

Asphaltenes Dispersion By Thermal Change And Petroleum Viscosity: Mesoscopic Model

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Abstract — The extraction and transport of asphaltic crude oils are associated with high pumping costs because of high viscosity. It is necessary to implement different methods leading to decrease it. Chemical products allow energy saving compared with procedures of temperature increase. Experimental studies to analyze a viscosity reducer's influence is proposed, where the results achieved for one type of crude clarifying the chemical-physical mechanism associated. According to viscosity reduction, we see that the high viscosity in heavy crudes is due to forming a dispersed phase of asphaltenes. This paper aims to propose a mesoscopic model that describes the aggregate size behavior and the viscosity of the crude. The obtained model was used to theoretically and experimentally analyze different improvers' influence on an asphaltenic crude

Keywords: Oil stochastic model, viscosity reduction, asphaltene aggregation.

I. INTRODUCTION

Asphaltenes conform to the polar fraction of the components of crude oil. Their presence at high concentrations causes numerous operational problems, including high pumping costs, asphaltene deposition on tube walls, and decreased product yield [1-3]. Asphaltenes generate a dispersed phase; poly dispersion depends on temperature, pressure, and flow, among other factors.

This colloidal characteristic of crude oils present is closely related to their physicochemical and transport properties [4]. The behavior of the dispersed fraction of asphaltenes is a complex process that depends on many factors and is not yet fully understood, and led to numerous experimental studies and established different hypotheses and theoretical models to describe this phenomenon [2, 5-7]. Research has also been carried out to develop practical methods reducing the size and concentration of asphaltene aggregates and mitigating their effects on crude oil extraction and transportation processes [8-10].

Investigations related to temperature and different chemical products relationship, acting as flow improvers on the dispersed phase of polar asphaltenes [11], must be made experimental and empirically because of the interaction

between the composition and molecular structure of mixtures, transport properties, and chemical-physical mechanism behavior. Viscosity reductions are reached dosing low improver concentrations correlated with the decrease in pipelines asphaltene deposition.

It is important to note that the improvers' action depends on the origin and composition of the crude oil, so that improvers for certain types of crude oil may be ineffective, and even counterproductive, for a different oil.

We hypothesize that asphaltenes aggregation behaves as a colloid in crude oil, influencing their rheology, and flow improvers act as surfactants.

This work aims to develop a mesoscopic model for molecular interactions related to crude oils' viscosity and distribution. The proposed model was used to experimentally study the effects of four flow improvers on an asphalt oil's viscosity and select which of these was the most effective on that particular oil.

II. METHOD

A. Model developed

The crude is visualized as a dispersed system. Aggregates of asphaltenes of the volume form the dispersed phase A. The dispersion media B by the non-polar hydrocarbons and a part of asphaltenes dissolved, v_A is the asphaltene total volume fraction and ϕ is the fraction of these obtained in the disperse phase. The medium is isotropic according to composition. System volume V (m^3) is where only a one-aggregate exists. In this way, All A molecules in V groups forming an aggregation with v_0 volume, obtaining:

$$V = \frac{v_0}{v_A} \quad (1)$$

Due to the molecular level processes, volume v fluctuates temporarily still in steady-state. Molecules diminishing n number in the aggregate, and an increase in n_1 asphaltene molecules (into the dispersion media) represented by:

$$n \xrightarrow{k_1} n_1$$

with transition probability per unit time W_1 supposing a priori:



$$W_1 = k_1 n \quad (2)$$

the aggregation of the molecules increasing in n and diminishing n_1 :

$$n_1 + n \xrightarrow{\frac{k_2}{V}} 2n$$

with transition probability per unit time W_2 :

$$W_2 = \frac{k_2}{V} n_1 n = \frac{k_2 v_A}{\nu_0} n_1 n \quad (3)$$

being k_1 and k_2 (s^{-1}), the kinetics constants associated with the aggregation and disaggregations processes, where relationship k_1/k_2 must increase with oil temperature T (K), increase in the kinetic energy at molecules, and with the possible interaction established by A and B . This is a closed system; the total number of molecules N does not change in the time writing according to eq. 3:

$$W_2 = \frac{k_2 v_A}{\nu_0} n(N - n) \quad (4)$$

$$N = \nu_0 \frac{\rho}{P_m} N_0 \quad (5)$$

where ρ is the density of the dispersed molecule ($kg \cdot m^{-3}$), P_m ($kg \cdot Kmol^{-1}$) is the average molecular weight of asphaltenes and $N_0 = 6.02 \times 10^{26} Kmol^{-1}$.

