International Journal of Academic Information Systems Research (IJAISR)
ISSN: 2643-9026
Vol. 4, Issue 7, July – 2020, Pages: 1-8

Development of Predictive Equation for Dissolution in Crude Oil Spill on Non – Navigable River

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Abstract: *Oil spill into rivers and reservoirs is of great concern as the contamination of water bodies has a devastating and obnoxious effect on marine ecology and local water supply systems. Dissolution of petroleum hydrocarbons into the water column poses risks to aquatic organisms because of the acute toxicity of the compounds that have significant water solubility. The objective of this study is to develop predictive equation for the dissolution of crude oil spill on non-navigable rivers. The equation was developed using dimension analysis. The spilled oil parameters used in the analysis were: oil solubility in water. The coefficients determined and used in the analysis were: dissolution mass transfer coefficient. These parameters were obtained from standards published in journal papers in the field of oil spill modeling. Other parameters used were: the volume of oil spilled and time elapsed. The developed equation was validated against a reference mass loss equation for dissolution using the coefficient of determination R^2 and percentage deviation. The equation predicted a dissolution loss of less than 0.03 percent of initial spill mass 24 hours after a spill. The developed predictive equation had R^2 value of 1.0, which indicates a good fit of the equation. In addition, percentage deviation values of -0.0066 between the predictive equation and reference equation indicate a good agreement between the two equations. The predictive equation will be useful in contingency planning, training, spill response and long – term damage assessment of oil spills in non-navigable rivers.*

Keywords: Dissolution, crude oil spill, non-navigable river

1. INTRODUCTION

An oil spill is the release of a liquid petroleum hydrocarbon into the environment as a result of uncontrolled well blow-out, pipeline rupture or tank failure. The term also refers to marine oil spills where oil is released into the river, sea, and ocean, coastal or inland waters. Oil may be a variety of materials including crude oil, refined petroleum products (such as gasoline or diesel fuel) or by – products, oily refuse or oil mixed in water [1].

According to [2], the persistence of spilled oil in water bodies are determined by physical, chemical and biological processes which are dependent on oil properties, hydrodynamics, meteorological and environmental conditions. These processes are: advection, turbulent diffusion, surface spreading, evaporation, dissolution, dispersion, emulsification, hydrolysis, photo-oxidation, biodegradation and particulation.

When liquid oil is spilled on the water surface it spreads to form a thin oil film – an oil slick. The composition/character of the oil changes extensively from the initial time of the spill, as light (low – molecular weight) fractions evaporate, water – soluble components dissolve in the water column, the immiscible compounds become emulsified and dispersed in the water column as small droplets,[3].

Dissolution is an important process from the point of view of possible biological harm to aquatic life and to humans who use the river water for domestic purposes. It is generally unimportant from the viewpoint of the spill mass balance because less than 1% of the oil slick may dissolve, [3].

Such a low dissolution of oil is a result of three factors which include: the low dissolution mass transfer coefficient, the very small water solubility driving force and the presence of relatively small quantities of the more soluble hydrocarbon hydrocarbons, most of which are more susceptible to evaporation [4]. Most components of oil have very low solubility, but few dissolve readily in water and become part of the water column. The most soluble compounds in water are the light aromatic like benzene and toluene; nevertheless, they are also the first to evaporate, [5]. This process should be distinguished from dispersion, which produces particles or droplets of oil in water. Dissolution could be estimated as a function of superficial area of slick, mass transfer coefficient, the oil solubility in fresh water, the decay exponent and time elapsed [6].

2. MATERIALS AND METHODS

2.1 Description of Non-navigable River

This research was carried out for small non-navigable rivers of the scale typical of a tributary to a navigable river, [7]. According to them, the river is assumed to exhibit a fair degree of meandering and is sheltered from wind by the river banks and vegetation. There may be areas of quiet water or eddies at the inside of river bends and other pools where flow velocities differ from that of the main current.

The cross channel profiles are irregular, with rapids at one extreme and quiet bay at the other. Turbulence results from shear in currents along the banks and river bottom. Increased velocity of flow and bed roughness has direct bearing on turbulence. The river currents and water level are usually increased by seasonal or episodic changes in runoff and rainfall.

