

# Mathematical modelling of combined mass transfer and biochemical reaction of biodesulfurization of diesel using immobilized cells

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## Abstract:

Environmental safety is one the global challenges that need attention of researcher to provide immediate solution. The research was conducted mainly to identified microorganism capable biodegrading the sulfur compounds in combustion fuel (Diesel) and also to carryout mathematical modelling of combine mass transfer and biochemical reaction Biodesulfurization (BDS) of Diesel was carryout by isolated bacterium pseudomonas stutzeri using sodium alginate as supporting media for cell immobilization. From the researched, the experimental value of thiophene was desulfurized from 6.9555mg/l to 1.105mg/l under 72-hour period. This means that 84.1% of thiophene in Diesel was desulfurized, while the results gotten from the simulated model (theoretical value), thiophene was desulfurized from 6.955mg/l to 1.054 mg/l. This implies that 84.8% of thiophene in Diesel was desulfurized. The experimental value (84.1%) is lower than the theoretical value (84.8%) due to the slight errors that might have occurred during the experiment and modelled equation is a little improves on previous models. The kinetic parameters obtained are  $\mu = 0.057 \text{ hr}^{-1}$ ,  $K_m = 0$ ,  $K = 0.399 \times 10^{-8} \text{ hr}^{-1}$ . When  $K_m = 0$ , it means that the rate of reaction is independent of sulfur concentration in the diesel. The study provides an alternative solution for the acid rain and global environmental pollution cause by combusted sulfur compounds in diesel.

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## 1. Introduction

Sulfur and its organic homologues are undesirable in the liquid fuels due to the cause of environmental pollution and hindrance in a variety of refining processes e.g., catalyst poisoning during catalytic hydro-treatment, resistance to octane boosting and corrosion of the equipment. Desulfurization has therefore become an unavoidable process for the refiners [1]. Currently the Hydrodesulfurization (HDS) process is the sole tool employed in the refineries all over the world to cater this problem. However, HDS process is inconvenient due to its uneconomic requirements like high temperature and pressure, hydrogen gas and costly catalysts, also its efficiency is low for removal of refractory sulfur compounds. It is therefore needed to develop more efficient and affordable processes for desulfurization of liquid fuels. Sulfur compounds are unwanted in refining process owing to their tendency to catalyst deactivation during processing of crude oil. They also have poisoning potential and can lead to the corrosion of pumping equipment and pipelines [1]. The government across the nations has enacted laws to reduce the emission of these pollutants. Regulations for the sulfur level in diesel oil have become increasingly stringent, thus global society is stepping on the road to zero-sulfur fuel, with only

differences in the starting point of sulfur level and rate reduction of sulfur content between different countries [2].

The concentration of sulfur in crude oil ranges from 0.05 to 5.0% (by weight), although values as high as 13.95% have been reported [3]. In general, the distributions of sulfur increase along with the boiling point of the distillate fraction. As a result, the higher the boiling range of the fuel, the higher the sulfur content will tend to be. Upon combustion, the sulfur in fuels can contribute to air pollution in the form of particulate material and acidic gases, such as sulfur dioxide. To reduce sulfur-related air pollution, the level of sulfur in fuels is regulated, and to meet these regulations sulfur must be removed from fuels during the refining process [3].

Sulfur oxide (SO<sub>2</sub>) and Hydrogen sulfide (H<sub>2</sub>S) are considered as one of the major air pollutants in the world today. The emission of sulfur dioxide is caused by naturally occurring sulfur compounds that are left behind in the fuels, which result into the emission of sulfur oxide gases. The reaction of water with these sulfur compounds in the atmosphere form sulphates and acid rain leading to destruction of buildings. It also acidifies soil and eventually results in destruction of forests and hence the ecosystems [4]. The emission of sulfur has resulted into related health issues, like heart diseases, asthma, and respiratory illnesses. In addition, the presence of sulfur compounds in

liquid fuels adversely affects vehicles. Sulfur levels in automotive fuels are responsible for lower efficiency of catalytic converters. In addition, high sulfur levels in petroleum distillates can promote the deactivation of catalysts through poisoning in Fluidized Catalytic Cracking (FCC) during hydrocracking of the heavy distillates to lighter ones [5]. The presence of high sulfur-containing compounds in the process streams could cause corrosion of piping and fitting, thereby damaging the pipelines and leading to air emissions of sulfur-containing compounds, which are undesirable for mankind and his environment. In many cases, a large quantity of SO<sub>2</sub> is released into the atmosphere when petroleum distillates that contain substantial number of sulfur-containing compounds are used as fuel and combust [6].

