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Development of Predictive Model for Wax and Asphalthene Deposition in Crude Oil Facilities

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Abstract
This study developed an effective and reliable model for the prediction of wax and asphaltene deposition in crude oil facilities. Regular solution theory was used to develop the model taking into account that four phases are present at the time of deposition. The crude oil was characterized into five pseudo-components using the result obtained from hydrocarbon analysis using Gas chromatography with flame ionization detector and SARA analysis. Equilibrium constants of the phases were determined for each of the pseudo-components thereafter, the regular solution model parameters were determined using recently developed corrections for solubility parameter, density, molar volume and gas phase fugacity. Equilibrium calculations were performed using the standard method of Rachford Rice and phase distribution was used to determine the amount of deposition at the desired temperature. Crude oil sample collected from Kaduna Refinery and Petrochemical Company (KRPC) was used in a laboratory setup comprising a pump, water bath, piping connections, storage tank and isolation valve to experimentally determine the amount of wax and asphaltene deposition at temperatures of 10, 20, 30 and 40 ^{o}C. The simulation of the model with the experimental result shows the validity of the model as a 0.9908 regression value was obtained, and the mean square error was 0.0013 which is low and within the acceptable limit. This model was compared with the Artificial Neural Network (ANN) model developed comparing of 10 neurons in its hidden layer, the ANN model regression was 0.9220 and mean square error of 0.0077 was obtained. This further strengthens the reliability of the developed regular solution model and can be recommended for practical use. With this modeling tool deposition of wax and asphaltene can be prevented right from design or during operations of crude oil facilities.
Keywords: Regular solution model, wax and asphaltene deposition

I. Introduction

Crude oil is a complex mixture of various hydrocarbons and hydrocarbon derivatives, water and other kinds of impurities. Complex and heavy organic compounds contained in crude oil, such as asphaltenes and waxes cause many problems in oil production, transportation and processing. When crude oil temperature is lower than its cloud point, these heavy organic compounds will begin to precipitate in oil reservoirs, pipes, separators, pumps, tanks and other equipment, which can cause a number of problems. When wax and asphaltene precipitate, the crude oil viscosity increases ten-fold or more, as such its velocity decreases leading to increase in load for fluid motive devices and blockage in process facilities (Adesina, Anthony, Ako, & Olawale, 2010). Therefore, one of the biggest problems facing the oil and gas industry in production and transportation of crude oil is to prevent the precipitation of heavy components. Another negative effect of wax and asphaltene deposition are; reduction and subsequent blockage of pipeline internal diameter, reduced oil flow, operation difficulty and leads to huge financial lost in the oil and gas sector or considerably increase production/transportation costs. (Obaseki & Paul, 2020).

The oil industry are currently preventing the deposition of wax and asphaltene formation problem using inhibitors (Obaseki & Paul, 2020). Inhibitors are injected into crude oil so as to prevent wax and asphaltene precipitation even when the crude oil temperature goes below it cloud point. Another approach employed in battling wax and asphaltene deposition is by heating the oil at some points along the pipeline in order to raise the temperature of the oil above it deposition temperature or by insulation to prevent exchange of heat with the surrounding that might reduce the system temperature. Furthermore, pigging (that is the mechanical removal of wax from pipe internal) can be used to treat wax and asphaltene deposition. The three methods stated thus far, result in long term high operation cost and unnecessary downtime in the process which is highly uneconomical and discouraged (Nazar & Dabir, 2001). The problem can however be minimized, if the wax and asphaltene formation potential and deposit amount can be predicted at any given time. One of the ways in which this can be achieved is by proper modeling of the system (Anand, 2018).

Modeling is a valuable tool to check wax and asphaltene precipitation and deposition that can occur in oil industry as crude oil flows in oil production facilities. These models help to predict where and by how much wax and asphaltene builds up in oil production and processing facilities, with such knowledge, the mitigation/inhibition of wax and asphaltene precipitation becomes easier and allows better design and operation that will ensure economic feasibility of petroleum production (Lonje & Liu, 2021; Kamari, Mohmmadi, Bahadori, & Zendehboudi, 2014).

From the forgoing, it is clear that excellent mathematical model that would encompass all the necessary factors of wax and asphaltene deposition during crude oil production, transportation and processing is highly vital.

Several researches have been carried out to model wax and asphaltene deposition using solubility parameter, thermodynamic phase behavior and artificial intelligent tools (like neural networks, support vector machine, fuzzy logic) but not a single model combines both wax and asphaltene deposition together only but recently, where researchers develop thermodynamic models which considers the four phase modeling (Xue, Li, & He, 2019). To that effect, this research like to further investigate and improve the 4-phase model, getting experimental data for wax and asphaltene deposition and analyzing deposits formed for the amount of both wax and asphaltene.

II. Crude Oil Characterization

Crude oil characterization is the first procedure to follow before the modeling process, this involve the division of the fluid into pure and pseudo-components and the attachment of thermodynamic properties to each component (Tharanivasan, 2012). Using the regular Solution Model, the required thermodynamic properties are mole fraction, solubility parameter and molar volume of each component (Ghotbi, Mashhadi, & Jafari, 2016).

The division of the components is based on the crude oil composition and the work of Xue, Li & He, to determine the percent distribution of the components (Xue, Li, & He, 2019).

2.1 Crude Oil Composition and Wax Estimation

The composition of crude oil was obtained from Gas Chromatography with Flame Ionization Detection (GC-FID) analysis to determine the saturates, polyaromatics and aromatics components. A C_{7+} characterization was used to categorize the components into a suitable number of pseudo-components and for assigning critical properties to the pseudo-components. The five pseudo-components employed in the research were light fraction, saturates, aromatics+resines, wax and asphaltene. The first three pseudo-components were obtained directly from GC-FID result. The wax forming potential was estimated using Pedersen method (Pedersen, 1995), the mole fraction, Z^s_i, of the potentially wax forming part of pseudo-component, i, was given as;

$$Z_i^S = z_i^{tot}\left[1-(A+B\cdot M_i)\cdot\left(\frac{\rho_i-\rho_i^p}{\rho_i^p}\right)^c\right] \qquad Eqn.1$$

Where, M_i is the molecular weight in g/mol and ρ_i is the density in g/cm^3 at standard conditions (temperature of 15^{o}C and 1atm pressure) while ρ_i^p is the density of its equi-molecular weight of normal paraffin. A, B and C are constants determined by performing estimation fit to experimental wax precipitation data for seventeen different oils by Pedersen et al, obtained the value of A, B and C as 0.8824, 5.353x10^{-4} and 0.1144 respectively (Pedersen, 1995). The calculation procedure were carried out in Microsoft excel workbook and presented here in appendix B with explanation of each column.