Now we establish the master equation describing the behavior of probability $P(n;t)$ of the existence of n molecules in the aggregate on-time t :

$$\begin{aligned} \frac{\partial P(n;t)}{\partial t} = & (\mathbf{E}^{+1} - 1)k_1 n P(n;t) \\ & + (\mathbf{E}^{-1} - 1)\frac{k_2 v_A}{\nu_0} n(N - n)P(n;t) \end{aligned} \quad (6)$$

$$P(n_0;0) = 1$$

\mathbf{E}^a is the step operator acting on the discrete variable functions and $\mathbf{E}^a [f(n)] = f(n + a)$. If n is high, then Δn at an individual microscopic level, may be negligible compared to n ; n considers it a continuum variable. Moreover, the Fokker - Planck equations correspond to the master equation (6) is:

$$\begin{aligned} \frac{\partial P(n;t)}{\partial t} = & -\frac{\partial}{\partial n} \left(\frac{k_2 v_A}{\nu_0} n(N - n) - k_1 n \right) P(n;t) \\ & + \frac{1}{2} \frac{\partial^2}{\partial n^2} \left(\frac{k_2 v_A}{\nu_0} n(N - n) + k_1 n \right) P(n;t) \end{aligned} \quad (7)$$

$$P(n_0;0) = 1$$

Considering that the dispersed phase fraction ϕ is the macroscopic variable, and relationship with the microscopic variable n is:

$$n = \phi \frac{\nu_0}{v_A} \frac{\rho}{P_m} N_0 \quad (8)$$

Then, probability behavior equation (ϕ,t), using equation 7 and 8:

$$P(n;t) = \left| \frac{\partial \phi}{\partial n} \right| P(\phi;t) = \frac{P_m v_A}{\rho \nu_0 N_0} P(\phi;t) \quad (9)$$

Obtaining de dimensionless equation:

$$\begin{aligned} \frac{\partial P(\phi;t)}{\partial \tau} = & -\frac{\partial}{\partial \phi} \left(\phi \frac{\theta}{\kappa} v_A - \phi^2 \frac{\theta}{\kappa} - \phi \right) P(\phi;t) \\ & + \frac{1}{2} \frac{v_A}{\theta \nu_0} \frac{\partial^2}{\partial \phi^2} \left(\phi - \phi^2 \frac{\theta}{\kappa} + \phi \frac{\theta}{\kappa} v_A \right) P(\phi;t) \\ P(n_0;0) = & 1 \end{aligned} \quad (10)$$

where:

$$\tau = k_1 t \quad (11)$$

$$\theta = \frac{\rho N_0}{P_m} \quad (12)$$

$$\kappa = \frac{k_1}{k_2} \quad (13)$$

Dimensionless parameter θ relates to the asphaltenes properties. κ represents the Dynamic relation between molecules velocity (scaled with the square root of temperature) and molecular interactions (asphaltene-asphaltene and asphaltenes-dispersion media). Suitable combining both parameters:

$$\frac{\kappa}{\theta} = \alpha^2 \sqrt{T} \quad (14)$$

where α ($K^{-0.5}$) is determined experimentally. In the vicinity of steady-state $P(\phi,t)$ is normal or gaussian, so it is enough to define the behavior of the expected value Φ and the variance σ_ϕ of ϕ , solving equation (10) using the linear noise approximation method and:

$$\Phi = v_A - \alpha^2 \sqrt{T} \quad (14)$$

$$\sigma_\phi = \alpha^2 \sqrt{T} \frac{v_A}{\theta \nu_0} \quad (15)$$

Where the temporal autocorrelation function of fluctuation $\Xi = \langle \xi(\tau + \tau_c) \xi(\tau) \rangle$ is described by differential equation:

$$\frac{d\Xi}{d\tau_c} = - \left(\frac{v_A}{\alpha^2 \sqrt{T}} - 1 \right) \Xi \quad (15)$$

$$\Xi(0) = \sigma_\phi$$

With solution:

$$\Xi = \alpha^2 \sqrt{T} \frac{v_A}{\theta v_0} \exp\left(-\left(\frac{v_A}{\alpha^2 \sqrt{T}} - 1\right) \tau_c\right) \quad (16)$$

