Gasoline biofiltration: an analytic model

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ABSTRACT

We present an analytical method of solution for a pair of models representing the removal of gasoline from air by biofiltration. The experimental data showed that the aromatic components of the gasoline were more readily digested than the aliphatics. The models, involving two or three fitted parameters, fitted the laboratory data well.

1 INTRODUCTION

Biofiltration is an increasingly used process to remove volatile organics (VOC) from a vapour stream. This involves the packed bed absorption of the VOC, followed by its biodigestion. The process can be competitive with condensation, incineration, adsorption and scrubbing when the VOC concentrations are low and the gas flow rates are high.

If biofiltration is used to remove gasoline vapour from air, it is found that the aromatic fraction is relatively easily and rapidly digested but the aliphatic fraction is consumed only when a substantial amount of the aromatics have been eliminated. Experimental work done at the ICT, Prague (Halecky *et al*., 2006) has measured these effects by sampling down the length of a bioreactor bed and obtaining the concentration profiles for both fractions of the gasoline.

2 MODELLING THE SYSTEM

This system can be modelled by a pair of component mass balances. Over a differential element in the bioreactor, we can write for the aromatics that:

$$QC_{ar} + r_{ar} A dh (1-\varepsilon) a = Q (C_{ar} + dC_{ar}) \tag{1}$$

where r_{ar} is the apparent rate of removal of the aromatics per unit of biomass, C is a concentration at depth h and Q is a volumetric flow-rate. (The remainder of the terms are defined in the nomenclature section.)

This can be rewritten as:

$$\frac{dC_{ar}}{dh} = A(1-\varepsilon) a r_{ar} / Q \tag{2}$$

and similarly for the aliphatics:

$$\frac{dC_{al}}{dh} = A(1-\varepsilon) a r_{al} / Q \tag{3}$$

The rates of removal were previously modelled by the following expressions:

$$r_{ar} = -\mu_1 \left[\frac{C_{ar}}{K_1 + C_{ar}} \right] \left[\frac{K_2}{K_2 + C_{al}} \right] \tag{4}$$

and

$$r_{al} = -\mu_2 \left[\frac{C_{al}}{K_3 + C_{al}} \right] \left[\frac{K_4}{K_4 + C_{ar}} \right] \tag{5}$$

Clearly, the first part of these expressions has the form of Monod kinetics, however note that, as a simplification, they are based on gas phase concentrations. The interference between the fractions was handled by allowing each fraction to inhibit the others' rate of digestion in the form shown by the second part of these equations.

This leads to a maximum of six kinetic parameters being needed to characterise the system. However, when the data was analysed, only three parameters were needed: two pseudo first order constants and a further constant to represent the effect of the aromatics on the aliphatic removal (with the multiplicative form: $[K_4/(K_4+Caromatics)]$.

The equations have been solved (Gerrard *et al.,* 2006) using Euler's numerical technique.

The purpose of this paper is to derive some analytic solutions to the fitting of this smaller, (three constant) kinetic model.

2.1 First analytic solution

The two component mass balances can be written in full as:

$$\frac{dC_{ar}}{dh} = -(A(1-\varepsilon)a/Q)\ \mu_1\left[\frac{C_{ar}}{K_1 + C_{ar}}\right]\left[\frac{K_2}{K_2 + C_{al}}\right] \tag{6}$$

$$\frac{dC_{al}}{dh} = -(A(1-\varepsilon)a/Q)\ \mu_2\left[\frac{C_{al}}{K_3 + C_{al}}\right]\left[\frac{K_4}{K_4 + C_{ar}}\right] \tag{7}$$

As mentioned above, the earlier work showed that equation (6) could be simplified to first order kinetics with no inhibition term, thus:

$$\frac{dC_{ar}}{dh} = \frac{-Am_1}{QK_1} C_{ar} \tag{8}$$

where

$$m_1 = (1-\varepsilon)a\mu_1 \tag{9}$$

Clearly, equation (8) can be immediately solved to give:

$$C_{ar} = C_{ar,in} \exp\left[\frac{-Am_1 h}{QK_1}\right] \tag{10}$$

For the aliphatics, we can write the equation (7) with first order kinetics again *plus* the inhibition term to represent the effect of the aromatics on the rate of removal of the aliphatic fraction:

$$\frac{dC_{al}}{dh} = \frac{-Am_2}{QK_3} C_{al}\left[\frac{K_4}{K_4 + C_{ar}}\right] = \frac{-Am_2}{QK_3}\ C_{al}\left[\frac{K_4}{K_4 + C_{ar,in} \exp\left[\frac{-Am_1 h}{QK_1}\right]}\right] \tag{11}$$

where $m_2 = (1-\varepsilon)a\mu_2$ (12)