Density of the crude oil components are obtained from the online data base Pub-Chem of the National Library of Medicine and National Center for Biotechnology Information while the density of the equi-molecular weight of normal paraffin is determined from the following correlation

$$\rho_i^p = 0.3915 + 0.0675\cdot\ln M_i \qquad Eqn.2$$

The characterization of asphaltenes were more challenging because they comprise of a mixture of different thousands of chemical species and they are known to self-associate (Tharanivasan, 2012). The parameters required to estimate the amount of asphaltene include aggregation number, shape distribution and associated molar mass were determined from the gamma distribution function as;

$$f(M) = \frac{1}{M_m\Gamma(\beta)}\left[\frac{\beta}{\bar{r}-1}\right]^{\beta}\cdot(r-1)^{\beta-1}\exp\left[\frac{\beta(1-r)}{\bar{r}-1}\right] \qquad Eqn.3$$

Where $\bar{r}$ is the average aggregation number of asphaltene fraction defined as the average molar mass of all self-associated asphaltene sub-fractions ($\bar{M}$) divided by the monomer molar mass as $\frac{\bar{M}}{M_m}$. And β the parameter for the shape distribution. The calculations were performed in Microsoft Excel workbook.

III. Model Development

3.1 Model Selection Process

In recent year thermodynamic models were developed in order to predict the precipitation of wax and the precipitation of asphaltene in crude oil facilities, however, those models seldom consider wax and asphaltene precipitations at the same time. Research by Li et al shows the effects of asphaltene on wax crystallization and provided that the wax would not delaminate without asphaltene but stratify with two clear layers when asphaltene is present in the crude however this is not applicable to crude with low asphaltene content (Li, et al., 2016), other research (Ruwoldt, Subramanian, Simon, Oschmann, & Sjoblom, 2018), (Lei, Han, & Zhang, 2016), (Sun, Wang, Gu, Xu, & Gong, 2017) also showed the effect of asphaltene on wax precipitation. In view of this, Xue et al (Xue, Li, & He, 2019) developed a four phase thermodynamic model to predict wax and asphaltene precipitation in crude oil using the simplified perturbed chain statistical associating fluid theory (sPC-SAFT) to account for the effect of asphaltene on wax precipitation (Xue, Li, & He, 2019). But the sPC-SAFT model requires the turning of parameter based on experimental result obtained, this means that different crude oil will have different turning parameter and the model cannot be applied generally to all crude oil type. In this research work, a four phase wax and asphaltene precipitation model is considered using a different thermodynamic model instead of sPC-SAFT model.

Most literature reviews indicate that models of wax and asphaltene precipitation can be categorized into two; the solid solution model and multi-solid phase model. In this work the solid solution model was used because it considers that all fractions are mutually miscible in the solid phase while multi solid model assumes the fractions are independent. The model implemented uses an equation of state for vapor–liquid equilibrium modeling and an activity coefficient for solid–liquid equilibrium modeling. There are several activity coefficient models for describing the non-ideality of solid (such as wax and asphaltene) and liquid phases, these include regular solution model, Flory-solid model, modified regular solution model and a universal quasi chemical activity coefficient (UNIQUAC) model (Xue, Li, & He, 2019). This work uses the regular solution model because the model avoids the use of estimated molecular mass of the pseudo-components which create high uncertainty especially for asphaltene which is difficult to characterize (Tharanivasan, 2012). The Equation of state model employed is the Peng-Robinson equation of state for the vapour-liquid equilibrium.

3.2 Regular Solution Model Development for Wax And Asphaltene Precipitation

The K values for vapour-liquid equilibrium, wax-liquid equilibrium and asphaltene-liquid equilibrium are given as;

$$K_i^v = \frac{x_i^v}{x_i^l} = \exp\left\{\frac{v_i^L}{v_{mix}^L} - \frac{v_i^v}{v_{mix}^v} + ln\left(\frac{v_i^v}{v_{mix}^L}\right) - ln\left(\frac{v_i^L}{v_{mix}^H}\right) + \frac{v_i^v}{RT}(\delta_i^v - \delta_{mix}^L)^2 - \frac{v_i^L}{RT}\left(\delta_i^v - \delta_{mix}^l\right)^2\right\} \quad Eqn.4$$

$$K_i^w = \frac{x_i^w}{x_i^l} = exp\left\{\frac{v_i^w}{v_{mix}^w} - \frac{v_i^L}{v_{mix}^L} + ln\left(\frac{v_i^L}{v_{mix}^L}\right) - ln\left(\frac{v_i^w}{v_{mix}^w}\right) + \frac{v_i^L}{RT}(\delta_i^L - \delta_{mix}^w)^2 - \frac{v_i^w}{RT}(\delta_i^L - \delta_{mix}^w)^2\right\} \quad Eqn.5$$

$$K_i^a = \frac{1}{x_i^l} = exp\left\{\frac{v_i^a}{v_{mix}^a} - \frac{v_i^L}{v_{mix}^L} + ln\left(\frac{v_i^L}{v_{mix}^L}\right) - ln\left(\frac{v_i^a}{v_{mix}^H}\right) + \frac{v_i^L}{RT}(\delta_i^L - \delta_{mix}^a)^2 - \frac{v_i^a}{RT}(\delta_i^L - \delta_{mix}^a)^2\right\} \quad Eqn.6$$

Where δ and v are the solubility parameter and molar volume of the liquid, vapour, wax and asphaltene phase. R is the rate gas constant and T is the temperature of the system. According to the phase equilibrium theory, if all of the vapor, liquid, wax-rich, and asphaltene-rich exist at a fixed temperature and pressure, the fugacities of fraction *i* that form wax or asphaltene in each phase must be equal:

$$f_i^s(p,T,x_i^s) = x_i^s\gamma_i^s f_{Pure,i}^s \quad Eqn.7$$

$$f_i^l(p,T,x_i^l) = x_i^l\gamma_i^l f_{Pure,i}^l \quad Eqn.8$$

$$f_i^s(p,T,x_i^s) = f_i^l(p,T,x_i^l) \quad Eqn\ 9$$

The equation for equal fugacity is obtained by combining the three equations above, which gives

$$\frac{f_{Pure,i}^L}{f_{pure,i}^s} = \frac{\gamma_i^s x_i^s}{\gamma_i^L x_i^L} \quad Eqn.10$$

