



Journal of Environmental Science and Technology

ISSN 1994-7887

science
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Vaporization Models of Varying Crude Oil Characteristics

¹A.P. Uzoije, ²F.N. Uzundu and ³P.C. Agu

¹Department of Environmental Engineering,

²Department of Chemical Engineering,

³Department of Material and Metallurgical Engineering, Federal University of Technology Owerri, P.M.B. 1526, Owerri-Imo State, Nigeria

Corresponding Author: Uzoije Atulegwu Patrick, Department of Environmental Engineering, Federal University of Technology Owerri, P.M.B. 1526, Owerri-Imo State, Nigeria

ABSTRACT

The purpose of this study is to provide models for quick assessment of vaporized hydrocarbon from an oil spilled soil. Vaporization is a dominant mechanism which manifests at the initial period of crude oil spill. Quantification of these vaporized hydrocarbons without going through the rigorous methods of weighing and other experimental methods is always beneficial to science and technology. Modeling of the crude oil vaporization rates enhances quick quantification of vaporized hydrocarbon concentrations. In this study, the experimental data obtained from the vaporization process of crude oil of different consistency (different hydrocarbon concentrations) spiked on different soil samples (soils of different textural characteristics) were fitted into the following kinetic models; zero, first and second order. It was observed that zero order kinetics best fitted the vaporization of sample A crude oil (crude oil of the highest hydrocarbon concentration) from different soil samples with vaporization from soil D (soil with the highest percentages of clay and organic matter) showing the highest linear coefficient (R^2) of 0.95. The kinetic study equally showed that first order kinetic model was sufficient to quantify the vaporization rate of crude oil sample C (crude oil sample with lowest hydrocarbon concentration) given the fact that the rate equation models for its vaporization from all the soil samples showed linear coefficients (R^2) of between 0.611-0.87. Vaporization rate of oil sample B obeyed the second order kinetic model. Generally, the results showed the dependability of the kinetic models to varying crude oil and soil types. The models help us get good insight into providing solution to our environmental problems as it pertains to crude oil spill on land.

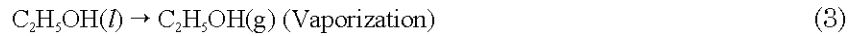
Key words: Reaction order, kinetic model, vaporization, crude oil, soil

INTRODUCTION

Vaporization is a dominant mechanism at the initial periods of crude oil spill on the environment (Ho and Aris, 1987). From the view point of inter-phase between soil and air, the air receives the bulk of the light transported contaminants such as chemical (crude oil) into land environment (Colyar and Wisdom, 1997). The vaporization process occupies only a brief period during the life of a spilled crude oil and vaporization rate can decrease by as much as two orders of magnitude in 8 days (Henry and Kenneth, 1991). The vaporization rate is quantified through the use of rate equations and rate equations are expressions that show the rates of reactions. Gautheir *et al.* (2007) suggested that rates of reactions are usually represented in the form of an empirical curve-fitting procedure.

Two methods are employed to find the values of rate equation constants. Levenspiel (1999) presented those methods as experimental and predictive methods. In most cases the predictive method is not usually adopted due to its inadequacy. In analyzing the data to test which rate equation satisfactorily fits the data, two procedures are adopted. These include; integral and differential methods. Levenspiel (1999) also presented the integral method as most convenient vis-à-vis its efficiency in testing simple rate expressions. The differential method has the inability to reliably determine the derivatives of the scattered data.

Equations can be used to describe physical reactions like melting, sublimation, evaporation and condensation. These equations are presented as:



where, s, l and g represent solid, liquid and gaseous states.

The rate equation is generally represented as:

$$K[A]^m[B]^n$$

where, [A] and [B] are the concentrations of A and B, respectively. K is the rate constant and m and n are the order of the reaction which can only be determined using experimental data.