Biodesulfurization (BDS) this is described as the process by which the use of a catalyst of biological nature enables the removal of sulfur content in oil fractions at moderate pressure and temperature conditions. Given its specificity, it is presented as a promising alternative for the removal of organic-sulfured molecules resistant to conventional technologies, such as dibenzothiophenes and their substituted forms [7]. Development of a BDS process includes the isolation and production of the biocatalyst (microorganism or enzyme), the desulfurization reaction (non-aqueous biocatalysis), and finally, the separation of products and quality controls. Different desulfurizing microorganisms have been isolated and characterized worldwide, including *Rhodococcus erythropolis* IGTS, *Rhodococcus erythropolis* D-1 and *Rhodococcus* sp strain WU-K2R [8]. These microorganisms transform Dibenzothiophene (DBT) into 2-hydroxybiphenyl (2-HBP), which remains in the organic phase while the sulfur is eliminated in the form of inorganic sulfate in the aqueous phase of the system. BDS takes place at low temperatures and pressure in the presence of microorganisms that are capable of metabolizing sulfur compounds. It is possible to desulfurize crude oil directly by selecting appropriate microbial species [9]. There are potential benefits to BDS, such as lower capital and operation costs. It has been reported that BDS requires approximately two times less capital and 15% less operating cost in comparison with traditional HDS [10]. The longevity of microorganisms in BDS processes used to be short, around 1–2 days, but this has been extended to 8–16 days (200–400 h) [10]. There were also advances made in reactor design. Reduced mass transport limitations enabled higher volumetric flow rates and led to improvement in the efficiency of BDS. The use of staging and air sparging (in the case of aerobic conversion) with a lower water-to-oil ratio enabled conversion in smaller reactors. These advances unfortunately also came with a trade-off. As the concentration of microorganisms increase, separation becomes more difficult and additional equipment to break the oil–water emulsion is required [11]. Modeling the fermentation kinetics by parameter estimation from experimental data and application of a reaction diffusion model for estimation of substrate concentration gradient inside the immobilization support. Moreover, fermentations with different initial substrate and biomass concentrations were carried out using strain SY025, aiming to evaluate

their influence over flavor compounds, using statistical models. Compared to free cells, immobilized yeasts showed both higher glycerol yield (SY025, 40%; SY067, 53%; SY001, 35 19%) and biomass yield in the system (SY025, 67%; SY067, 78%; SY001, 56%). On the other hand, free cells presented higher ethanol yields when compared to immobilized ones (SY025, 9%; SY067, 9%; and 37 SY001, 13%). According to the model developed, a substrate gradient inside the support was predicted, but 38 with low mass transfer limitations [12].

## 2. Materials and Method

The chemicals used in this study were Sodium alginate D-glucose (G), D+fructose (F) and MgSO<sub>4</sub>·7H<sub>2</sub>O (R and M Chemical, UK). some brown cylindrical shaped granules of diameter 0.3 to 1.0 mm, length 1.0 to 1.5 mm and activity of 350 IGIU/g (Sweetzyme, Novozymes, Denmark). For the high-performance liquid chromatography (HPLC) analysis, deionized water and acetonitrile (ACN) (HPLC grade) are used. Different series of glucose concentrations from 10 to 50% w/v were prepared. All analytical samples were diluted with distilled water and filtered through 0.45 µm Nylon filters prior to the HPLC analysis [13].

### 2.1 Biochemical reaction and Mass transfer

The regions near the surface of the particles where the fluid velocity was very low. In such regions around the exterior of particles, a near-stagnant film of fluid was present, through which the substrate needs to be transported. This transport takes place primarily by molecular diffusion; since this rate may be quite slow, the observed reaction rate can be significantly decreased by this external film diffusion. The local rate of film diffusion of the substrate from the fluid bulk to the surface of the immobilized cells may be considered to be proportional to the area for mass transfer and the driving force for mass transfer, i.e. the concentration difference between the bulk and the external [14]. The first-order rate of the biochemical reaction is equal to rate mass transfer [14]. Therefore, since the enzyme concentration is a function of biomass growth, then Michelis-Menten equation can be modified as:

$$-r_c = k C_A C_c / C_A + C_M \quad (1)$$

Equation (1) can be simplified into;

$$\frac{dC_A}{dt} = k C_A C_c / C_A + C_M \quad (2)$$

Where  $C_c = X_0 e^{\mu t}$ ,  $C_M = K_M$

Enzymes concentration is a function of biomass concentration

$$-\frac{dC_A}{dt} = (k X_0 e^{\mu t} C_A) / (K_M + C_A) \quad (3)$$

Re-call

$$-\frac{dC_A}{dt} = k C_A \quad (4)$$

$$1 = \frac{X_0 e^{\mu t}}{K_M + C_A}$$

Cross multiplying, it becomes;