2.2 Determination of spilled oil parameters

The spilled oil parameters required for the development of the predictive equation were obtained from standards in papers published by researchers in the field of oil spill modeling. This is because at the initial period of real-life spills, more attention usually is paid to oil combating operations rather than to rigorous measurements. Besides a direct measurement of vast areas, typically affected by such a dynamic event as an oil spill, is an extremely difficult task, [2].

Bonny light crude oil was considered as the specimen for this study as it is the most common crude blend exported from Nigeria, [8].

The spilled oil parameters obtained are as follows:

- Solubility (Kg/m^3): Oil solubility value for Bonny light crude oil in water was obtained from [9]. This parameter (variable) will be used in the determination of mass loss due to dissolution in an oil spill.
- Mass transfer co-efficients (m/s): The values of standard mass transfer coefficient were provided by [7]. These parameters (variables) will be used in the determination of mass loss due to evaporation and dissolution in an oil spill.

2.3 Other relevant data:

- Volume of Spill (m^3): A spill volume in the category of a major spill was assumed for this study, according to [10].

2.4 Reference equation:

- Dissolution could be calculated as a function of superficial area of slick [7]; using the following equation:

$$\frac{d}{dt} = [k_{dis}C_{0.}W]dx \quad (1)$$

$$dx = \left(K_{lv}\left(\frac{\Delta g.V^2t^{1.5}}{v^{0.5}}\right)^{0.25}\right) \quad (2)$$

Where,

d = dissolution loss

K_{dis} = the dissolution rate coefficient

C_0 = oil solubility in fresh water

dx = change in length of slick resulting from spreading in one direction.

W= the width of the slick

k_{1v} = the spreading law coefficient for viscous spreading (k_{1v} = 1.5)

υ = the kinematic viscosity of water

Δ = the ratio of density difference between water and oil to density of water, (Δ =0.14)

g = acceleration due to gravity

t = time

V = the volume of slick per unit length normal to the direction of spreading (per unit width of the river).

2.5 Theory

The governing equations required to evaluate the weathering processes for spilled oil in a river system was established using dimension analysis. With the help of dimensional analysis the equation of physical phenomenon were developed in terms of dimensionless groups or parameters. The methods of dimension analysis are based on the Fourier principle of homogeneity, [11].

- Buckingham's π-theorem: The Buckingham's π-theorem states as follows: If there are n-parameters (governed and governing parameters) in a dimensionally homogenous equation and if these contain m – fundamental dimensions (such as M, L, T, θ and mol), then the parameters are arranged into (n-m) dimensionless terms, called π – terms.

  Mathematically, if any parameter K_1, depends on governing parameter, K_2, K_3, K_4…Kn; the functional equation may be written as:

  $$K_1 = f\ (K_2, K_3, K_3 \ldots K_n)\ = 0 \qquad (3)$$

  Equation (3) may be written as:

  $$f\ (K_1, K_2, K_3, K_4 \ldots K_n)\ = 0 \qquad (4)$$

  It is a dimensionally homogenous equation and contains *n* parameters. If there are *m* fundamental dimensions, then according to Buckingham's π- theorem (4) can be written in terms of a number of π-terms (dimensionless groups) in which number of π-terms is equal to $(n - m)$. Hence (4) become:

  $$f_1\ (\pi_1, \pi_2, \pi_3 \ldots \pi_{n-m})\ = 0 \qquad (5)$$

  Each dimensionless π-term is formed by combining *m* parameters with one of the remaining (*n-m*) parameter i.e. each π-term contains (*m*+1) parameter. These *m* parameters which appear repeatedly in each of π-terms are consequently called repeating parameters and are chosen from among the parameters such that they together involve all the fundamental dimensions and they themselves do not form a dimensionless parameter.

  The final general equation for the phenomenon may be obtained by expressing anyone of the π-terms as a function of the other as:

- Transformation of π–terms: To ensure simplicity in the experimentation process, the present π-terms (π_2, π_3, and π_4,) were adjusted to generate new π-terms by multiplying or dividing with each other [12], while maintaining the independency condition.

- Functional relationship between dimensionless terms (π-terms): The experimental/calculated values of the governed parameter and other governing parameters are substituted into the dimensionless groups. A plot is made of the π-terms containing the governed parameter against the other π-terms. The functional relationship is determined by analyzing the nature of the plot, [13].

