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Original Research Article

Optimal Formulation of a Wax Deposition Inhibitor using Design of Experiment Approach

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ABSTRACT

Wax deposition in crude oil production and transportation pipelines from offshore to onshore facilities is a serious concern in the oil and gas industry, especially under low temperature conditions. Despite the different methods adopted to mitigate this problem, the use of wax inhibitors is generally accepted to be the most efficient solution to this problem. The aim of this study was to develop a wax inhibitor optimally formulated from two bio-based precursors (jatropha oil and castor oil) and xylene. The bio-based precursors used to formulate the inhibitors (jatropha oil and castor oil) were extracted from the respective oil-bearing seeds via Soxhlet extraction and they were subsequently characterised to elucidate their properties. The formulation of the wax inhibitor was done according to a three variable D-Optimal mixture design. The independent variables considered were the components of the mixture while the response was the viscosity of the inhibitor-doped crude oil. The inhibitor was optimally formulated from a mix of 20.50% jatropha oil, 39.50% castor oil and 40% xylene. The formulated inhibitor was able to reduce the viscosity of crude oil by 62.8%, thus demonstrating its excellent capability as a flow improver.

1. INTRODUCTION

Crude oil is a complex mixture of different hydrocarbon compounds. The hydrocarbons present in crude oil are typically categorized into three classes namely paraffins, asphaltenes, naphthenes and aromatics with the paraffins accounting for the largest percentage in terms of composition (Leckel, 2009). Beyond the hydrocarbons, crude oil also contains other elements nitrogen, oxygen and sulphur. These constituents of crude oil may interact together to form more complex compounds.

Crude oil is categorised into light crude with API gravity less than 31.1 °API, medium crude with gravity between 22.3 and 31.1 °API and heavy crude with gravity less than 22.3 °API. In particular, heavy crude oil exhibits very complex flow behavior because of the high content of wax in this type of crude oil. It has been reported that over 20% of global crude oil reserves is made up of waxy crude while heavy crude accounts for almost 50% (Kumar et al., 2015). With the depletion of conventional inland oil reserves, there has been an increasing push for the production of crude oil from nonconventional reserves such as those of waxy crude oil (Li et al., 2015). These crude oil reserves are typically in deep water offshore regions which are characterised by extremely low temperatures (Hao et al., 2019).

Crude oil production in these low temperature environments is usually faced with the problem of wax deposition. High molecular weight paraffins which are waxes are generally responsible for the production and transportation problems encountered during crude oil exploitation in these regions (Aiyejina et al., 2011). Under reservoir conditions of temperature and pressure in the range of 70-150 °C and 50-100 MPa respectively, these waxes are soluble in crude oil and are thus dissolved in crude oil which behaves as a Newtonian fluid. However, at lower temperatures and pressures which are encountered as the crude oil flows through the subsea pipeline or through onshore pipelines in cold environments, the high molecular weight paraffins or waxes begin to form micro and macro crystalline structure that precipitates out of the oil and deposits on the surface of the cooler walls of the pipeline. The deposited wax confers non-Newtonian flow characteristics to the crude oil which makes it difficult to convey to the surface (Chang et al., 1998).

Reports have shown that so long as the temperature of the pipeline is less than or equal to the wax appearance temperature, wax deposition can occur in crude oil containing wax as small as 2 wt% (Kasumu, 2014). As the temperature of the crude oil goes below its wax appearance temperature, immediate precipitation of wax begins. The precipitated wax transforms subsequently to a gel with high yield strength and covers the entire cross-section of the pipe through which the crude oil flows (Hao et al., 2019). If this process is not mitigated, the precipitation and subsequent deposition of wax on the surface of the pipe continues and ultimately leads to gelation of the crude oil at via three successive phase changes (Chala et al., 2018).

Despite being common, the use of these chemicals is not sustainable because of their high cost, oil specificity, and ecotoxicity. This necessitates the search for less expensive, environmentally benign, and renewable alternatives. Natural plant seed oils have interesting possibilities as additives for flow improvement wax deposition inhibition of waxy crude oil (Kumar et al. 2015). As wax inhibitors, and viscosity reducers for waxy crude oils, jatropha, rubber, and castor seed oils rich in oleic, linoleic, and ricinoleic acid glycerides as well as crude palm oil and palm kernel oil have all shown promise (Akinyemi et al., 2018; Ragunathan et al., 2020).