Where γ is the activity coefficient, estimated with the regular solution theory in terms of solubility parameters for the solid and liquid phase as;

$$Eqn.11$$

$$ln\gamma_i^L = \frac{v_i^L\left(\bar{\delta}^L - \delta_i^L\right)^2}{RT} \quad Eqn.12$$

$$ln\gamma_i^S = \frac{v_i^S\left(\bar{\delta}^S - \delta_i^S\right)^2}{RT} \quad Eqn.13$$

$$Eqn.14$$

$$\bar{\delta}^L = \sum_i \varphi_i^L \delta_i^L \quad Eqn.15$$

$$\bar{\delta}^S = \sum_i \varphi_i^S \delta_i^S \quad Eqn.16$$

$$\varphi_i^L = \frac{x_i^L v_i^L}{\sum_i x_i^L v_i^L}$$

$$\varphi_i^S = \frac{x_i^S v_i^S}{\sum_i x_i^S v_i^S}$$

Where φ_i^S and φ_i^L are the volume fraction of component i in the solid and liquid phase respectively, v_i^S and v_i^L are the solid and liquid molar volumes, δ_i^S and δ_i^L are the solubility parameters of component i in the solid and liquid phase respectively, the solubility parameter in the liquid phase for paraffins is expressed as;

$$\delta_i^L = 8.6 - \exp(2.219195 - 0.54907 MW_i^{0.3}) \quad Eqn.17$$

While for napthenic components is given as;

$$\delta_i^L = 8.7 - exp(2.219195 - 0.54907 MW_i^{0.3}) \quad Eqn.18$$

And for aromatics is given as

$$\delta_i^L = 8.8 - exp(2.219195 - 0.54907 MW_i^{0.3}) \quad Eqn.19$$

The solubility parameter of the components in the solid phase is given as;

$$\delta_i^S = \left(\frac{\Delta h_i^f}{v_i} + \delta_i^{L^2}\right)^{0.5} \quad Eqn.20$$

The solid and liquid molar volumes are expressed as;

$$v_i = v_i^S = v_i^L = \frac{MW_i}{D_{i,25}^L} \quad Eqn.21$$

Where $D_{i,25}^L$ is the liquid phase density of component i at 25 ^oC which can be evaluated as

$$D_{i,25}^L = 0.8155 + 0.672 \times 10^{-4} MW_i - \frac{13.06}{MW_i} \quad Eqn.22$$

The calculation of the solubility parameter and molar volume with Molecular weight of each component were done using Microsoft Excel worksheet. The fugacity of pure (pseudo) components in wax-rich phase or asphaltene-rich phase is generally obtained according to its liquid fugacity, heat of fusion, melting point and heat capacity of fusion.

$$\ln\left(\frac{f^s}{f^l}\right) = -\frac{\Delta H_{f,i}}{RT}\left(1 - \frac{T}{T_{f,i}}\right) + \frac{1}{R}\int_{T_{f,i}}^{T} \frac{\Delta C_{pi}}{T} dT - \frac{1}{RT}\int_{T_{f,i}}^{T} \Delta C_{p,i} dT \quad Eqn.23$$

$$\ln\left(\frac{f^s}{f^l}\right) = -\frac{\Delta H_{f,\ i}}{RT}\left(1 - \frac{T}{T_{f,\ i}}\right) - \frac{\Delta C_{pi}}{R}\left[1 - \frac{T}{T_i^f} + \ln\left(\frac{T_i^f}{T}\right)\right] \quad Eqn.24$$

Where superscript s stands for wax-rich phase or asphaltene-rich phase. The melting point $T_{f,\ i}$ and the heat of fusion $\Delta H_{f,i}$ of paraffinic, naphthenic and aromatic carbohydrates with the same molar mass are quite different. The paraffin's melting point and heat of fusion are obtained by the correlation proposed by

$$T_{f,\ i} = 374.5 + 0.02617 M_i - \frac{20172}{M_i} \qquad M_i \leq 450 \quad Eqn.25$$

$$T_{f,\ i} = 411.4 - \frac{32326}{M_i} \qquad M_i > 450 \quad Eqn.26$$

$$\Delta H_{f,\ i} = 0.5969 M_i \cdot T_{f,\ i} \quad Eqn.27$$

Lira-Galeana et al. suggested that the melting point and heat of fusion for naphthenic and aromatic carbohydrates are calculated with the following equation (Xue, Li, & He, 2019);

$$T_{f,\ i} = 333.46 - 419.01 \exp(-0.008546 M_i) \quad Eqn.28$$

$$\Delta H_{f,\ i} = 0.2208 M_i \cdot T_{f,\ i} \quad Eqn.29$$

According to the correlation from Pedersen et al, the heat capacity is considered as a function of system temperature and molar mass (Pedersen, 1995);

$$\Delta C_{pi} = 1.2695M_i - 1.94014 \times 10^{-3} M_i \cdot T \qquad Eqn.30$$

3.3 Equation of State (Eos) Model

The Peng Robinson EOS was developed by D. Peng and D. B. Robinson by fitting experimental data in 1976 and has become the most popular equation of state in estimating crude oil properties like fugacity (Ghotbi, Mashhadi, & Jafari, 2016). This equation of state is selected because it provides good estimation accuracy near the critical point of the components, good prediction of vapour-liquid equilibria and it incorporates acentric factor to take into account gas molecule shape and attraction between gas molecules to improve temperature dependency of the model. The EOS is given as

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \qquad Eqn.31$$

Where, P, T and V are the pressure (Pa), temperature (K) and molar volume (m^3 mol^{-1}) of the system, R is the rate gas constant (8.314J mol^{-1} K^{-1}), while a and b are Peng-Robinson constant which can be determined as follows;

$$a(T) = \alpha a(T_c)$$

$$a(T_c) = \frac{0.45724(\alpha R^2 T_c^2)}{P_c} \qquad Eqn.32$$

$$b = \frac{0.07780(RT_c)}{P_c} \qquad Eqn.33$$

$$\alpha = 1 + k\left(1 - \sqrt{\frac{T}{T_c}}\right)^2 \qquad Eqn.34$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad Eqn.35$$

Equation 3.34 can be expressed in term of compressibility factor (Z) as

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - 9AB - B^2 - B^3) = 0 \qquad Eqn.36$$

Where A and B are equivalent expression give as;

$$A = \frac{(a\alpha)_i P}{R^2 T^2} \quad \& \quad B = \frac{b_i P}{RT} \qquad Eqn.37$$

Considering the equation of fugacity,

$$lnf = lnP^* + \frac{1}{RT}\left[PV - RT - \int_{v^*}^{v} Pdv\right] \qquad Eqn.38$$

The equation relating fugacity with Peng Robison equation of state is obtained by substituting equation into equation 3.42 and integrating

$$f_i^v = \exp\left\{\frac{(Z-1)B_i}{B} - ln(Z-B) - \frac{A}{2.828427B}\left\{\frac{2A_i}{A} - \frac{B_i}{B}\right\} ln\left\{\frac{Z + 2.41421536B}{Z + 0.41421536B}\right\}\right\} \qquad Eqn.39$$

Thus the fugacity of the vapour phase can be calculated.