$$K_M + C_A = X_0 e^{\mu t} \quad (5)$$

Where  $X$  = biomass concentration,  $X_0$  = initial biomass concentration

$$\ln K_M + \ln C_A = X_0 e^{\mu t} \quad (6)$$

Dividing through by  $X_0$  gives,

$$\frac{\ln K_M}{X_0} + \frac{\ln C_A}{X_0} = \mu t \quad (7)$$

Equation (4) is an equation of a straight line. Also linearizing equation (3)

$$-\frac{dC_A}{dt} = (kX_0 e^{\mu t} C_A) / (K_M + C_A) \quad (8)$$

$$K_M + \frac{C_{A0} - C_A}{\ln(C_{A0}/C_A)} = \frac{K_X t}{\ln(C_{A0}/C_A)}$$

The Growth rate ( $\mu$ ) of bacterium *psedomona stutzeri* was calculated using equation 9.

$$\ln\left(\frac{X}{X_0}\right) = \mu t \quad (9)$$

Theoretical Values of Concentration of Diesel in (mg/l) was calculate using equation 3.

$$-\frac{dC_A}{dt} = (kX_0 e^{\mu t} C_A) / (K_M + C_A)$$

At  $C_A \gg K_M$ , we have

$$-\frac{dC_A}{dt} = kX_0 e^{\mu t}$$

$$C_A(t) = C_{A0} - \frac{K_X X_0}{\mu} (e^{\mu t} - 1) \quad (10)$$

Equation 9 is general model equation from which a simulated values were obtained

### 3. Results

The new values of  $C_A$  (i.e., the theoretical or simulated values of  $C_A$ ) can be gotten at various time intervals from equation (8) where  $k = 0.399 \times 10^{-8} \text{ hr}^{-1}$ ,  $C_{A0} = 6.955 \text{ mg/l}$ ,  $X_0 = 1.412 \times 10^6 \text{ mg/l}$ . Also, the kinetics parameters in Table 1 were used to obtained a particular solution for developed model.

Table 1: Kinetics Parameters

Specific Growth Rate $\mu \text{ (hr}^{-1}\text{)}$	$K_M \text{ (mg/l)}$	Rate Constant $K \text{ (hr}^{-1}\text{)}$
0.057	0	$0.399 \times 10^{-8}$

Table 2: The Theoretical Values of Concentration of Thiophene with respect to Time

Time (hr)	CA (mg/l) Simulated result	Experimental Result (mg/l)
0	6.955	6.955
12	6.857	5.759
24	6.665	4.980
36	6.285	3.773
48	5.529	2.609
60	4.032	1.844
72	1.105	1.054

### 4. Discussion of Results

In the experimental values, 84.1% of thiophene was desulfurized using *bacterium pseudomonas stutzer* while, for the theoretical values, 84.8% of thiophene was desulfurised. This implies that the theoretical values obtained using modified Mechilis – mente's equation has a higher desulfurizing rate than the experimental value (84.1%). The experimental values are lower than the theoretical values due to experimental and model assumption that might have occurred during the experiment. The growth rate of *bacterium pseudomonas stutzer* grows at an exponential rate. The  $\mu = 0.057 \text{ hr}^{-1}$  which implies that the microorganisms grow at growth rate of  $0.057 \text{ hr}^{-1}$ ,  $K_M = 0$  it's implying that the rate of reaction is independent of sulfur concentration in the diesel. However, the rate of reaction is dependent on microbial population. The developed model certified the initial boundary conditions and its shows an improvement compared with [15, 16].

The general equation for calculating the concentration of substrate at any given time is shown below;

$$C_A(t) = 6.955 - \frac{0.399 \times 10^{-8} \times 1.412 \times 10^6}{0.057} (e^{0.057t} - 1)$$

### 5. Conclusion

The particular solution for calculating the substrate concentration from for the BDS for the developed modelled shows perfection when validated with experimental values. The experimental value is 84.1% and is lower than the theoretical value (84.8%) due to the slight errors that might have occurred during the experimental setting. The kinetic parameters obtained from Monod's equation are  $\mu = 0.057 \text{ hr}^{-1}$ ,  $K_M = 0$ ,  $K = 0.399 \times 10^{-8} \text{ hr}^{-1}$ . Conclusively the developed model has validity from its initial values or boundary conditions because, from the developed model at time  $t$  equal to zero  $C_A(t) = C_{A0}$ .

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