Separating the variables:

$$\int_{C_{al,in}}^{C_{al}} \frac{dC_{al}}{C_{al}} = \frac{-Am_2}{QK_3} \int_0^h \left[\frac{dh}{1+\frac{C_{ar,in}}{K_4}\exp\left[\frac{-Am_1 h}{QK_1}\right]} \right] \tag{13}$$

Thus,

$$\ln\frac{C_{al}}{C_{al,in}} = -B_2 \int_0^h \left[\frac{dh}{1+\frac{C_{ar,in}}{K_4}\exp[-B_1 h]} \right] \tag{14}$$

where:

$$B_1 = \frac{-Am_1}{QK_1} \tag{15}$$

$$B_2 = \frac{-Am_2}{QK_3} \tag{16}$$

Thus,

$$\ln\frac{C_{al}}{C_{al,in}} = -B_2 \int_0^h \frac{\exp(B_1 h)dh}{\exp(B_1 h)+\frac{C_{ar,in}}{K_4}} \tag{17}$$

Letting: $u = \exp(B_1 h)$ (18)

then

$du = B_1 \exp(B_1 h)\, dh$ (19)

Hence integral becomes:

$$\ln\frac{C_{al}}{C_{al,in}} = -B_2 \int_{1}^{\exp(B_1 h)} \frac{du / B_1}{(u + (C_{ar,in} / K_4))} \tag{20}$$

Of course, this can be directly integrated to give:

$$\ln\frac{C_{al}}{C_{al,in}} = -\frac{B_2}{B_1}\ln\frac{\exp(B_1 h) + \dfrac{C_{ar,in}}{K_4}}{1 + \dfrac{C_{ar,in}}{K_4}} \tag{21}$$

Finally:

$$C_{al} = C_{al,,in}\exp\left\{-\frac{B_2}{B_1}\ln\frac{\exp(B_1 h) + \dfrac{C_{ar,in}}{K_4}}{1 + \dfrac{C_{ar,in}}{K_4}}\right\} \tag{22}$$

This model will be fitted to the experimental data later.

2.2 Second analytic solution

A new formulation of the model to represent the effect of the aromatics on the aliphatic rate of removal uses a different multiplying factor namely: [1-k*Caromatic].

Clearly, as the aromatic concentration falls, there is a progressively smaller effect on the rate of aliphatic removal. (This will allow an analytical solution to be found which can predict the concentration profiles almost as well as the solution given above, but with a simpler equation.)

In more detail, we now re-write equation (11) as

$$\frac{dC_{al}}{dh} = \frac{-Am_2}{QK_3} C_{al}\left[1 - kC_{ar}\right] \tag{23}$$

Introducing equation (10) here we have:

$$\frac{dC_{al}}{dh} = \frac{-Am_2}{QK_3} C_{al} \quad [1 - kC_{ar,in}\exp\left[\frac{-Am_1 h}{QK_1}\right]] \tag{24}$$

Separating the variables gives:

$$\int_{C_{al,in}}^{C_{al}} \frac{dC_{al}}{C_{al}} = \frac{-Am_2}{QK_3} \int_0^h [1 - kC_{ar,in} \exp\left[\frac{-Am_1 h}{QK_1}\right]] \mathrm{dh} \tag{25}$$

Integrating gives:

$$\ln \frac{C_{al}}{C_{al,in}} = \frac{-Am_2}{QK_3} \{[h + \frac{kC_{ar,in}}{\frac{Am_1}{QK_1}} [\exp\left[\frac{-Am_1 h}{QK_1}\right] - 1]\} \tag{26}$$

or:

$$C_{al} = C_{al,in} \exp\{ \frac{-Am_2}{QK_3} \{[h + \frac{kC_{ar,in}}{\frac{Am_1}{QK_1}} [\exp\left[\frac{-Am_1 h}{QK_1}\right] - 1]\} \tag{27}$$

This equation can also be used to predict the shape of the concentration profiles.

