitored using dry cell weight method. The concentration of sulfur has been determined by ''trace sulfur in petroleum distillate by nickel reduction'' (UOP 357-80) method. From the growth curve, it is observed that the system follows uninhibited Monod type model within the range of substrate studied. A systematic and programmed investigation has been carried out to determine the growth kinetic parameters, namely maximum specific growth rate, saturation constant K_s and yield coefficient $Y_{X/S}$. A deterministic mathematical model for the TBR has been developed using judicious assumptions to predict its performance characteristics.

Keywords: Bio-desulfurization; Uninhibited Monod model; Intrinsic kinetic parameters; Trickle bed reactor; Immobilized; Two phase mathematical model

1. Introduction

Sulfur is the most undesirable element present in petroleum fractions. Diesel contains various organo-sulfur compounds, which not only contribute to air pollution, but causes severe hazardous impact on environmental safety leading to serious damage to eco-system. Most of the major developed countries have already been compelled to legislate almost sulfur-free highway diesel fuel. In this direction, U.S. Environmental Protection Agency (EPA) has proposed a new set of fuel standards for highway diesel fuels and emissions to be phased in the beginning of 2007, according to which the new standard for fuel includes a reduction of sulfur of maximum 15 ppm. In the existing hydrodesulfurization process, using available range of catalyst (CoMo, NiMo, etc.) diverse sulfur containing compounds present in oils react in different extent and sterically hindered poly aromatic sulfur compounds, namely alkylated di-benzothiophenes, naphthothiophenes remain unconverted [1,2]. Hence, removal of sulfur to an ultra low level of 10–15 ppm is not achievable. Because of increasingly stringent regulations concerning with the sulfur content of motor fuels, sulfur removal by biocatalytic means is often considered as a potential alternative to the conventional process. Bio-desulfurization, a process in which sulfur is removed by enzymatic process, may provide a complementary technology for lowering sulfur level from 100 ppm to ultra low level of 15 ppm [8]. Microbial biocatalysts have been identified that can biotransform

* Corresponding author. Tel.: +91 33 24146378; fax: +91 33 24146378.
E-mail address: ftbe_bon@yahoo.com (R. Chowdhury).

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Nomenclature

A	cross-sectional area of the reactor (m)
A_L	bio-film area loss per unit packing sphere in contact (m)
b_d	biomass decay rate coefficient (s^{-1})
C_B	substrate concentration (mg/dm^3)
D_p	diameter of each packing sphere (m)
F_A	volumetric flow rate of the liquid stream (dm^3/h)
F.B.P.	final boiling point
I.B.P.	initial boiling point
K_s	saturation constant
L_f	bio-film thickness over each packing material (m)
N	number of packing spheres in contact with one sphere within the TBR
ΔP	pressure drop
R	radius of each packing sphere (pith ball) (m)
V	volume of the TBR (m^3)
V_0	average velocity of the liquid (m/s)
V_L	bio-film volume loss per unit packing sphere in contact (m^3)
X_{A0}	initial biomass concentration (mg/dm^3)
X_{b0}	initial biomass density (mg/dm^3)
X_b	final biomass density (mg/dm^3)
$Y_{X/S}$	yield coefficient = mass of biomass produced/mass of substrate consumed
Z	axial position within the reactor
Greek letters	
ε_0	initial bed porosity
ε_f	porosity in bed with bio-film
η	effectiveness factor
μ	viscosity of the liquid (diesel) (cp)
μ_{max}	maximum specific growth rate of biomass
Φ	sphericity of the packing materials
Subscript	
max	maximum

sulfur compounds that are very difficult to be removed by the 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 organo-sulfur compounds [3–7,9–15]. Under the present study, bio-desulfurization has been carried out to assess the actual behaviour of natural organo-sulfur compounds occurring in diesel as the behaviour of pure model organo-sulfur compounds towards bio-desulfurization is expected to be different from that of a real system. A deterministic mathematical model, based on mechanistic approach, has been developed to simulate the system behaviour.

2. Experimental

2.1. Materials

Beef extract (E. Merck), peptone (E. Merck), NaCl (Ranbaxy), methanol (E. Merck), acetone (E. Merck), benzothiophene (Lancester), N_2 (Prakash traders), dithiozone (E. Merck), NaOH (E. Merck), acetic acid (Process chemical industries), mercuric oxide (E. Merck), HCl (E. Merck), isopropyl alcohol (Process chemical industries) and nickel–aluminum alloy (E. Merck) were used during the present investigation.

2.2. Microorganism

The pure bacterial strain of *Rhodococcus* sp. (NCIM 2891) was purchased from National Collection of Industrial Microorganisms (NCIM), India. Cells were cultivated and enriched using sulfur-free medium supplemented with diesel oil in 50 ml Erlenmeyer flasks.

2.3. Diesel used

Hydrodesulfurized diesel samples were purchased from Indian Oil Corporation (IOC), Kolkata, having the characteristics given in Table 1.

2.4. Composition of the growth medium for microorganisms

Basis: 1 dm^3, beef extract: 10 g, NaCl (AR): 5 g, peptone (for bacteriology): 10 g.

3. Analytical methods

3.1. Dry weight method for the determination of bacterial mass

The biomass concentration in the reaction broth was determined by dry weight method. In this method, 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 aluminum cup and dried at 50 °C overnight. The exact weight of the bacterial mass was determined by subtracting the weight of dry cup from that of the cup containing dry bacterial mass.

Table 1
Specification of diesel used

Compound	Diesel
I.B.P. (°C)	140
F.B.P. (°C)	370
Specific gravity (basis: density of water = 1000 kg/m^3)	0.8216
Sulfur (ppm)	200–540
Aromatic (w/w) (%)	27.16