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Modelling the Bio desulfurization of Kerosene in a Batch Reactor

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ABSTRACT: *Direct combustion of fossil fuels leads to sulfur oxide emission that contributes to acid rain and air pollution. Biodesulfurization is considered a complimentary or an alternative to hydrodesulfurization currently used in refineries. In this paper, the biodesulfurization of kerosene is modelled by taking a mass balance on the substrates, the sulfur-containing organic compounds in the kerosene. The resulting equation was a First order differential equation which was solved numerically using the Finite Difference Method. The simulated results were found to have a high correlation with known and reliable experimental data. The maximum velocity rate constant, and the Michaelis – Menten constant, K_M were obtained by subjecting the obtained parameters from linear plots to the Macquardt's non-linear regression analysis, The partition (distribution) coefficients of the organic sulfur compounds in the kerosene used in the simulation were estimated through the efficacy of combining linear solvation energy relationships (LSERs) developed for pure systems through the application of linear solvent strength theory. The quantitative parameters estimated in the course of modelling the anaerobic biodesulfurization of kerosene would be useful in bioreactor design of the process that would eventually take the technology to the market.*

Keywords: *Biodesulfurization, Mass Balance, Partition (Distribution) Coefficients, Linear Solvation Energy Relationships (LSERs) and Finite Difference Method.*

I. INTRODUCTION

Kinetic equations, which describe the activity of an enzyme or a microorganism on a particular substrate, are crucial in understanding many phenomena in biotechnological processes. Quantitative experimental data is required for the design and optimization of biological transformation processes. A variety of mathematical models have been proposed to describe the dynamics of metabolism of compounds exposed to pure cultures of microorganisms or microbial populations of natural environment [1]. Characterization of the enzyme or microbe-substrate interactions involves estimation of several parameters in the kinetic models from experimental data. In order to describe the true behavior of the system, it is important to obtain accurate estimates of the kinetic parameters in these models [2].

It is a known fact that sulfur-containing hydrocarbons in petroleum products are insoluble in water and the microorganisms capable of biodesulfurization are normally suspended in aqueous solution, thus the process takes place at the interface between the organic and aqueous phases. When this happens, the overall biodesulfurization rates may not necessarily depend on only the bio-kinetic factors but also on physic-chemical constrains that control bio-availability. [3] Reported that DBT appeared to partition into the aqueous phase prior to cellular uptake by *Escherichia coli* and *Pseudomonas putida* during the biodesulfurization of DBT by these microorganisms. The implication of this is that the availability of DBT to the microorganisms is a function of its uptake mechanism which could be directly between the cells of the organism and the oil phase or by solubilisation in the aqueous medium. This brings to the fore the exchange of mass between the aqueous phase that houses the microorganisms and the oil phase containing the substrates needed by the microorganisms for growth and sustenance. The kinetics of chemical analyses of catalytic reactions without the incursion of transport processes is a normal practice for two main reasons. In the first place, if fundamental knowledge of a reaction is available through the mechanism of the reaction, it will enhance the chances of catalyst design that will take advantage of the optimal reaction pathways to the desired products. Secondly, the usual procedure for reactor design of an industrial process involves the coupling of the intrinsic rate kinetics of the reaction with the transport relationships. These relationships are important for industrial processes since any of the various diffusion processes may be the limiting factor(s) [4 & 5].

The kinetics biodegradation rate of pharmaceutical and personal care products was investigated, [6] found out that the kinetics followed a first order rate. The half-lives of these products were also investigated. The kinetics of Polyaromatic hydrocarbons, PAH by *sphingomonas paucimobilis EPA 505* was modelled in engineered and natural systems based on probalistic and statistical criteria, [7] inferred underlying interaction mechanism based on model fits. The model was fully predictive and relied only on parameters determined in the sole PAH experiments. However, [8] reported that sole substrate model is inadequate to describe multi substrate kinetics of a broad range of PAH mixtures. The potential of pseudomonas fluorescence to degrade synthetic phenol in water was investigated [9], it was observed that the culture followed substrate inhibition kinetics while the specific phenol consumption rates fitted Haldane model based on which the bio kinetic parameters were estimated. Orthogonal collocation and Gear's method were used to modelled the kinetics of phenolic waste water biodegradation by [10], the simulated results agree with the experimental ones. [8] used simple Monod type kinetic model to simulate the biodegradation of diesel fuel by some consortium of microorganisms, their results revealed that the consortium of organisms function at high hydrocarbon concentrations. The biodegradation kinetics of benzene and toluene were modelled separately and as a mixture by [11], their work showed that better description of pure substrate can be achieved by Andrew's model while mixtures could be best modelled with sum kinetics interaction parameters, SKIP models are employed.