3 FITTING DATA TO THE MODELS

The experimental data from the Institute for Chemical Technology, Prague came from a small biofilter of height equalling 75 cm, with a diameter of 10 cm. The concentrations of aliphatic and aromatic gasoline fractions were measured at the inlet, outlet and four other intermediate points. The trials were organised to give one set of results with approximately constant inlet concentration and a varying gas flow-rate together with another set having constant organic load (eg a high flow-rate and a correspondingly low inlet concentration).

The table lists the seven experiments used in the analysis. The third row gives the sum of squares of the errors, SOS, (between the actual and predicted concentration profiles) assuming the simple first order models for both gasoline fractions, ignoring any interaction.

The fourth row shows the considerable improvement when equation (22) was used, (which, of course, includes both the first order characteristic *plus* the inhibition effect of the aromatics on the aliphatic components). The values of the parameters are given in rows five to seven. These are the same as previously reported (Gerrard *et al.,* 2006) which required the use of a numerical solution of the equations. As expected, the aromatic (first order) constants are typically around three times the values of the aliphatic. The K_4 values for the inhibition constant are seen to average 16 mg m^{-3}.

Table 1.
Results of curve fitting.

	Run 1	**2**	**3**	**4**	**5**	**6**	**7**
$Q\ m^3/hr$	0.015	0.03	0.06	0.006	0.015	0.03	0.06
$C_{ar\ and\ al}$ mg/m^3	120, 129	122, 127	136, 113	267, 231	106, 90	54, 44	25, 20
SOS no inhibition	323.	203.	78.	1557.	337.	81.	27.
SOSeqn 22	87.	54.	75.	443.	80.	23.	10.
m_1/K_1	21.1	18.4	9.2	7.4	16.9	21.8	33.4
m_2/K_3	4.0	5.4	5.4	1.2	5.3	10.2	11.0
K_4	29.9	24.1	18.1	8.10	18.9	6.64	9.5
SOSeqn 27	112.	66.	75.	1060.	103.	33.	8.
m_1/K_1	20.8	18.3	9.2	7.3	16.6	21.6	32.1
m_2/K_3	3.5	3.8	1.8	0.59	4.1	5.9	10.5
k	0.0083	0.0082	0.0054	0.0037	0.0094	0.018	0.04

The last four rows give the values of the fitted parameters which minimised the SOS using equation (27). (The Solver routine in Excel was used here.) As before, the m_1/K_1 parameter is again larger than the m_2/K_3 constant. This again reflects the relative ease of removal of the aromatic components. (The m_1/K_1 values for both models are very close, the m_2/K_3 values do differ somewhat.)

The values of k used as the parameter to quantify the inhibition effect in the second model were small and positive, as expected. If we recollect the form of the equation used: [*1-k*Caromatic*], then clearly, the minimum value of this term is zero. This would occur at the highest aromatic concentrations, ie at the inlet, thus $k <= 1/C_{ar,\ in.}$

Most of the k values were indeed at this upper limit. Hence, the multiplicative inhibition factor can be written as $[1-C_{ar}/C_{ar,in}]$. Thus, the rate of digestion of the aliphatics is linearly related to the aromatic concentration and the model reduces, in this instance, to a two parameter system.

4 CONCLUSIONS

Two simple, analytic solutions to the modelling of gasoline biofiltration have been produced.

The kinetic parameters are listed to aid the designer of such bio-reactors.

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6 NOMENCLATURE

A	area of cross section of the bed, m^2
a	microbial mass per volume of solids, $mg_{bio}\ m^{-3}$
B	constants defined in equations (15 and 16), m^{-1}
C	concentration in gas phase, mg m^{-3}
h	bed height, m
k	inhibition constant, $m^3\ mg^{-1}$
K	kinetic constant, mg m^{-3}
m	constants defined in equations (9 and 12), mg $m^{-3}\ h^{-1}$
Q	volumetric flow-rate, $m^3\ h^{-1}$
r	rate of bio reaction, mg $mg_{bio}^{-1}\ h^{-1}$
u	defined in equation (18)
ε	bed voidage
μ	kinetic constant, mg $mg_{bio}^{-1}\ h^{-1}$

Subscripts

al	aliphatic compounds
ar	aromatic compounds
bio	microbial mass
in	inlet

REFERENCES

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