The probability density function is given by:

$$P(\phi) = \frac{1}{\sqrt{2\pi}\sigma_\phi} \exp\left(-\frac{(\phi - \Phi)^2}{2\sigma_\phi^2}\right) \quad (17)$$

So that the accumulative probability in which ϕ is less than x corresponds to:

$$P(\phi < x) = \frac{\operatorname{erf}\left(\frac{(x-\Phi)}{\sqrt{2}\sigma_\phi}\right) + \operatorname{erf}\left(\frac{\Phi}{\sqrt{2}\sigma_\phi}\right)}{\operatorname{erf}\left(\frac{(1-\Phi)}{\sqrt{2}\sigma_\phi}\right) + \operatorname{erf}\left(\frac{\Phi}{\sqrt{2}\sigma_\phi}\right)} \quad (18)$$

At steady-state, ergodicity property is established (equality in temporal average) by solving the master equation, or the N observed results in a specific time interval. The average followed by análisis of N observed systems of volume V at the same time. The observed system includes an individual conglomerate, volume v is calculated by:

$$v = \phi v_0 \quad (19)$$

So that probability (17) is equivalent to the asphaltenes agglomerates size distribution.

Theoretically, it is established that viscosity η (Pa.s) of a dispersed system in a linear function of the volume fraction of the disperse phase Φ and the μ_0 (Pa.s) of the dispersion media:

$$\eta = \mu_0 \left(1 + \frac{\Phi}{4}\right) \quad (20)$$

Substituting (14) in equation (20) we obtain:

$$\eta = \mu_0 \left(1 + \frac{1}{4} \left(v_A - \alpha^2 \sqrt{T}\right)\right) \quad (21)$$

On the other hand, the dispersion media's viscosity is also affected by temperature, system composition, and distribution of the aggregates size and asphaltenes fraction $(1 - \Phi)$ dissolved within. More studies on the area must propose useful models and first approximations with relativity easy experimental adjustment and the theoretical description from equation (21). This equation is described then:

$$\eta = A - B^2 \sqrt{T} \quad (22)$$

We applied:

$$\exp(x) = 1 + x + \frac{1}{2} x^2 + O(x^3) \quad (23)$$

Furthermore, we proposed the model to predict viscosity

concerning temperature for asphaltenic crudes:

$$\eta = A \exp\left(-B^2 \sqrt{T}\right) \quad (24)$$

B. Model Evaluation

Equation (24) is proposed to evaluate viscosity. It was applied to analyze the effect of for viscosity Flow improvers on asphaltenic crudes. Properties of oil crude are shown in Table 1.

Table 1. Properties of oil crude

Parameter	Value
Sediment	0%
Emulsión	0%
Water	0.8%
pH	7
Viscosity @25 °C	55,779 cP

We determined the viscosity change concerning temperature for three concentrations (1%, 2% y 3% weight/weight) using an Anton Paar rheometer to evaluate Flow improver feasibility. Non-linear regression techniques adjusted experimental results to the model (24)

III. RESULTS AND DISCUSSION

According to equation (21), the average fraction of asphaltene aggregates decreases with temperature in such a way, it is possible, for a given temperature, that this fraction tends to zero. However, due to this variable's stochastic nature, there is a probability that part of the asphaltenes is forming aggregates. Figure 2 shows the size distribution behavior for different temperature values, where it can be seen that the fraction of smaller particles increases with temperature.

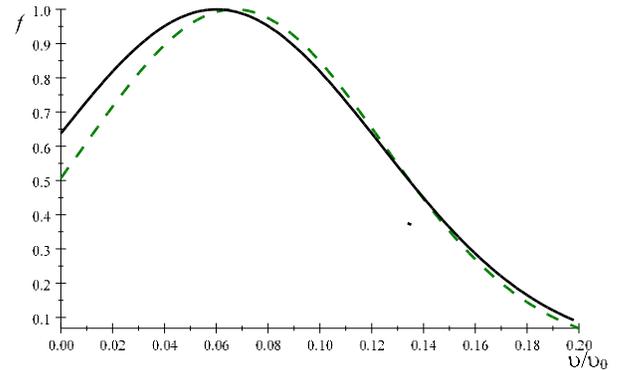


Figure 2. Particle size distribution $f = n/N$ for a hypothetical system with $\alpha = 0.002$, $\theta v_0 = 1$, $v_A = 0.1$ para $T = 300$ K (continuos line) and $T = 400$ K (no continuos line)