3.4 Model Development Procedure

The steps used in developing this model were as follows;

1. Peng Robison equation of state is use to determine the vapour phase fugacity, equation 3.
2. Equilibrium constant of the vapour and liquid phase is then evaluated from the critical property of the vapour equation

$$\ln K_i = \ln\left(\frac{P_{ci}}{P}\right) + \frac{5.37(1+\omega)}{1 - \frac{T_{ci}}{T}} \qquad Eqn.40$$

3. Liquid fugacity f^L is then evaluated from equation 3.4
4. Fugacity of the solid state (wax and asphaltene) are then evaluated using fugacity ratio according to equation 24
5. Equilibrium calculations are then performed using equations 5 & 6 for wax and asphaltene respectively according to standard technique from Rijkers & Heidemann.
6. Rachford Rice flash calculations is then performed to determine the phase separation of wax and asphaltene into light and heavy phase, the criteria are as follows;

$$h(v) = \sum \frac{(K_i - 1)z_i}{1 + (K_i - 1)v} = 0 \qquad Eqn.42$$

where i represent the pseudo-components (light, liquid, asphaltene and wax), v is the ratio of and k_i is equilibrium constant. The only unknown in the above equation is the ratio of , which is evaluated using iteration.

7. The phase distribution is then evaluated as

$$x^L = \frac{z_i}{1 + (K_i - 1)v} \; and \; x^h = \frac{K_i z_i}{1 + (K_i - 1)v} \qquad Eqn.43$$

8. The model convergence is checked using equation 3.13. If the fugacity of the light and heavy are equal, then the model converges but if otherwise the Ki value is updated using the equation below and steps 5 to 7 are repeated until model converges.

$$lnK_i^{(n+1)} = lnK^{(n)} - g^{(n)} \qquad Eqn.44$$

Where $g^{(n)}$is convergence step change given as the natural logarithmic ratio of the two fugacity $\ln\left(\frac{f_i^v}{f_i^l}\right)$.

3.5 Experimental Data Collection Procedure

A schematic of the experimental setup is shown in Figure 1; it consists of a pump, water bath, metallic pipe, crude oil reservoir, pipe connectors and a valve.

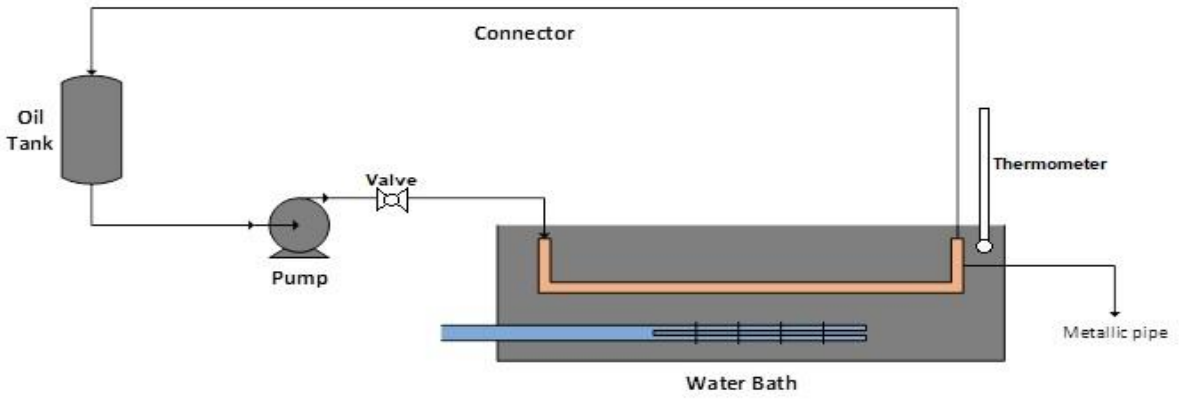


Figure 1. Schematic diagram of wax and ashpaltene deposition experimental setup

A valve was used to regulate the flow and pressure of the crude in the system so that variation of pressure will be noticed. The temperature of the system was controlled by a water bath. The temperature was varied based on the crude oil pour point and asphaltene appearance temperature. Each experimental run took 1 hour before stopping and scrapping of the pipe. The amount of asphaltene deposited was analysed and recorded.

The wax content of the sample was determined using the procedure outlined by Mahto and Singh (Mahto & Singh, 2013). For the determination of wax content, 6.0 g of the crude oil sample was taken in a 500 ml conical flask then 200 ml of petroleum ether was added and heated mildly with little agitation. 45 g of fuller earth clay was added to the solution and stirred uniformly, the solution is then placed on a water (stem) bath at temperature above 60 ^{O}C and evapourated to dryness. The residue is allowed to cool to room temperature after which 150 ml of acetone and 5 ml of petroleum ether were added and stirred uniformly. Wax precipitate out of the resultant solution after it have settled for 15 minutes, the solution is carefully filtered using a normal filter paper, the filter paper is allowed to dry for 10-12 hours at room temperature then weighed. The difference in weight of the filter paper before and after filtration gives the weight of wax content in the sample.

For the determination of asphaltene, 2 cm^3 of the sample was taken in a conical flask then 60 cm^3 of n-heptane was added to precipitate the asphaltene from the sample. The precipitate was filtered and weighed.

3.6 Artificial Intelligent Model

In order to develop an intelligent model based on Artificial Neural Network for predicting asphaltene and wax deposition in crude oil facilities, a comprehensive experimental dataset was used for developing the models from (Ghotbi, Mashhadi, & Jafari, 2016). The experimental data measured wax and asphaltene precipitation amount using

variation in temperature ranging from 273K to 300K. The characterization of sample crude oil is presented in Table 1.

Table 1. Characterization of crude oil used for ANN model

S/N	SARA Components	Weight percent
1.	Saturate	35.8
2.	Aromatic	48.5
3.	Asphaltene	2.5
4.	Resin	13.2

A total of 5 experimental data set were used to develop the model in MATLAB application software, this is because the software facilitates ease of simulation, provides great accuracy, produces standard algorithm and saves time (Agwu, Akpabio, Alabi, & Dosunmu, 2018). Four experimental data from the crude sample in this research was used in model validation to determine the model accuracy.

3.6.1 Artificial Neural Network Model Description

This model was developed in MATLAB application software using the inbuilt nntool user interface, 5 input and output data sets were used to train the model while 4 data set were used to test and validate the model. In modelling ANN, the input, hidden and output layer must be determined. The number of input neurons is specified by the number of input variables while the output neuron is determined by the number of output variable. The hidden layer neuron was determined by trial and error, because the hidden layer extracts the underlying dependence between the input and output data, as such the neurons and number of hidden layer varies for any set of input and output (Lonje & Liu, 2021). However one hidden layer networks are more popular for practical applications due to their simple structures and time saving (Ashoori, Abdini, Abedini, & Nasheghi, 2010). The training algorithm used for the hidden layers is also an important factor that determine the accuracy of the neural network, during training phase, the network output is compared with the desired output of the experimental dataset. The error between these two values is used to adjust the weights and bias of each neuron in the hidden layer until they are fully optimized based on the number of iteration input (Abedini & Abedini, 2011). The training algorithm is also determined using trial and error with the following combination been the best trainlm, trainsg and trainsic in the order of first to last will be use for the input, hidden and output layer. And the number of iteration is set at 1,000 epochs, because if the number of weights in a network is higher than useable data, the error in fitting the non-trained data firstly decreases, but then increases as the network become over trained and over fitting problem is occurred (Ahmadi, 2012).