Thus, the aim of this study was to develop a wax inhibitor optimally formulated from two bio-based precursors (jatropha oil and castor oil) and xylene.

2. MATERIALS AND METHODS

2.1. Sample Collection and Preparation

The crude oil sample used were sourced from the Nigerian Petroleum Development Company, Benin City, Nigeria. The jathropha and castor seeds used as source of oil were sourced locally in Benin City, Edo State, Nigeria. The seeds were separated from the chaff and dried for 5 days in the sun at ambient temperature for easy dehulling. The seeds were further dried in an electric oven at 60 °C for 5 hours so as to reduce the moisture content to an appreciable value in order to ease the extraction process. The prepared seeds were grounded using an electric mill so as to improve the surface area for extraction (Betiku and Adepoju, 2013).

2.2. Jathropha and Castor Seed Oil Extraction

Jathropha and castor seed oil were extracted from their respective seeds using the Soxhlet extraction procedure. For this procedure, the grinded seed was weighed and wrapped in a muslin cloth and put in the thimble of the extractor. Following this, the extractor was connected to a round bottom flask containing n-hexane and the set up was completed with a condenser which was tightly fixed at the bottom. The whole setup was heated up in a heating mantle at a fixed temperature of 70 °C. Multiple runs were carried out in order to have enough amount of oil for the intended purpose. At the end of each run, the residue was discarded, and the extractor was charged

again with fresh seed. Furthermore, the excess solvent in the oil was recovered using a rotary evaporator (Betiku and Adepoju, 2013). The oils were used as pour point depressant and flow improver alongside xylene.

2.3. Formulation of Wax Inhibitor

In this study, a three variable D-Optimal mixture design was used to plan and conduct the experiments for formulating the wax deposition inhibitor from the three pour point depressants considered in this study. For the chosen D-Optimal mixture design, the input variables were representative of the constituent of the inhibitor formulation. The input variables were the amount of jatropha oil (X_1), amount of castor oil (X_2), and amount of xylene (X_3). The constraints binding all three components of the mixture is presented in Equation 1 such that the levels of all three input variables are not independent, meaning that changes in the level of one variable affect the others (Spanemberg et al., 2019).

$$0 \leq X_i \leq 100 \tag{1}$$

For a three-variable design, i = 1, 2,3 such that:

$$X_1 + X_2 + X_3 = 100 \tag{2}$$

In this study, the response chosen to optimize the formulation of the inhibitor was crude oil viscosity. The range and levels of the input variables are shown in Table 1. This was chosen on the basis of preliminary experiments and previous work (Anisuzzaman et al., 2019). The information in Table 1 was used to generate the experimental design using Design Expert software version 7.

Table 1: Coded and actual levels of the factors for wax deposition inhibitor formulation

Factors	Unit	Symbols	Variable levels	
			Low level	High level
Jatropha oil (%)	%	X_1	20	60
Castor oil (%)	%	X_2	20	60
Xylene (%)	%	X_3	10	40

3. RESULTS AND DISCUSSION

3.1. Statistical Analysis

The quadratic model analysed by fitting it to the experimental data which was obtained from the 16 experiments carried out according to the D-Optimal mixture design. This process was done using multiple regression analysis and resulted in the estimation of the unknown model parameters. The estimated model parameters were then fixed into the general quadratic equation to obtain the final model for formulating the inhibitor in terms of actual values of the input factors (Equation 3). The equation represents the viscosity of crude oil doped with inhibitor (which was used as the measure of performance of the inhibitor) as a function of Jatropha oil (X_1), Castor oil (X_2), and Xylene (X_3). Equation 3 was used to predict the doped crude oil viscosity and the results are shown in Table 2. For all the results obtained, it was observed that the predicted viscosity values were very similar to the experimental values. This is an indication of the validity of the statistical model.

$$Viscosity\ (cP) = 107.29X_1 + 21.50X_2 - 563.86X_3 - 2.46X_1X_2 + 828.73X_1X_3 + 958.30X_2X_3 \tag{3}$$