The system polydispersion grade β represents the relative magnitude of the fluctuation:

$$\beta = \frac{\sqrt[2]{\sigma_\phi}}{\Phi} = \frac{1}{\sqrt[2]{\theta v_0}} \frac{\sqrt[2]{\alpha v_A^4 \sqrt{T}}}{(v_A - \alpha \sqrt[2]{T})} \quad (25)$$

Figure 3 shows the relative magnitude average of fluctuation concerning temperature for a system with $\theta v_0 = 1$, $\alpha = 0.002$ y $v_A = 0.1$.

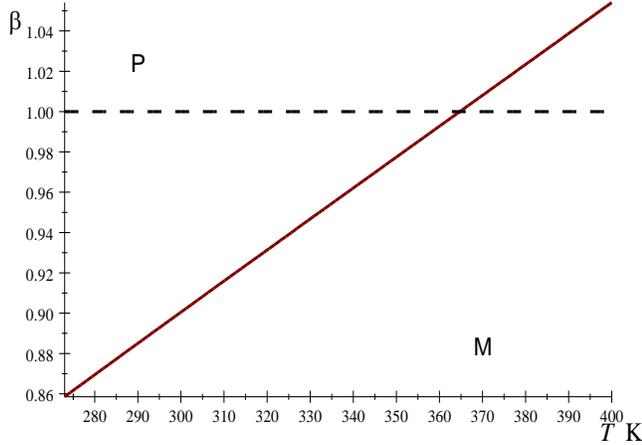


Figure 3. Polydispersion behavior concerning temperatures, where M zone under noncontinuous line corresponds to mono-disperse and P a poly-dispersed system. $\alpha = 0.002$, $\theta v_0 = 1$, $v_A = 0.1$

Figure 4 shows the behavior obtained by a Montecarlo simulation of the particle size is observed behavior in 20 sites from the system for two temperature values. For particle size equals zero, it corresponds to empty spaces. In this case, we observe the prediction of an increase of empty spaces with temperature and according to our hypothesis.

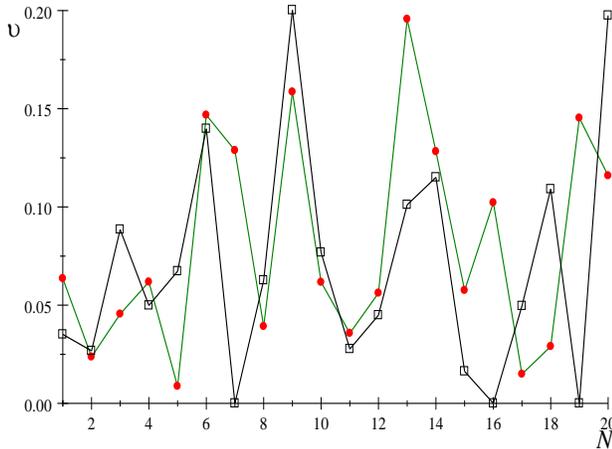


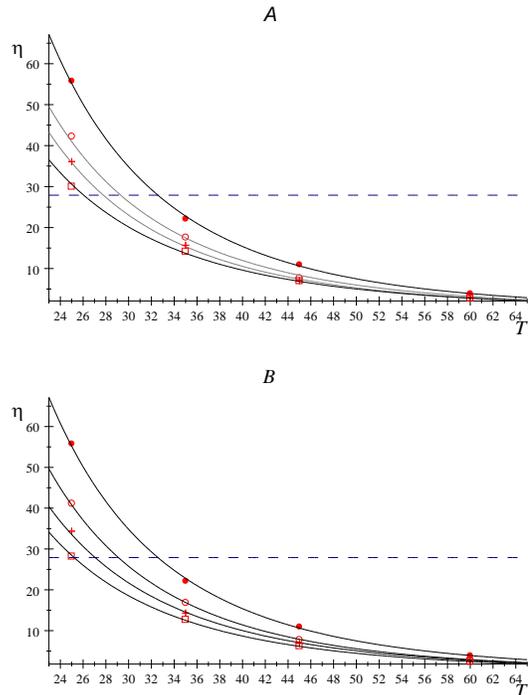
Figure 4. prediction of v in N spatial sites obtained by our model and Montecarlo Method where (\bullet) $T = 300$ K; (\square) $T = 400$ K. $\alpha = 0.002$, $\theta v_0 = 1$, $v_A = 0.1$