In this study, the modelling of kerosene biodesulfurization was done taking mass balance on the sulfur containing organic compounds in kerosene. The type of biodesulfurization modelled is the selective reductive pathway in a batch reactor.

II. METHODOLOGY

Mass balance of the substrates, the sulfur containing hydrocarbons in the fuel, kerosene is presented as follows:

The material balance on the solute (substrates in kerosene) over the time period from t to $t+\Delta t$ over the element of volume of a batch reactor from z to $z+\Delta z$ is obtained thus:

(Input at z) – (output at $z+\Delta z$) – (Reaction due to biodesulfurization) – (Rate of transfer to the cell surface) = Accumulation over time period. 1

In a batch reactor, there is no inflow or outflow of material thus,

Accumulation over time period = (Rate of transfer of the substrate to the cell surface) - (Reaction due to biodesulfurization)

Mass transfer rate to the solid, $r_m = ak_L(C - C_S)A\Delta z$ 2

Accumulation in the fluid phase, $r_{ac} = A\Delta z\left(\frac{dC}{dt}\right)$ 3

There is no reaction in the fluid phase in the reactor since all the reactions take place on the cell surface. Hence the reaction term is equal to zero.

Substituting equations 2 and 3 into equation 1

$$k_L a(C - C_S)A\Delta z = A\Delta z\left(\frac{dC_i}{dt}\right) \quad 4$$

Dividing equation 4 by $A\Delta z$ we have

$$k_L a(C - C_S) = \frac{dC}{dt} \quad 5$$

C_S is the concentration of the substrate on the surface of the organism and is not measurable.

The solution to the problem can be obtained by applying the law of conservation of mass to the adsorbable solute contained in the fluid phase and the solid.

It should be noted that adsorption transfer material from the fluid phase and adds to the solid phase (the microorganism, *Desulfobacterium indolicum*)

The solid phase loses material by desulfurization and generates none.

Then the solid phase mass balance for the sulfur specific reductive pathway of biodesulfurization is

$$A\Delta z\frac{dq}{dt} - A\Delta z\frac{v_{max}C}{K_M + C} = k_L a(C - C_S)A\Delta z \quad 6$$

Dividing Equation 6 through by the elementary volume, $A\Delta z$ yields Equation 7

$$\frac{dq}{dt} - \frac{v_{\max} C}{K_M + C} = k_L a(C - C_S) \quad 7$$

Substituting Equation 7 into equation 5, we have

$$\frac{dq}{dt} - \frac{v_{\max} C}{K_M + C} = \frac{dC}{dt} \quad 8$$

Solutions to equation 8 are simple when q is a linear function of C, that is, the adsorption, is assumed to be linear. Then $\frac{dq}{dt}$ can be replaced by $-K\frac{dC}{dt}$.

Then, $\frac{dq}{dt} = K\frac{dC}{dt}$ 9

K is Distribution coefficient

$$-\frac{v_{\max} C}{K_M + C} = \frac{dC}{dt} + K\frac{dC}{dt} \quad 10$$

$$\frac{v_{\max} C}{K_M + C} = -(1 + K)\frac{dC}{dt} \quad 11$$

Equation 11 represents the mass transfer based kinetic rate expression for the sulfur specific reductive pathway of biodesulfurization and is a first order differential equation.

The resulting differential equation was solved numerically using the Implicit Finite Difference Method. The choice was guided most importantly by convenience. Furthermore, it is accurate, consistent and stable. Equations arising from implicit method may be difficult to solve, but their solution is not restricted by stability criteria. There is also no restriction on the size of the time step. The simulated profile was compared to the experimental data of [12].

III. RESULTS AND DISCUSSION

The kinetic parameters, the maximum rate constant, $v_{\max}$ and the Michaelis – Menten constant, K_M were obtained by subjecting the obtained parameters from Eadie-Hofstee, Lineweaver-Burk and Hanes plots to the macquardt's non-linear regression analysis. This was done because the obtained parameters from these plots are not the same (see Table 1). For instance, in the case of the thiophene that has the same maximum rate constant, $v_{\max}$ for all the linear plots but different Michaelis-Menten constant, $K_{M.}$ then, the question would be which of them is the appropriate to choose. In reality, Michaelis – Menten equation is not a linear equation, transforming it linearly to obtain parameters would always introduce errors in such parameters.