3.2. Analysis of Variance

The statistical significance and level of fit of the inhibitor formulation model was assessed by carrying out analysis of variance (ANOVA). This was implemented in the ANOVA module of the Design Expert software. The results of this exercise are presented in Table 3. Statistically, for a model term to be considered significant, the p value for that term should be less than 0.05. Otherwise, the term is said not to be significant. A model term that is significant means that changes in the values of the factor represented by that model term will have a significant effect on the response under consideration and the reverse is also the case (Montgomery 2005). For the results obtained as presented in Table 3, all the first order effect model terms were significant. The interaction terms were also significant apart from the term representing the interaction between amount of

jatropha oil and amount of castor oil (X_1X_2). This shows that changes in the values of all other model terms apart from the jatropha oil-castor oil interaction will have a significant effect on the viscosity of the doped crude oil sample. Table 3 also shows that the p value of the model was very small ($p < 0.0001$) showing that the model was very useful for predicting the response (Montgomery, 2005). The model did not show significant lack of fit as the "lack of fit" p value was greater than 0.05 (p=0.6001). This is an indication of a good fit between the model and the experimental results.

Table 2: Experimental and predicted results for inhibitor formulation

Run	Actual values of factors			Viscosity (cP)	
	Jatropha oil (%)	Castor oil (%)	Xylene (%)	Experimental value	Predicted value
1	41.31	20.00	38.69	38.58	36.89
2	20.50	60.00	19.50	75.15	69.89
3	20.50	60.00	19.50	73.25	69.89
4	25.40	47.10	27.50	56.66	64.04
5	48.19	26.08	25.73	80.10	78.98
6	60.00	24.28	15.72	90.01	95.34
7	50.30	39.70	10.00	86.50	85.36
8	57.62	32.38	10.00	101.21	90.72
9	60.00	24.28	15.72	89.85	95.34
10	41.31	20.00	38.69	38.87	36.89
11	33.78	56.22	10.00	67.11	73.35
12	33.78	56.22	10.00	67.54	73.35
13	37.75	38.00	24.26	73.40	75.75
14	21.46	38.54	40.00	22.95	24.43
15	21.46	38.54	40.00	24.23	24.43
16	35.11	47.26	17.62	88.40	79.16

Table 3: ANOVA results for model inhibitor formulation model

Source	Sum of squares	Degree of freedom	Mean square	F value	p value
Model	8416.60	5	1683.32	38.50	< 0.0001
Linear mixture	7286.21	2	3643.11	83.32	< 0.0001
X_1X_2	0.01	1	0.01	0.00	0.9872
X_1X_3	646.58	1	646.58	14.79	0.0032
X_2X_3	839.31	1	839.31	19.20	0.0014
Residual	437.25	10	43.73		
Lack of fit	434.48	5	86.90	156.77	< 0.6001
Pure error	2.77	5	0.55		
Corrected totals	8853.85	15			

The goodness of fit statistics for assessing the adequacy of the model predictions is shown in Table 4. The coefficient of determination (R^2 value) was obtained as 0.9506. The R^2 value is an important statistical parameter used to assess model fit. It is desired that the high R^2 value be as close to one as possible. The case of perfect fit between model and experimental observations is when the high R^2 value is exactly equal to one. As seen from the results presented in Table 4, the model was characterised by a high R^2 value indicating very good fit between the experimental observations and model predictions. Furthermore, the adjusted R^2 value obtained was within reasonable agreement with the R^2 value further confirming the fit of the models (Yi et al., 2009). As shown in Table 4, the value of standard deviation was small compared with the mean of the observations and this shows that there was very little deviation between the individual experimental results compared with the mean value (Montgomery, 2005). This is a further confirmation of the very good fit of the model to the experimental data. The value of coefficient of variation was obtained as 9.85. This parameter is

evaluated as the ratio of the standard deviation to the mean expressed as a percentage and it is usually used to measure and assess the reliability and repeatability of the experiments (Myers and Montgomery, 1995). A low value like that obtained in this study for the model representing hardness indicates that the experiments were run with high precision and reliability and hence the runs are repeatable (Myers and Montgomery, 1995). Table 4 also shows that the adequate precision value was 17.511. The adequate precision value measures the signal to noise ratio of model predictions and values greater than 4 are usually desirable (Cao et al., 2009). A value of 17.511 obtained in this work indicates that the model for model has adequate signal and can thus be used to navigate the design space (Montgomery, 2005).