We found an R^2 greater than 0.98 for all the adjustments, which indicates our proposed model's validity for the type of crude oil, flow improvers, and temperature interval. The values of the parameters A and B calculated for each case, the observed behaviors, and the fitted models are shown in Table 2 and Figure 5. Note that the reduction in viscosity for temperature is more significant at lower temperature values. In contrast, at higher temperatures, for which the asphaltene's dispersed phase's fraction is predicted to have been significantly reduced, the decreased viscosity is less significant. These results corroborate the established hypothesis that the flow improvers' chemical-physical action mechanism is based on the increase in the dissolution of asphaltene in the dispersion medium in such a way that the volume fraction of the dispersed phase decreases, which is manifested precisely in the reduction in viscosity observed

Table 2. Parameters A; B obtained by the statistical adjustment from the observed results and the proposed model

$$\eta = A \exp(-B \sqrt[2]{T})$$

Concentration n	1%	2%	3%
Crude + A	4283.8; 0.930	3635.0; 0.924	2415.2; 0.874
Crude + B	5002.9; 0.962	3221.2; 0.913	2507.9; 0.896
Crude + C	4927.2; 0.968	3066.0; 0.921	1752.4; 0.875
Crude + D	4867.4; 0.959	2601.1; 0.887	2076.9; 0.883
Crude	6836.8; 0.964		



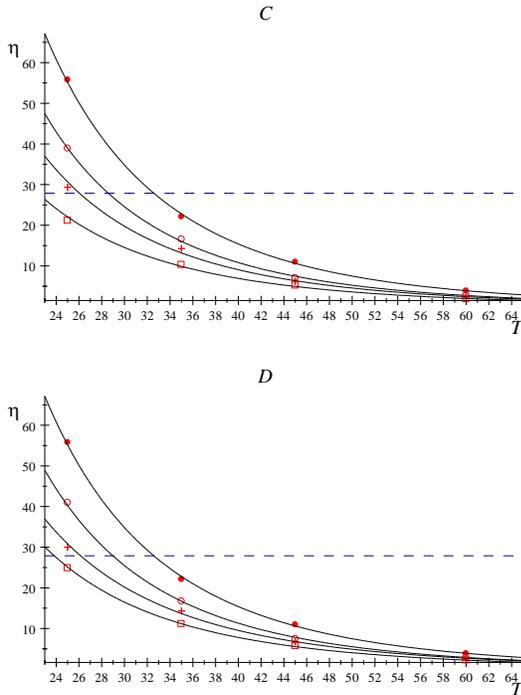


Figure 5. Predicted behavior for the adjusted model and experimental results for different concentrations of the Flow improvers A, B, C y D. (●) 0% or blank; (°) 1% ; (+) 2% and (□) 3% concerning to temperature (°C). The non-continuous line represent the 50% of the crude oil viscosity @ 25°C

For selecting the most appropriate improver for the crude oil studied, the minimum temperature necessary to achieve a 50% reduction in the crude oil's viscosity at 25°C was taken as a criterion. The calculated temperature values are shown in Table 2. It was obtained that the most appropriate flow improver is C since the reduction in viscosity for all the temperatures analyzed was achieved at the lowest temperature.

Table 2. Temperature values (°C) for which oil crude reduces viscosity by 50%

Concentration	1%	2%	3%
Product			
Crude + A	29.301	27.778	26.053
Crude + B	29.099	27.057	25.210
Crude + C	28.57	26.039	22.390
Crude + D	28.972	26.143	23.827
Crude (Blank)	32.571		

The above results show characteristics for transport in crude. This knowledge is useful for oil transport, and energy save, although there are other ways to produce energy [12] for crude heating.

IV. CONCLUSION

A Stochastic-mesoscopic model was obtained due to the aggregation/disaggregation process. It predicts the behavior of the grade of poly dispersion of this dispersed system and the crude oil's viscosity concerning the system's temperature. We exposed our model and the adjusted parameters from the experimental results that implicitly take into account the relationship between the kinetic energy of the molecules, which depends on the temperature, and the molecular interactions that exist in the system. that rely on the composition and molecular structures of the substances present. The proposed model was used to study the experimentally observed effect of four flow improvers on viscosity's behavior concerning the temperature of specific crude oil and select the most effective improver.