Order of reaction: Reaction processes take place mainly in zero, first and second order. A reaction process is said to be in a zero order if the rate of reaction is independent of the concentration of materials. The zero order rate law for the general reaction is written as the equation:

$$\frac{dA}{dt} = K \quad (4)$$

Integrating both sides of the equation and inserting the boundary condition of $t = 0$ at $A = A_0$, transforms the integrated form of zero-order kinetics to:

$$[A] = -Kt + [A]_0 \quad (5)$$

First order reactions are generally unimolecular. The rate is proportional to the concentration of a single reactant raised to the first power and this is represented as:

$$\frac{d[A]}{[A]} = Kdt \quad (6)$$

Integrating the equation and inserting the boundary conditions of $t = 0$ at $[A] = [A]_0$ gives:

$$\ln \frac{[A]}{[A]_0} = -Kt \quad (7)$$

The second order reaction is characterized by a reaction between two materials hence the definition that the rate of second order reaction is proportional to either the concentration of a reactant squared, or the product of concentrations of the reactants (Gautheir *et al.*, 2007). The second order reaction is represented in a differential form as:

$$\frac{d[A]}{dt} = K[A]^2 \quad (8)$$

Separating the variables and performing the integration operations with the boundary conditions of $[A] = [A]_0$ at $t = 0$ transform the equation to:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = Kt \quad (9)$$

Several studies have been done on the order of reaction processes. For instance, the degradation of Poly Aromatic Hydrocarbon (PAH) showed compliant with first-order degradation kinetics (Xu and Obbard, 2004). First order kinetic behavior was equally observed in the photochemical degradation of crude oil in seawater carried out by Wang *et al.* (1994). Cumene and all low-boiling aromatics got from south shore of Grand Bahama Island disappeared within 90 min of exposure to ambient temperature and the disappearance of these hydrocarbons is a good first order estimate of the vaporization (Duddy *et al.*, 2004). This study is a supplement to a previous study that investigated vaporization kinetics of various crude oil samples of Niger Delta from different soil samples of the same area (Uzoije, 2008). In the previous study, the crude oil samples spiked on the soil samples of sufficient clay and organic matter content vaporized within few days and vice versa. This manuscript will study the derivation and determination of the reaction order(s) that satisfactorily fits the crude oil vaporization process studied by Uzoije (2008).

MATERIALS AND METHODS

Crude oil samples A, B and C collected from Brass, Qua Iboe and Bonny light oil wells respectively, were each serially mixed with four Niger delta soil samples (A, B, C and D) of different textual characteristics and these mixtures were subjected to vaporization process at ambient temperature by Uzoije (2008). The hydrocarbon concentration of the crude oil samples decreases in this order $A \rightarrow B \rightarrow C$ while the organic matter and the clay content of the oil samples decrease in the following order $D \rightarrow B \rightarrow A \rightarrow C$. The detailed methodology was explained by Uzoije (2008). Order(s) of reaction that fit the data obtained for the vaporization process conducted by Uzoije, 2008 was carried out adopting the integration rate law method. Zero, first and second order reactions were tested to find which of the reaction orders fits the vaporization process. To gain the information about the reaction order, the concentration-time data designed in zero, first and second order-reaction patterns were derived and the three plots of concentration of vaporized hydrocarbon

as a function of time of vaporization were also made. The regression analysis was used to estimate the rate order (K). Coefficient of determination (R^2) and y intercept of each crude oil hydrocarbon concentration vaporized form various crude oil-spiked soil samples. The reaction order or rate equations that showed a straight line curve with the concentration-time experimental data satisfactorily fits the process. Here, it is describe various reaction orders using integrated rate law with respect to crude oil vaporization.

RESULTS AND DISCUSSION

The vaporization kinetics data of various crude oil samples used for this work was first studied using the zero order kinetic equation (Xu and Obdard, 2003) which is represented as:

Zero order reaction: Usually, the zero order reaction is written as:

$$\frac{\Delta C}{\Delta t} = KC^0 \quad (10)$$

The law of indices that says that anything raised to power zero is 1, transformed equation to:

$$\frac{\Delta C}{\Delta t} = K \quad (11)$$

The rate law above is rearranged to,

$$\begin{aligned} \Delta C &= -K\Delta t \\ C_t - C_0 &= -K(t - t_0) = -Kt \\ C_t &= -Kt + C_0 \end{aligned} \quad (12)$$

where, C_t , C_0 , K , t represent concentrations of vaporized crude oil at time t and at $t = 0$, the rate constant and time of vaporization, respectively. C_0 and K can be calculated form the plot of C_t versus time (t). A straight curve of this equation will be made to test the fitting ability of the rate law into the crude oil vaporization data.