Table 4: Goodness of fit statistics for inhibitor formulation model

Parameter	Value
R^2	0.9506
Adjusted R^2	0.9259
Predicted R^2	0.8853
Mean	67.1100
Standard deviation	6.6100
C.V %	9.8500
Adequate precision	17.5110

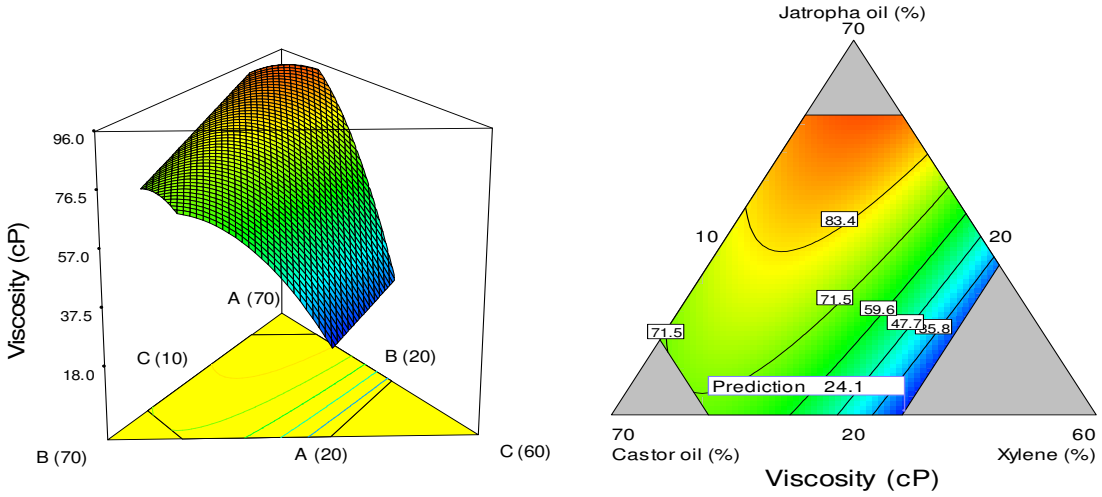
3.3. Optimisation of Inhibitor Formulation

The optimisation results are shown in Table 5. This optimal point was chosen with the highest desirability of 0.985. As seen from the results, the optimally formulated wax inhibitor was comprised of 20.50% of jatropha oil, 39.50% of castor oil and 40% of xylene. With this optimally formulated wax inhibitor, the crude oil viscosity was minimised to 24.11 cP. The efficacy of the wax inhibitor can be seen in the fact that it also functioned as a flow improver by reducing the viscosity of the crude oil in its virgin state (39.24 cP) to a value of 24.11 cP after applying the formulated inhibitor. This represents a 62.8% reduction in viscosity which is desirable for the flow of crude oil in pipelines. High viscosity is not desirable as it presents transport problems as well as increasing energy consumption and associated costs of equipment such as pumps (Martínez-Palou et al., 2011). The results obtained in this study indicates that seed oils such as jatropha and castor oil could interact with wax in crude oil to reduce viscosity. This has been attributed to the presence of fatty acids such as oleic acid and ricinoleic acid in jatropha and castor oil (Alpandi et al., 2022). The mechanism of the reduction in viscosity has been proposed to involve the interaction between the hydroxyl groups or the double bonds in the fatty acids and the functional groups in the wax molecules. This observation is in agreement with previous reports (Akinyemi et al., 2016).

The relationship between the input factors and the response at the optimised conditions is shown in Figure 1. It can be seen that a combination of high level of jatropha oil, intermediate levels of castor oil and high level of xylene were necessary to minimise the viscosity of crude oil.

Table 5: Optimisation results for inhibitor formulation

Variable	Value
Jatropha oil	20.50%
Castor oil	39.50%
Xylene	40.00%
Minimum viscosity	24.11 cP



(a) (b)

Figure 1: Optimal formulation of mixture component presented in (a) 3D plot and (b) contour plot [X1=A=Jatropha oil; X2=B=Castor oil; X3=C=Xylene]

4. CONCLUSION

The focus of this study was to optimally formulate a wax inhibitor from jatropha oil, castor oil and xylene to be used for mitigating wax deposition in crude oil during flow in pipelines. The following conclusions have been drawn on the basis of the findings of the work. An efficient wax inhibitor was successfully formulated from jatropha oil, castor oil and xylene using mixture experimental design which successfully improved the flow properties of crude oil (viscosity) by 62.8%.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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