The iterative method for estimating the kinetic parameters $v_{\max}$ and K_M using the Marquardt's algorithm of non-linear regression analysis entails that the multi-response nature of the problem will be accounted for by the minimization of the sums of the squares of the residuals Φ on the molar quantities of the reaction [9]. This technique resulted in good estimates of the rate constants. The parameters obtained from the linear plots were used as seed for the Marquardt's algorithm. The $v_{\max}$ and K_M are 0.103 and 0.575 for thiophene and 1.350 and 54.700 for 2, 5 – Dimethylthiophene respectively.

Table 1: The Kinetic Parameters Obtained from the Linear Plots of Hane, Lineweaver-Burk and Eadie-Hofstee from the Experimental Data of Biodesulfurization of Kerosene by *Desulfobacterium indolicum*

	Hanes Plot	Lineweaver-Burk Plot	Eadie-Hofstee Plot
Maximum Rate Constant, $v_{\max,}$ (mg/L.hr)	**1.03**	**1.03**	**1.03**
Michaelis-Menten constant, $K_{M,TH,}$ (mg/L)	**0.574**	**0.560**	**0.561**
Maximum Rate Constant, $v_{\max DMT,}$ (mg/L.hr)	**1.350**	**1.348**	**1.349**
Michaelis-Menten constant,$K_{M, DMT,}$ (mg/L)	**54.68**	**54.52**	**54.66**

Source: [12] Keys: TH, Thiophene and DMT, 2, 5 - Dimethylthiophene

The distribution coefficients of the substrates between the oil and the aqueous phases were estimated using a model developed by [7] for sulfur-containing organic substances in the fuel phase. It is represented as,

$$\log K_{i,fw} = \log\left[\frac{RT}{V_f P_i^0}\right] - \left(C_{aw} + r_{aw}R_2 + S_{aw}\Pi_2^H + a_{aw}\alpha_2^H + b_{aw}\beta_2^H + V_{aw}V_x\right) \quad 12$$

The parameters R_2 describes the excess molar refraction of solute i [13], Π_2^H describes the polarity/polarizability of solute i [14], α_2^H describes the hydrogen-bonding acidity of solute i [4], β_2^H describes the hydrogen bonding basicity of solute i [11 & 16], and *V*x, describes the group-contributable molecular volume of solute i [19] while *c*, *r*, *s*, *a*, *b*, and *v* are adjusted coefficients specific to the two-phase system, in this case air and water.

Equation 12 accurately predicted fuel-water Distribution coefficients of a wide range of non polar hydrocarbon and thiophene compounds in agreement with previous findings [7]. However, predictions were highly unreliable for polar solutes.

Table2: The Distribution coefficients of Thiophene and 2, 5 Dimethylthiophene

Substances	$K_{i,fw}$
Thiophene	**1.281**
2,5 Dimethylthiophene	**1.054**

Source: [12]

The concentration-time profiles obtained from solving Equation 11 by the Finite Difference Method compared with the experimental data of [12] is presented in Figure 1. The multi-component nature of the feed was taken into consideration in the solution of the model equation because there are many sulfur-containing hydrocarbons in kerosene, four of them, thiophene, 2, 5 – Dimethylthiophene, benzothiophene and dibenzothiophene. Only the first listed two are present in the kerosene analysed. The level of agreement between the simulated and experimental data was determined by the sum of variances between the simulated and experimental data. It is important to mention that the growth kinetics of the organisms was neglected for reasons previously explained.

The sum of variances between the simulated concentration-time profile and the experimental one is 16.82. The variances at the points range from 0.28 at the 60th hour to 9.92 at the 72nd hour. The next large variation to that of the 72nd hour is that at the 36th hour which is 2.9, the reason for very large variation at the 72nd hour is not clearly understood but it may be attributed to product inhibition and further work is needed to prove this assertion. In terms of percentage, this is 2.66% and 25.61% respectively, the next large deviation to 25.61% being 6.45%. The level of agreement between the simulated and experimental concentration – time profiles can be described as being good.