Abbreviation and Acronyms

- k_1 y k_2 : Kinetics constants (s^{-1})
- n : number of molecules of asphaltenes forming an aggregate.
- N : total asphaltenes molecules
- N_0 : Avogadro number ($6.02 \times 10^{26} \text{ Kmol}^{-1}$)
- P : density probability function
- P_m : asphaltenes molecular weight (kg.Kmol^{-1})
- T : temperature (K)
- V : System volume (m^3)
- v_A : volume fraction of the asphaltene total volume
- ϕ : asphaltene volume fraction that produces aggregates
- θ : nondimensional parameter related to the asphaltenes properties.
- κ : the quotient of the kinetics aggregation constants and disaggregation of the asphaltenes molecules
- Φ : expected value for the disperse fraction
- σ_ϕ : variance of the disperse fraction
- Ξ : autocorrelation function for the temporal fluctuation
- α : parameter related to molecules velocity and molecular interaction potential ($\text{K}^{-0.5}$)
- η : dispersed media viscosity (Pa.s)
- μ_0 : dispersion media viscosity (Pa.s)
- v : individual asphaltene aggregate volume (m^3)
- ρ : dispersed particle density (kg.m^{-3})

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REFERENCES

- [1] Alimohammadi, S., Zendejboudi, S., & James, L., A comprehensive review of asphaltene deposition in petroleum reservoirs: Theory, challenges, and tips. *Fuel*, 252(2019) 753-791.
- [2] Rajan Babu, N., & Vargas, F. M., Modeling of Asphaltene Deposition in a Packed Bed Column. *Energy & Fuels*, 33(6)(2019) 5011-5023.
- [3] Bemani, A., Poozesh, A., Bahrami, M., & Ashoori, S. (2019). Experimental study of asphaltene deposition: Focus on critical size and temperature effect—*Journal of Petroleum Science and Engineering*, 181, 106186.
- [4] Ghorbani, M., & Maddahian, R., Investigation of asphaltene particle size and distribution on fouling rate in the crude oil preheat train. *Journal of Petroleum Science and Engineering*, 196(2021) 107665.
- [5] Sulaimon, A. A., De Castro, J. K. M., & Vatsa, S., New correlations and deposition envelopes for predicting asphaltene stability in crude

- oils. *Journal of Petroleum Science and Engineering*, 190(2020) 106782.
- [6] Emani, S., Ramasamy, M., & Shaari, K. Z. K., Discrete phase-CFD simulations of asphaltene particles deposition from crude oil in shell and tube heat exchangers. *Applied Thermal Engineering*, 149(2019) 105-118.
- [7] Pu, W. F., Wang, L. L., Peng, X. Q., Li, N., & Zhao, S., Effects of aromatics, resins, and asphaltene on oxidation behavior and kinetics of heavy crude oil. *Petroleum Science and Technology*, (2020) 1-8.
- [8] Jadhav, R. M., & Sangwai, J. S., Interaction of Heavy Crude Oil and Nanoparticles for Heavy Oil Upgrading. In *Nanotechnology for Energy and Environmental Engineering (2020)* (231-255). Springer, Cham.
- [9] Taheri-Shakib, J., Hosseini, S., Rajabi-Kochi, M., & Shekarifard, A., Investigating the Impact of Microwave Technology on the Interaction between Asphaltene and Reservoir Rock Surface. In *82nd EAGE Annual Conference & Exhibition 1(2020)* 1-5. European Association of Geoscientists & Engineers.
- [10] Ghloum, E. F., Rashed, A. M., Safa, M. A., Sablit, R. C., & Al-Jouhar, S. M., Mitigation of asphaltene precipitation phenomenon via chemical inhibitors. *Journal of Petroleum Science and Engineering*, 175(2019) 495-507.
- [11] Yao, B., Chen, W., Li, C., Yang, F., Sun, G., Wang, G., & Xu, H. (2020). Polar asphaltene facilitates the flow improving the performance of polyethylene-vinyl acetate. *Fuel Processing Technology*, 207(2020) 106481
- [12] Le-ol, A. K., & Koate, C. (2019) Energy Recovery from Municipal Solid Waste in the Port Harcourt Metropolis, Nigeria. *SSRG-IJME* 6(1) 7-13.