Levenberg Marquardt training algorithm was used as the training algorithm. After the model development, it was validated using 4 experimental data from the result obtained from the Nigerian waxy crude oil.

Figure 2. ANN model architecture

IV. Results and Discussion

The regular solution model algorithm used in this work is represented in Figure 3, detailed calculations were carried out in Microsoft Excel worksheet.

4.1 Crude Oil Composition

The results of the compositions of the crude oil samples used are given in Figure 4. A total of 35 components were detected in the crude oil sample by the Flame Ionization Gas Chromatography, the crude oil contained more of the saturate hydrocarbon as they constitute 84.80% of the total crude oil composition with Pentadecane been the highest of all the components. The aromatic content of the crude is also high with Drbenze(a_h)anthracene constituting 10 % of the total crude oil composition. Due to the high paraffinic content of the crude, the wax precipitation and deposition potential is high because long chain hydrocarbon such as pentacosane, hexacosane, nonacosane, tritriacontane, hexatriacotane contributes majorly in the formation of wax. The asphaltene component are mainly present in long chain polyaromatics component of the crude, however from the crude oil analysis the long chain polyaromatics constitute less than 5 % of the total crude oil component as such the potential of asphaltene deposition is low. Furthermore, the presence of resins in the crude will reduce the deposition potential of wax and asphaltene in the crude oil facilities, because resins tend to equilibrate and stabilize the asphaltenes in crude oil (Gholami, Mohammadzadeh, Kord, Moradi, & Dabir, 2015).