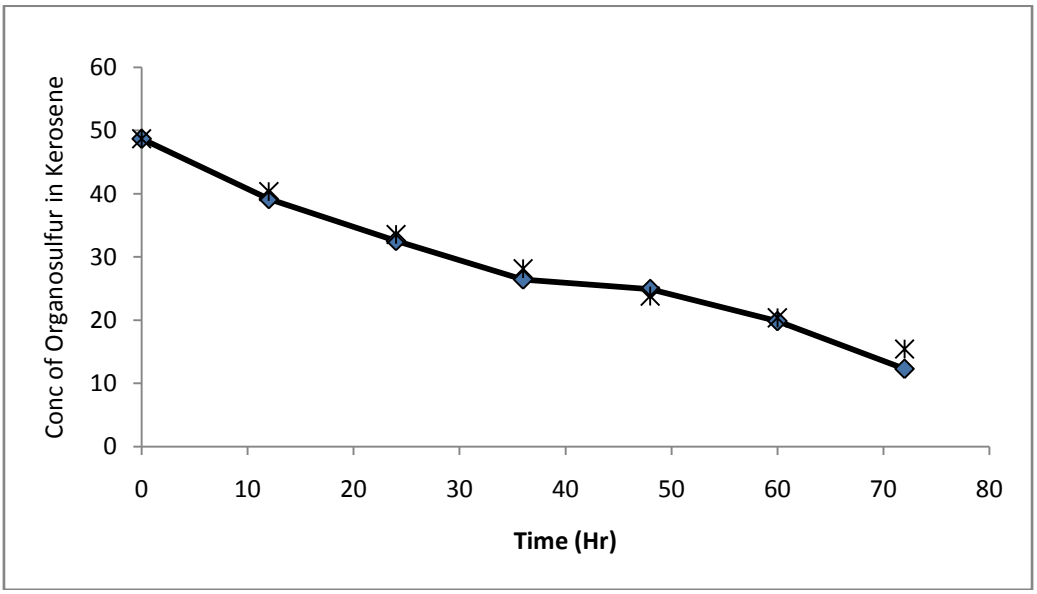

Figure 1: The Experimental and Simulated Concentration – Time Profile Kerosene Bio desulfurization by *D indolicum*.

The quantitative parameters (measured, calculated and estimated) represent a valuable pool of information that can be used for reactor design of anaerobic biodesulfurization of kerosene by *Desulfobacterium indolicum.* Further, all the assumptions made in the development of the biodesulfurization model are true to a reasonable extent and thus the rate at which the substrates are transported will play a significant role on the overall rate of the biodesulfurization. Also, *Desulfobacterium indolicum* desulfurized the kerosene by selectively removing the sulfur from the various organosulfur compounds in the fuel without any significant distortion in the carbon frameworks of the fuel was reasonable. The choice of the anaerobic route is borne out of the fact that it is a potentially attractive biodesulfurization route to apply because of its sulfur specificity. From the pathway, it follows that the calorific value is maintained because C – C bonds are not altered. Furthermore, the reaction pattern is similar to hydrodesulfurization which is the current method used in removing sulfur in the refineries, this means that it can fit into the existing structures in use.

NOMENCLATURE

$\prod_2^H$	**Polarity/Polarizability of Solute i**
α_2^H	**The Hydrogen-Bonding Acidity of Solute i**
β_2^H	**The Hydrogen Bonding Basicity of Solute i**
P_i^0	**Hypothetical liquid vapour pressure of solute i,**
v_{max}	**Maximum Velocity Rate Constant, (mol/m^3) $^{n-1}$s^{-1}**
A	**Cross Sectional Area of the Batch Reactor, m^2**
a	**Interfacial Area of the Biocatalyst, m^{-1}**
C	**Concentration of Substrate, mol/unit volume**
c, r, s, a, b,* and *v	**Adjusted Coefficients Specific to the Two-Phase System, in this case Air and Water.**
C_S	**Equilibrium Concentration of Substrate, mol/unit volume**
fw	**Fuel–Water Phase**
K	**Distribution Coefficient of the Substrate**
k_L	**Mass Transfer Co-efficient of the Liquid Phase, m^3 /m^2.s**
K_M	**Michaelis – Menten Constant, mol/unit volume**
q	**Amount of Substrate Adsorbed**
R	**Molar Gas Constant, J/mol.K**
R_2	**Excess Molar Refraction of Solute i**
r_m	**Rate of Mass Transfer, mol/unit volume**
T	**Temperature, K**
t	**Time, s**
V_f	**Molar Volume of the Fuel Phase, m^3/mol**
***V*x,**	**Group-Contributable Molecular Volume of Solute i, m^3**
z	**Element Length in a Batch Reactor, m**

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