3. Development of Predictive Equation

3.1 Determination of Π – terms

The losses in an oil slick as a result of dissolution into the water column are dependent on the following factors:

- Volume of oil spill V (m^3)
- Dissolution rate co – efficient K (m/s)
- Oil solubility in water S (Kg/m^3)
- Time t (s)

The dissolution loss from an oil slick d (kg) is a function of:

V, K, S, t

Mathematically,

$$d\ =\ f\ (V, K, S, t)\ or\ f\ (d, V, K, S, t)\ =\ 0 \qquad (8)$$

Total no. of variables, n = 5

Table 1 show variables expressed in terms of fundamental dimensions:

Table 1: Variables expressed in terms of fundamental dimensions

d	**V**	**K**	**S**	**t**
M	L^3	LT^{-1}	ML^{-3}	T

The fundamental dimensions are:

- Mass (M)
- Length (L)
- Time (T)

Number of fundamental dimensions, m = 3

Thus, number of π- terms = 5 – 3 = 2

From (5):

$$f\ (\pi_1, \pi_2)\ = 0 \qquad (9)$$

Selecting repeating variables as: V, S, K

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π_1 = V, S, K, d (10)

π_2 = V, S, K, t (11)

π_1 –term:

$\pi_1 = V^{a_1}.S^{b_1}.K^{c_1}.d$ (12)

$M^0L^0T^0 = (L^3)^{a_1}.(ML^{-3})^{b_1}.(LT^{-1})^{C_1}.M$ (13)

Equating indices:

$M: 0 = b_1 + 1$

$L: 0 = 3_{a1} - 3_{b1} + c_1$

$T: 0 = -c_1$

Solving the above equations,

$a_1 = -1, b_1 = -1, c_1 = 0$

$\pi_1 = V^{-1}.S^{-1}.K^0.d$ (14)

$\pi_1 = \frac{d}{VS}$ (15)

π_2 – term

$\pi_2 = V^{a_2}.S^{b_2}.K^{C_2}.t$ (16)

$M^0L^0T^0 = (L^3)^{a_2}.(ML^{-3})^{b_2}.(LT^{-})^{c_2}.T$ (17)

Equating indices:

$M: 0 = b_2$

$L: 0 = 3a_2 - 3b_2 + c_2$

$T: 0 = -c_2 + 1$

Solving the above equations

$a_2 = {}^1/_3, b_2 = 0, c_2 = 1$

$\pi_2 = V^{-1/3}.S^0.K^1.t$ (18)

$\pi_2 = \frac{Kt}{V^{1/3}}$ (19)

From the above calculations the determined π-terms are:

$$\frac{d}{VS}, \frac{Kt}{V^{1/3}}$$

According to the π-theorem:

$\pi_1 = \Phi\,(\pi_2)$ (20)

$\frac{d}{VS} = \Phi \frac{Kt}{V^{1/3}}$ (21)

3.2 Determination of functional relationship

Table 2 shows the values of the π – terms after the calculated and pre-determined values of the governing and governed parameters have been substituted:

Table 2: Values of π – terms

$\pi_2 = \frac{Kt}{V^{1/3}}$	$\pi_1 = \frac{d}{VS}$
0.0140	11.9185
0.0280	23.8491
0.0420	35.7710
0.0560	47.6930
0.0700	59.6150

Fig. 1 shows the plot of π_1 (y – axis) against π_2 (x – axis). The functional relationship between the π terms may now be established from the plot.