Table 1 shows the orders of reaction of vaporization processes of crude oil samples A. Table 2 shows that of crude oil sample B and Table 3 shows the order of reaction and vaporization processes of crude oil sample C. Each table contains various soil samples from where the crude oil samples vaporized, the order of reaction, the straight line models and degree of linearity (R^2). Wide variations of reaction order were observed in the vaporization of crude oil samples form the soil samples. Vaporization of crude oil sample A from various soil samples tends to obey the zero order. The vaporization data of oil sample A are well represented by zero order reaction kinetic models. The values of the levels of linearity (R^2 obtained are between 0.5-0.984). This is shown on Table 1. it was also observed that zero order model yield a somewhat better fit with the vaporization data of oil sample A from soil D considering its highest linearity value of 0.9524 (Table 1).

It could be concluded that the recalcitrant nature of oil A on soil D due to its high hydrocarbon concentration couple with the high organic matter and clay properties of the soil was a factor. This conclusion is in support of the study demonstrating that vaporization of high alkane hydrocarbon

Table 1: Reaction orders of vaporization process of crude oil A

Crude oil samples	Soil samples	Order	R ²	Model	Integrated rate law	Straight line plot
A	A	0	0.5955	$y = -0.4635x + 3.7279$	$C_c = -kt + C_0$	C_c vs. t
		1	0.0297	$y = 38.632x - 428.01$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.8834	$y = 0.8874x - 1.1299$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	B	0	0.8418	$y = -0.008x + 0.1081$	$C_c = -kt + C_0$	C_c vs. t
		1	0.0902	$y = 0.2239x - 4.378$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.4023	$y = 31.848x - 133$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	C	0	0.5368	$y = -0.2525x + 3.1393$	$C_c = -kt + C_0$	C_c vs. t
		1	0.6335	$y = -0.3244x + 1.6185$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.3927	$y = 3.9207x - 16.771$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	D	0	0.9523	$y = -0.0129x + 0.1025$	$C_c = -kt + C_0$	C_c vs. t
		1	0.9310	$y = -0.2903x - 1.9842$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.8860	$y = 7.843x - 3.3656$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t

Table 2: Reaction orders of vaporization process of crude oil C

Crude oil samples	Soil samples	Order	R ²	Model	Integrated rate law	Straight line plot
C	A	0	0.7343	$Y = -0.2359x + 2.9568$	$C_c = -kt + C_0$	C_c vs. t
		1	0.8713	$Y = -0.6257x + 3.0921$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.7136	$Y = 3.8373x - 12.886$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	B	0	0.6485	$y = -0.0601x + 0.8123$	$C_c = -kt + C_0$	C_c vs. t
		1	0.6123	$y = -0.1857x - 0.1032$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.8274	$y = 0.8603x - 0.271$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	C	0	0.0003	$y = 0.0102x + 1.4201$	$C_c = -kt + C_0$	C_c vs. t
		1	0.6116	$y = -0.2769x + 1.3255$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.4077	$y = 4.8571x - 23.79$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	D	0	0.3202	$y = -0.0324x + 0.3847$	$C_c = -kt + C_0$	C_c vs. t
		1	0.6584	$y = -0.247x - 1.5712$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.8449	$y = 7.4x + 1.85$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t

Table 3: Reaction orders of vaporization process of crude oil B

Crude oil samples	Soil samples	Order	R ²	Model	Integrated rate law	Straight line plot
B	A	0	0.6233	$y = -0.1501x + 1.9611$	$C_c = -kt + C_0$	C_c vs. t
		1	0.9566	$y = -0.2573x + 1.0957$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.8816	$y = 0.9288x - 2.9343$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	B	0	0.2592	$y = -0.0258x + 0.3551$	$C_c = -kt + C_0$	C_c vs. t
		1	0.3149	$y = -0.1336x - 1.549$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.0605	$y = 1.7421x + 13.972$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	C	0	0.4948	$y = -0.188x + 2.2155$	$C_c = -kt + C_0$	C_c vs. t
		1	0.9444	$y = -0.6402x + 1.8226$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.7724	$y = 89.985x - 392.92$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t
	D	0	0.0077	$y = -0.0079x + 0.1897$	$C_c = -kt + C_0$	C_c vs. t
		1	0.9112	$y = -0.2355x - 1.4446$	$\ln C_c = -kt + \ln C_0$	$\ln C_c$ vs. t
		2	0.7358	$y = 95.89x - 419.83$	$1/C_c = Kt = 1/C_0$	$1/C_c$ vs. t