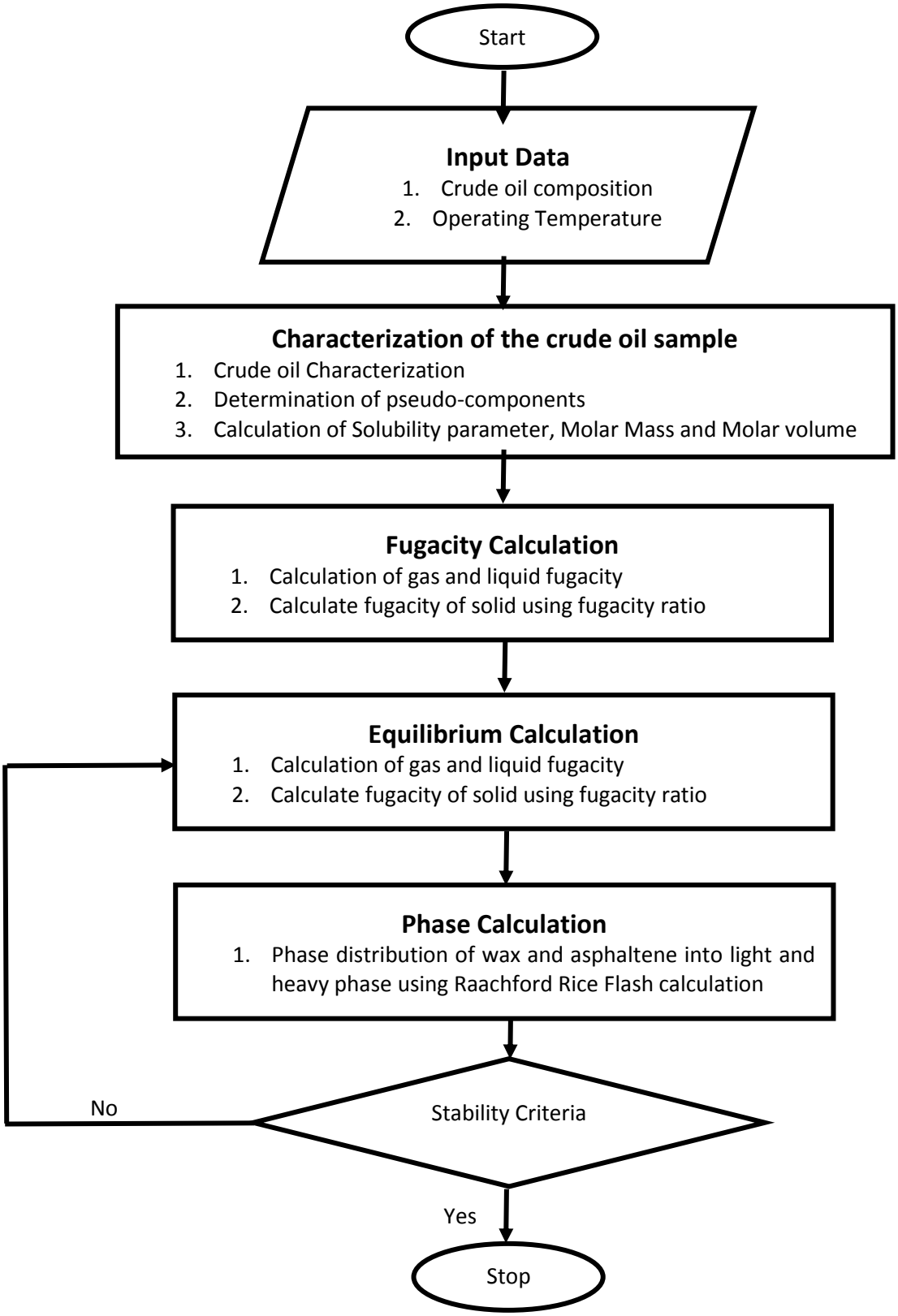


Figure 3 Modeling algorithm of the regular solution model

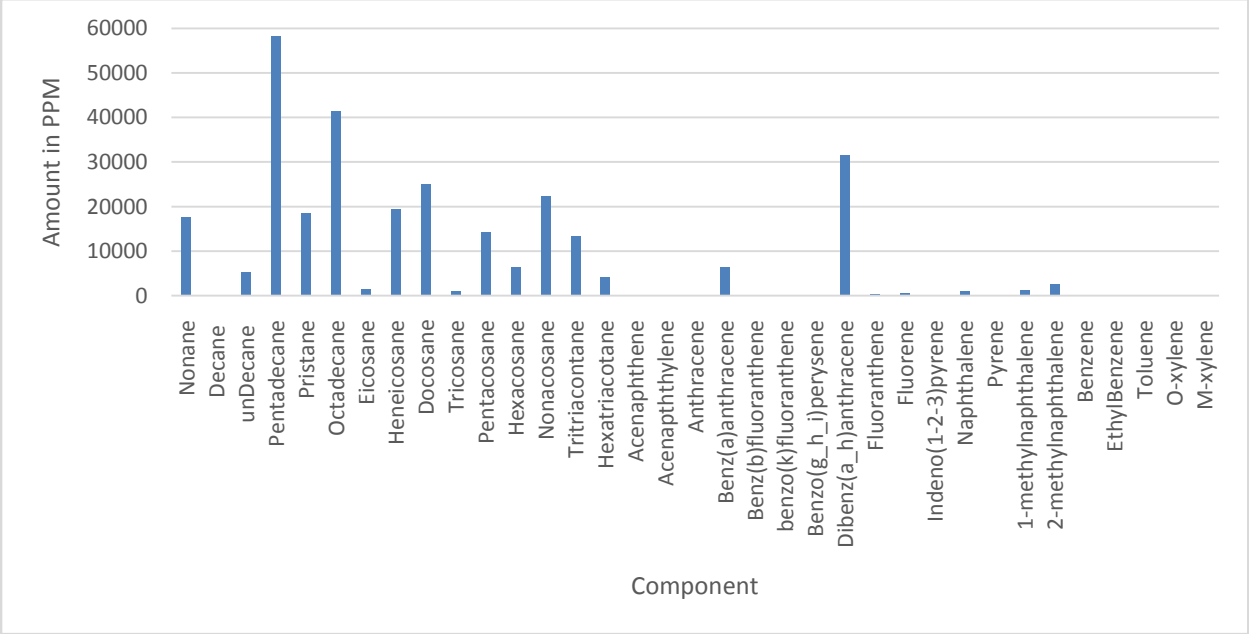


Fig.ure 4 Amount of individual components in the sample crude oil detected by GC-FID

For the purpose of developing a thermodynamic model, the crude oil components were divided into five pseudo components; light, saturates, aromatics+resin, wax and asphaltene, the fractional compositions determined are represented in Table 2.

Table 2 Pseudo-components division of the crude oil

S/N	Component	Mole fraction percent
1.	Light	3.82
2.	Saturates	38.77
3.	Aromatics + resin	12.75
4.	Wax	30.90
5.	Asphaltene	13.76

The pseudo components of the crude oil tell very much about the potential of deposition of the wax and asphaltene in crude oil, according to a study by Zhu et al. (2008) crude oil with more than 50% fraction of saturates (flocculants which include paraffinic wax) are most likely to precipitate and deposit wax in the crude oil facilities. As shown in the table above, crude oil sample contains more than 50% of wax and saturates contained, which indicate high paraffin content. As such the crude oil for this study is termed to be unstable with respect to wax deposition. On the other hand, the aromatic components are more polarizable differently their presence in crude oil gives more stability to the asphaltene molecules, they act as binders between the missed micelle and saturates with asphaltene (Makwashi, 2020). Also resin molecules prevent any significant aggregation of asphaltene therefore, the crude oil in this work with aromatic and resin content of 12.75% that is slightly lesser then the mole fraction of asphaltene, which indicates that the asphaltene fraction cannot easily precipitate to solid phase and deposit in the oil processing facility.
The SARA analysis is also an indication of the rheological behaviour of the crude oil such as viscosity, shear stress and density.

4.2 Thermodynamic Model Result

The model developed in this work was coined from the work done by Xue et al (Xue, Li, & He, 2019) that modeled wax and asphaltene precipitation using 4-phase thermodynamic equilibrium with multi-solid solid theory, the model is then modified in this work using regular solution theory that uses solubility parameter instead of molecular weight, additionally a new approach of estimating the fusion properties of crude oil pseudo components was used. The SARA fraction result obtained was used to obtain the solubility parameter with the new approach presented in Table 3. The regular solution model developed in this work and detailed calculations were carried out in

Microsoft Excel, the performance of the model was compared with the Multicomponent solution model and presented in Figure 5 (Ghotbi, Mashhadi, & Jafari, 2016).

Figure 5 represent the simulation of experimental data of wax and asphaltene deposition at temperature range of 273 to 300 K. Five experimental data points represented here were obtained from (Ghotbi, Mashhadi, & Jafari, 2016) along with their developed thermodynamic model using multi-component solution theory. The major drawback of the multicomponent solution model is that it mostly overestimates the wax and asphaltene deposition amount at a given temperature. As indicated in figure 4.2, the multicomponent solution model estimates the deposition fraction at 273K to be 0.0072 while the experimental value is 0.00604 thus having a deviation of 0.00116 more than the experimental value on the other hand, the deviation of the regular solution model at the same temperature was found to be 0.000036.

However, as the temperature increase there is an observed reduction in deviation for both models, this is because the deposition of wax and asphaltene reduces with the given temperature range and the thermodynamic parameters of the multicomponent model have better estimate at temperature close to the critical temperature. The regular solution model on the other hand, as a closer range with the experimental data with four out of five having close overlapping, the initial value deviates the most with a value of 0.00036, other deviation values are less than 0.0001.

Table 3 Solubility parameters of the regular solution model

S/N	Pseudo-Component	Solid solubility parameter	Liquid solubility Parameter
1.	Light	7.297416346	7.297416346
2.	Saturates	8.010588097	8.010588097
3.	Aromatics + resine	7.873964438	7.873964438
4.	Wax	16.5942746	8.293529629
5.	Asphaltenes	17.3216918	8.417250944

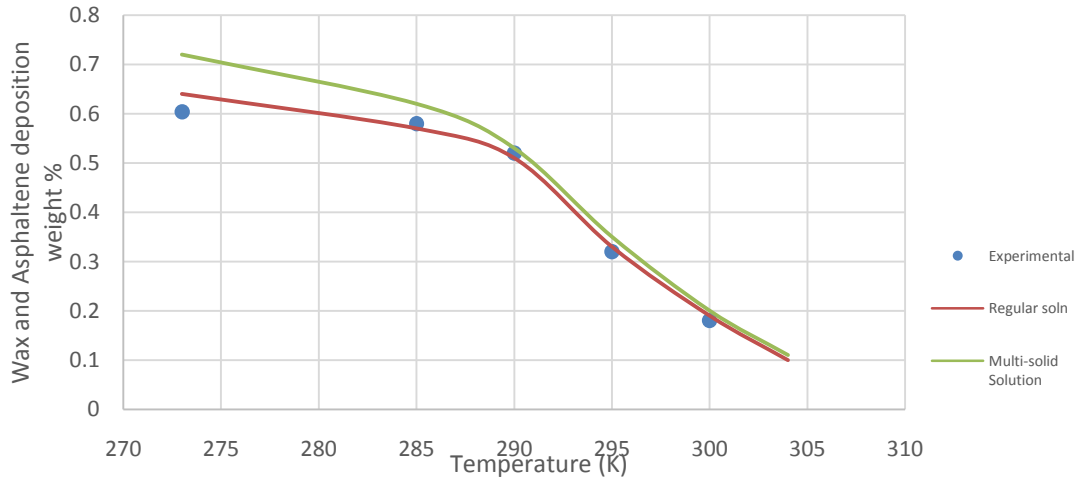


Fig.ure 5 Comparison between regular solution model and multi-solid solution model

Furthermore, comparing the two model base on the average deviation from the experimental data considered, the multi-solid solution model has a higher deviation of 0.000432 while the regular solution model deviates with an average value of 0.000152. This is thus showing the arrangement of the regular solution model developed with the experimental data in lieu to the multi-solid solution model.