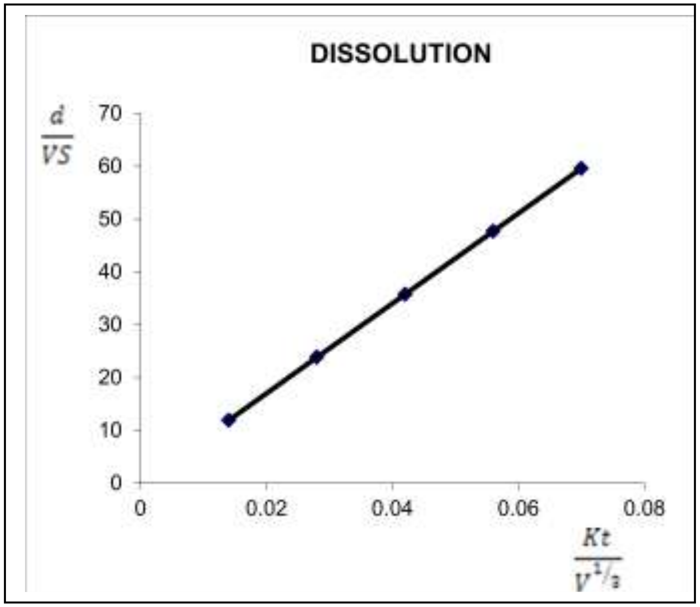

Figure 1: The plot of π_1 term against π_2 term

The plot shows that a line of best fit can be drawn between the points. This line is represented by the expression:

$$y = mx + c \quad (22)$$

Where

m = the slope of the line

C = the intercept of the line on the y – axis

The equation of the line is thus expressed:

$$y = 851.57x + 0.0051 \quad (23)$$

The relationship between the π – terms may now be written as:

$$\frac{d}{VS} = 851.57 \frac{Kt}{V^{1/3}} + 0.0051 \quad (24)$$

The dissolution loss (kg) may be calculated thus:

$$d = VS\left(851.57 \frac{Kt}{V^{1/3}} + 0.0051\right) \quad (25)$$

3.3 Validation

The predictive equations were validated by comparison of computed results from developed and reference equations using coefficient of determination R^2 and percentage deviation. According to [14], the coefficient of determination R^2 is used in the context of equations whose main purpose is the prediction of future outcomes on the basis of other related information. It provides a measure of how well future outcomes are likely to be predicted by the equation. It is a statistic that gives information about the 'goodness of fit' of an equation. A R^2 value of 1.0 indicates a perfect fit of the equation. Percent deviation formula is very useful in determining how accurate the data collected by research really is. The data is usually compared to reference data. If the percent deviation is a negative number that means the student data is lower than the standard value.

Using the equation for coefficient of determination provided by the above mentioned author and percentage deviation formula, the predictive equations were validated against the reference equations for dissolution.

- Coefficient of determination

$$R^2 = \frac{a\sum Y + b\sum XY - n\bar{Y}^2}{\sum Y^2 - n\bar{Y}^2} \quad (26)$$

Where,

R^2 = coefficient of correlation.

$\bar{Y}$ = mean value of Y

X = independent variable (calculated values).

Y = dependent variable (predicted values).

n = number of measurements / calculations.

- Percentage deviation

$$\%\ deviation = \frac{Predicted\ value - Standard\ value}{Predicted\ value} \quad (27)$$

4. Result and Discussion

4.1 Spilled oil parameters (variables)

The parameters (variables) which determine the rate of mass loss due to dissolution, in an oil spill on a river system were identified. Table 3 shows the values of the parameters (variables) that determine the rate of mass loss due to dissolution in an oil spill on a non – navigable river.

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Vol. 4, Issue 7, July – 2020, Pages: 1-8

Table 3: Values of the parameters (variables) that determine the rate of mass loss due to dissolution, in an oil spill on a non – navigable river

S/no.	Parameters (variables)	Value
1	Oil solubility	0.0213 mg/m^3
2	Volume of oil spilled	5,000 barrels = 794.5m^3
3	Dissolution mass transfer coefficient	1.5 x 10^{-6} m/s

- Oil Solubility (mg/m^3): Oil solubility in water is a function of temperature, salinity, oil weathering and water-to-oil volume ratio, [15]. He stated that monoaromatic hydrocarbons have higher solubilities, than similar weight alkanes.
- Mass transfer co-efficient (m/s): In engineering, the mass transfer coefficient is a diffusion rate constant that relates the mass transfer rate, mass transfer area and concentration gradient as driving force. This can be used to quantify the mass transfer between phases, immiscible and partially miscible fluid mixtures. Quantifying mass transfer allows for design and manufacture of separation process equipment and estimate what will happen in real life situations e.g. chemical spills etc., [16].
- Volume of Spill (m^3): A major spill is defined as a discharge of oil in excess of 5000 barrels in inland water ways, land or coastal waters, [10].