which obeyed the zero order kinetic models (Ostendorf *et al.*, 2007). The study of Lin *et al.* (1987) on the thermal cracking of heavy crude oil also proved that the vaporization of hydrocarbon gas from the reactor obeyed the zero order kinetic.

First order reaction: The integrated rate law allows the calculation of the concentration of substance as a function of time. Using calculus,

$$\frac{\Delta C}{\Delta t} = KC \quad (13)$$

Calculus was applied on Eq. 13 above to derive the results suitable to determine the rate of reaction on first order basis. With this, the equation is transformed to,

$$\frac{d[C]}{dt} = K[C] \quad (14)$$

Separating the variables of Eq. 14 above changed it to,

$$\frac{d(C)}{(C)} = -K(C) \quad (15)$$

Performing the integration function on Eq. 15 gives:

$$\int_0^c \frac{d[C]}{[C]} = -K \int_0^t dt = \ln[C_c - C_0] = -K[t_1 - t_0] \quad (16)$$

As the volatilization/vaporization process started at the time approximately equal to zero, Eq. 16 is transformed to

$$\ln[C_c - C_0] = -K[t_1] \quad (17)$$

The Eq. 17 can be rearranged to,

$$\ln C_c = -Kt - \ln C_0 \quad (18)$$

where, C_c represents the concentration of the vaporized hydrocarbon with time, t represents time of vaporization, C_0 represents the initial concentration, i.e., concentration of hydrocarbon at $t = 0$ and K represents rate constant.

Then, a plot of $\ln C_c$ versus t was made and the level of its linearity also assessed. The least square estimate of the data evaluated K and C_0 . The rate of vaporization of crude oil sample C from all the soil samples exhibited a first-order reaction kinetic behaviors. This is shown by the level of linearity of the curve (R^2) ranging between 0.61-0.87. Table 2 shows the results of the findings.

The observation of Uzoije (2008) that the rate of vaporization of crude oil sample C being fast within few hours due to its light-hydrocarbon-molecule consistency, could be responsible for this behavior, implying that the study of Uzoije (2008) is in support of the work. The observation that vaporization of light crude oils obeys the first order kinetics is also in line with that of Guipeng *et al.* (2006), where they observed the photochemical degradation of light crude oil in

seawater. Disappearance of light crude oil spiked in the soil amended with nutrients also obeyed the first order kinetic process (Henry and Kenneth, 1991).

Second order: The suitability of Second order reaction rate was also tested in the vaporization process of the crude oil samples. The reaction rate order was presented thus;

$$\frac{dC}{dt} = KC^2 \quad (19)$$

Separating the variables and performing the integration function transform the equation to:

$$\frac{1}{C_c} = Kt + \frac{1}{C_0} \quad (20)$$

A plot of $1/C_c$ versus time of vaporization, t was also made to assess the linearity of the curve by determining its R value. The vaporization rate data obtained were tested with the second order kinetics. Vaporization of crude oil sample B from virtually all the soil samples, except from soil sample B which showed no inclination to any of the reaction orders, obeyed the second order reaction equations with their level of linearity hovering between 0.7-0.8 (Table 3).

CONCLUSION

The rate order equation models for vaporization of crude oil samples from different soil samples of Niger Delta have been studied. It can be concluded that vaporization of crude oil sample A, C and B data obeyed zero, first and second kinetic order models respectively. The results of the study indicate the dependence of the kinetic order model to the crude oil hydrocarbon concentration and the textural properties of the soil.

ACKNOWLEDGMENTS

Our profound gratitude goes to the research unit of the federal university of technology owerri for approving a research grant to enable us carry out this research. The effort of the lab attendant who was on hand to provide necessary laboratory material that facilitated the lab work is highly commendable.

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