4.3 Experimental Results

The results obtained for each sample analyzed is tabulated and presented in Table 4, for each test (at a specific temperature) 6.0 g of crude oil sample, the percentage of deposition was determined as the difference in weight of filter paper after filtration and drying with the initial weight of the filter paper before filtration divided by the weight of crude oil sample (6.0 g).

The deposition of wax and asphaltene in crude oil facilities generally decrease with temperature, however from some literatures the deposition increase or decrease depending on the temperature range considered (Lonje & Liu, 2021). From the result in Table 4, the deposition amount decreases with increase in temperature for the

temperature range of 10^{O}C to 40^{O}C. The trend of the deposition decrement with temperature is observed to be closely linear for the four data point with slope of 0.0168, this agrees with most literature consulted for crude oil with similar SARA content and specified temperature range (Ghotbi, Mashhadi, & Jafari, 2016).

Using the experimental temperature range, wax and aspaltene deposition amount was simulated using the developed regular solution model, the values obtained were in close proximity with the experimental data. The deviation ranges from 0.00067 to 0.05833 expect for the last data at 40^{O}C that the model output was indicating no deposition because the value obtained was a negative value. By extrapolating the developed model predict that there will be little to insignificant deposition of wax or asphaltene above 36^{O}C. This indicate that the crude oil can be transported and easily circulated in any facility without much fear of deposition, however it will be recommended that preventive measures are put in place for long time accumulation of deposit in the facility.

The average deviation of the developed model to the experimental readings is calculated as 0.02642. This value indicates the agreement between the model developed and experimental data obtained. The plot of the model developed with the experimental is presented in Figure 6.

Model accuracy is further determined with statistical measuring tools that includes regression R, mean square error MSE, coefficient of determination R^2, efficiency coefficient E2, mean absolute error MEAE% and maximum absolute error MAAE%.

Table 4 Experimental data of wax and asphaltene deposition at various temperature

S/N	Temperature (^{o}C)	Amount deposited per 6 g sample	Percentage deposition
1.	10	0.032	0.533
2.	20	0.025	0.417
3.	30	0.011	0.183
4.	40	0.002	0.033

According to the values obtained in Table 5, the developed thermodynamic model has a good performance in terms of predicting the amount of wax and asphaltene deposition for the crude oil used in this research. High value of determination coefficient and regression indicates the success of the model in predicting the deposition amount of wax and asphaltene, the low value of the mean square error also confirms the accuracy of the model. However, the mean absolute error and mean average absolute error values are high and this is because the developed model predicted no deposition will occur for the given crude oil sample for temperature above 36^{o}C.

4.4 Artificial Intelligent Model

An Artificial Neural Network (ANN) model for wax and asphaltene deposition was developed in MATLAB application software using the inbuilt nntool, 5 data set were employed from (Ghotbi, Mashhadi, & Jafari, 2016) with temperature and weight percentage of precipitate as input and target data respectively. The developed ANN has a one input layer with one neuron (the input variable; temperature), one hidden layer with 10 neurons and one output layer with one neuron. The model ran successfully with 3 iterations and error performance of 6.82E-17.

Figure 7 showed the training performance of the model, the regression (R) value indicates a good agreement between the model output and input data, the closer the regression value is to unity the more accurate is the model. The maximum deviation of the model to the five experimental data was determined to be 0.01 and mean absolute relative error of 11.78%.

The ANN model is validated and tested with the experimental data obtained in this research work, the model performance is presented in Figure 8. From the graph the predicted ANN model made some over and under estimation of the experimental data. The first and the last data (283 K and 303 K) were underestimated while the second and third data were overestimated. Meanwhile the closest prediction the model made was for the experimental

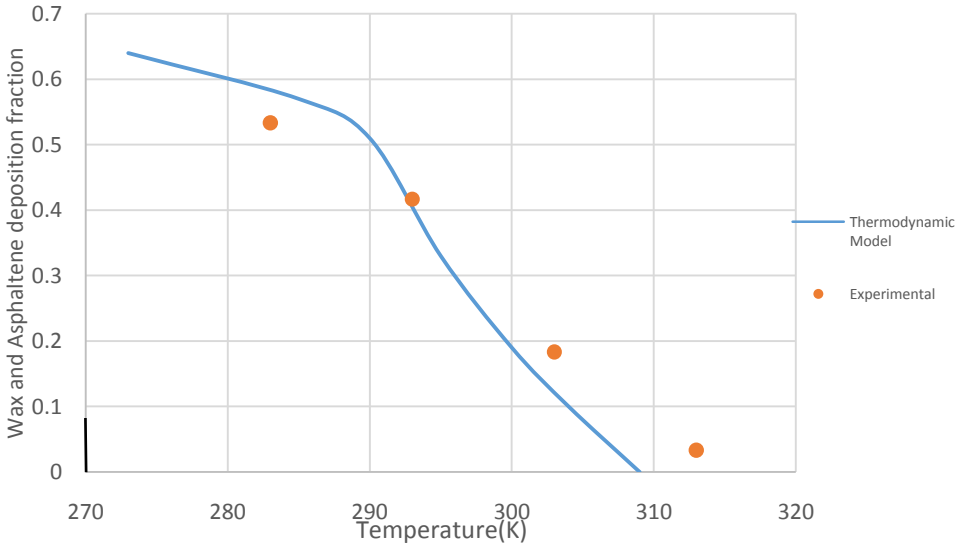
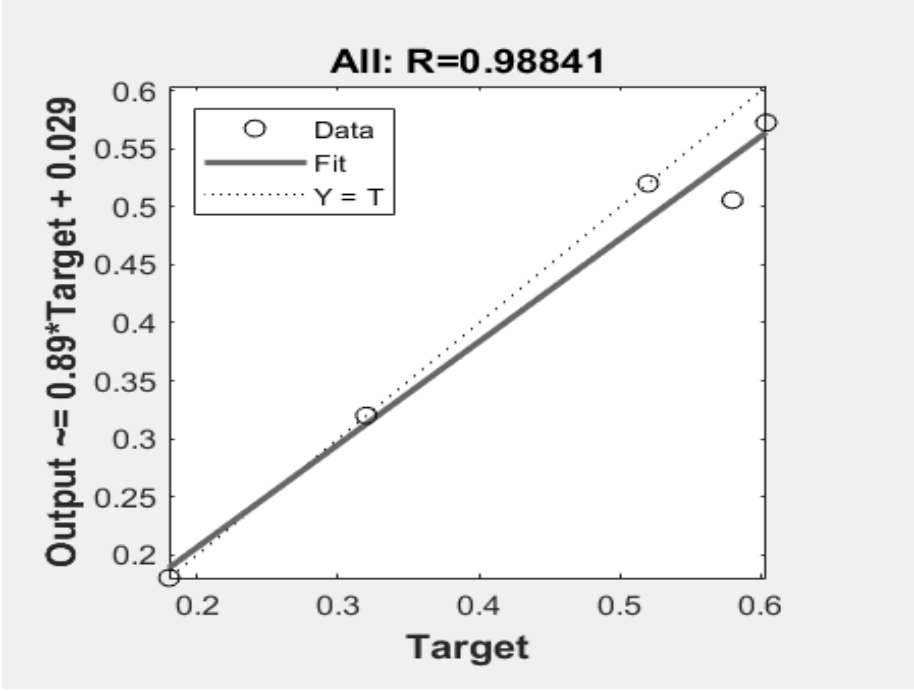