4.2 Predictive Dissolution Equation

Predictive equation was developed from the previously described parameters (variables), using dimension analysis. These equations were used to evaluate the percentage mass loss due to evaporation within a period of 24 hours.

Table 4 shows the developed predictive equations and the percentage mass loss due to evaporation, dissolution and dispersion respectively, after a period of 24 hours.

Table 4: Developed predictive equation and the percentage mass loss due to dissolution after a period of 24 hours.

Weathering Process	Predictive Equation	Mass loss (%) (after 24 hours)
Dissolution	$d = VS\left(851.57\frac{Kt}{V^{1/3}} + 0.0051\right)$	0.03

Mass loss due to dissolution from an oil slick is usually less than 1% of the mass of oil spilled, [9], and [4]. This loss is quantitatively not important and seems negligible from the recovery process point of view [9]. From an environmental impact point of view, it is a cause for concern. This is because dissolution of petroleum hydrocarbons into the water column poses risks to aquatic organisms because of the acute toxicity of the compounds that have significant water solubility, [5]. The predictive equation quantifies dissolution loss as 0.03% of total mass in the first 24 hrs.

4.3 Validation of Predictive Dissolution Equation

Table 5 shows the comparison between the results of the dissolution equation of [7] and the predictive dissolution equation. The results of the predictive equation show a cumulative mass loss of 1,009 kg after a period of five (5) days.

The developed predictive equation for dissolution shows a good fit with the reference equation of [7]. The predictive equation has a coefficient of determination R^2 value of 1.00 and an average percentage deviation of -0.0066, indicating a reasonable agreement between the two equations. A graph showing percentage mass loss due to dissolution with respect to time elapsed was plotted for both equations.

Table 5: Comparison between the results of the dissolution equation of [7] and the predictive dissolution equation

Time Elapsed (days)	1	2	3	4	5
	Cumulative dissolution loss (kg)				
Gulliver dissolution equation. $\frac{d}{dt} = [k_{dis}C_{0.}W]dx$	210.8	403.58	605.33	807.05	1008.74
Predictive dissolution equation $d = VS\left(851.57\frac{Kt}{V^{1/3}} + 0.0051\right)$	210.82	403.55	605.3	807.0	1008.8
Coefficient of determination R^2	1.00				
Average percentage (%) deviation	-0.0066				

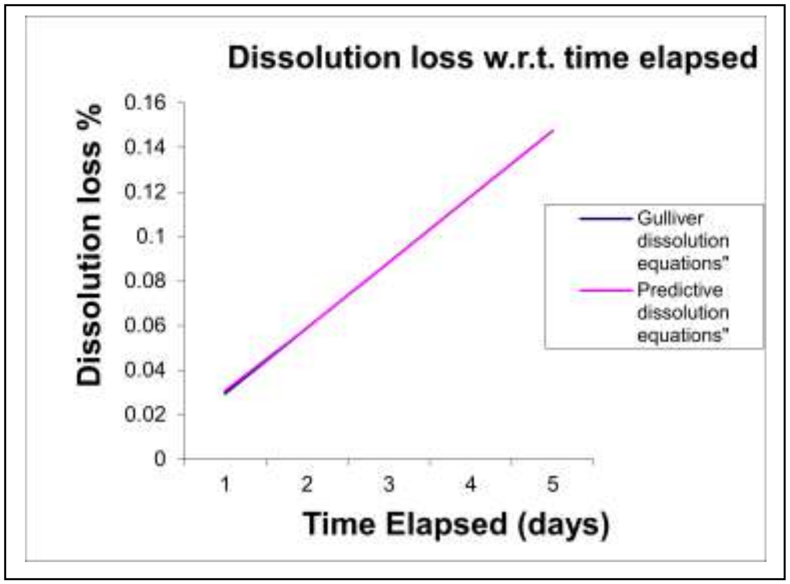

Fig. 2: Percentage mass loss due to evaporation from slick with respect to time

4.4. Conclusion

This study explored the development of predictive equation for dissolution of spilled oil in non-navigable rivers. Dissolution is one among the physico – chemical processes that occurs in an oil spill on a water body. This process results in loss of mass and changes in physical characteristics of the spilled oil. A predictive equation has been developed to evaluate the mass loss due to dissolution process in an oil spill on non-navigable river. Parameters considered in the development of the predictive equation are: spilled oil properties and rate coefficients. The predictive equation was developed from first principles using dimension analysis. The developed predictive equation is as follows:

- Mass loss due to dissolution: $d = VS\left(851.57\frac{Kt}{V^{1/3}} + 0.0051\right)$

The result of the predictive equation showed a mass loss of 0.03% for evaporation, after a period of 24 hours. The result of the predictive equation for evaporation was validated using coefficient of determination. The result obtained was compared with the dissolution equation of [7]. The developed predictive equation had R^2 value of 1.0, which indicates a good fit of the equation. In addition percentage deviation values of -0.0066 between the predictive equation and reference equation indicate a good agreement between the two equations.

5. Acknowledgment

All Praise, Honour and Glory to Almighty God; the greatest inspiration. We are grateful to our family and friends for their unflinching support, love and encouragement, through the duration of this research.

6. References

[1] Wikipedia Online Encyclopaedia (2009). Oil Spill. Retrieved from: http://en.wikipedia.org/wiki/Oil_spill

[2] Tkalich P., Huda K., & Gin K.Y. (2003). A Multiphase Oil Spill Model. Journal of International Association of Hydraulic Engineering and Research, 41(2), 115 – 125.

[3] ESSO (1999). General Oil Spill Response Plan, Section 04 - Fate and Effects of Spilled Oil. Retrieved August 21, 2009, from: http://www.esso.com

[4] Korotenko K. A., Mamedov R. M., & Mooers C. N. K. (2002). Prediction of the Transport and Dispersal of Oil in the South Caspian Sea Resulting from Blowouts. Environmental Fluid Mechanics, 1, 383- 414.

[5] Michel J. (2002). Oil Behavior and Toxicity. Retrieved from: http://www.response.restoration.noaa.gov/book_shelf/678_Chapter2.pdf

[6] Cohen, Y., Mackay, D., & Shiu, W. (1980). Mass Transfer Rates between Oil Slicks and Water. The Canadian Journal of Chemical Engineering, 58, 569-575.

[7] Gulliver J.S., Vaughan V.R., & Hibbs D.E. (2002). Modeling Oil Spills on River Systems: Evaluation of Aqueous Concentrations. Retrieved February 25, 2009, from: http://www.knovel.com

[8] International Tanker Owners' Pollution Federation (2009). Fate of Oil spills & Weathering Processes. Retrieved March 24, 2009, from: http://www.itopf.com/marine-spills.

[9] Bentacourt F., Palacio O., & Rodriguez A. (2005). Effects of the Mass Transfer Process in Oil Spill. American Journal of Applied Sciences, 2 (5), 939 -946.

[10] Egberongbe, F., Nwilo, P., & Badejo, O. (2006). Oil Spill Disaster Monitoring Along the Nigerian Coastline TS16.6', Marine and Coastal Zone Management – Environmental Planning Issues TS16. In Proceedings of 5th FIG Regional Conference, Accra Ghana, 2006.

[11] Rajput R.K. (2003). Heat and Mass Transfer (pp 208 – 210). New Delhi: S.Chand & Company Ltd.

[12] Langhaar, H. L. (1980). Dimensional Analysis and Theory of Models (pp 173 – 174). Florida: R. E. Krieger Publishing Co

[13] Barenblatt, G.I. (1987). Dimensional Analysis (pp. 38 – 48). London: Gordon and Breach Science Publishers.

[14] Kazmier L. J. (1976). Theory and Problems of Business Statistics (pp 265 – 267). New York: McGraw Hill Inc.

[15] McAuliffe C.D. (1986) Organism Exposure to Volatile/Soluble Hydrocarbons from Crude Oil Spills – A Field and laboratory Comparison. In Proceedings of 1987 Oil Spill Conference American Petroleum Institute, Washington. D.C., 275 – 288.

[16] Wikipedia Online Encyclopaedia (2009). Mass transfer coefficient. Retrieved from: http://en.wikipedia.org/wiki/Mass_transfer_coefficent