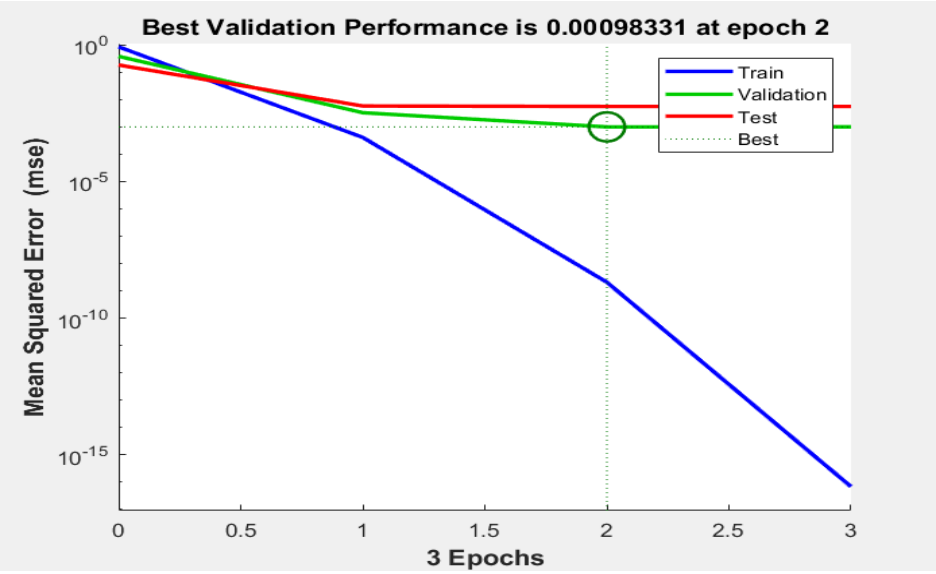
Fig.ure 6 Plot of the thermodynamic model developed and experimental data

Table 5 Statistical tool for model accuracy of the regular solution model

S/N	Accuracy tool	Value
1.`	Regression	0.99081202
2.	Mean square error	0.00139525
3.	Coefficient of determination	0.96340327
4.	Efficiency coefficient	0.96340327
5.	Mean absolute error %	10.1822954
6.	Maximum absolute error %	59.6590909



(a)



(b)

Figure 7 Training performance of the ANN model

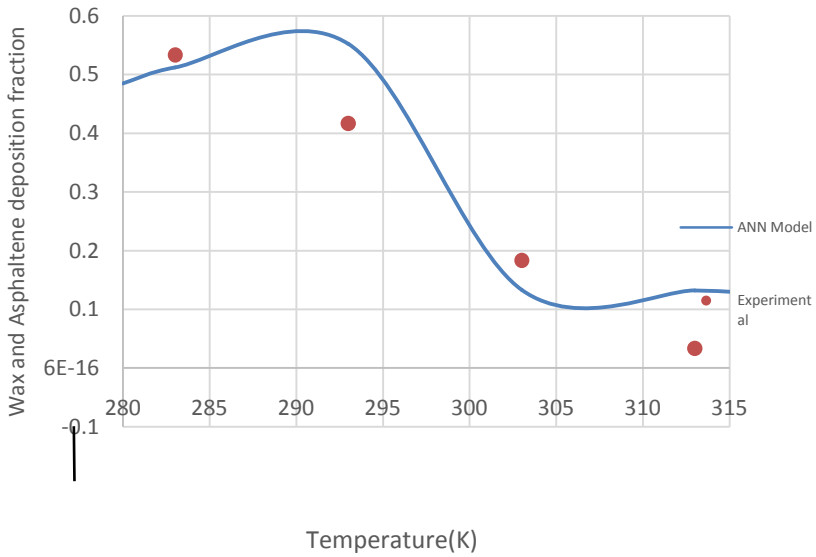


Fig.ure 8 Plot of ANN model with experimental data

deposition at 283 K that gave a deviation of 0.02145 while 0.1355 deviation was measured for the experimental data at 293 K. However, the average deviation of the ANN model was 0.07649 this is higher when compared to the regular solution model with a deviation of 0.0262. The poor performance of the ANN model when compared to the regular solution can be attributed to the reason that the model requires numerous data sets in order to make accurate prediction, the data contained in this research is however five data set which prove not to be sufficient for proper prediction.

Statistical tools such as regression and coefficient of determination were also used to determine the model accuracy and tabulated in Table 6. From the table the regression shows how much the predicted values correlate with the actual data however, the thermodynamic model shows more agreement with the actual data. Overall, in comparing the regular solution model with the ANN model using the statistical tools, the regular solution model shows more accuracy than the ANN model.

It is also worth considering that these model has two potential problems that affect network training these include overfitting of the data and overtraining of the network, if there is repeated training cycles. For this research the training was done twice to avoid the aforementioned problems. Despite the model low accuracy, it gave a better prediction then other intelligent models (such as support vector machine, adaptive neural fuzzy inference system etc) tested in the course of this research.

Table 6 Statistical tool for model accuracy of the ANN model

S/N	Accuracy tool	Value
1.	Regression	0.92201
2.	Mean square error	0.007772489
3.	Coefficient of determination	0.796131446
4.	Efficiency coefficient	0.796131446
5.	Mean absolute error %	89.99946136
6.	Maximum absolute error %	555

V. Conclusion

The newly developed model demonstrate good reliability for predicting wax and asphaltene deposition at the given temperature range with high accuracy, the model considers the precipitation of wax and asphaltene to be simultaneous contrary to other models that considers their deposition to be different or one dominating the other. The regular solution model developed was able to predict the wax and aspahltene deposition in crude oil facilities with great accuracy, hence the model is highly reliable. The research shows that when wax and asphaltene precipitates from crude oil, it forms four phases which are solid, liquid, wax and asphaltene as proposed by many researchers. And finally been able to predict when deposition will occur can prevent unnecessary time lost in oil and gas industry and will help design engineers to provide necessary measures to prevent deposition from occurring. It is recommended that the effect of pressure is considered in order to be able to predict the deposition in real pipeline condition in subsequent modeling.

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