Original article

Investigation of wax precipitation in crude oil: Experimental and modeling

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A B S T R A C T

In this work, a series of experiments were carried to investigation of rheological behavior of crude oil using waxy crude oil sample in the absence/presence of flow improver such as ethylene-vinyl acetate copolymer. The rheological data covered the temperature range of 5—30 °C. The results indicated that the performance of flow improver was dependent on its molecular weight. Addition of small quantities of flow improver, can improve viscosity and pour point of crude oil. Also, an Artificial Neural Network (ANN) model using Multi-Layer Perceptron (MLP) topology has been developed to account wax appearance temperature and the amount of precipitated wax and the model was verified using experimental data given in this work and reported in the literature. In order to compare the performance of the proposed model based on Artificial Neural Network, the wax precipitation experimental data at different temperatures were predicted using solid solution model and multi-solid phase model. The results showed that the developed model based on Artificial Neural Network can predict more accurately the wax precipitation experimental data in comparison to the previous models such as solid solution and multi-solid phase model with AADs less than 0.5%. Furthermore, the number of parameters required for the Artificial Neural Network (ANN) model is less than the studied thermodynamic models.

1. Introduction

Crude oil is a complex mixture of hydrocarbons, consisting of waxes, asphaltenes, resins, aromatics, and naphthenics. Among these, wax precipitation is a major problem in oil productions and transportations facilities. This phenomenon can result in many problems such as decreased production rates, increased power requirements and failure of facilities. Wax is the high molecular weight paraffin fraction of crude oil that can be separated with reduction in oil temperature below pour point of crude oil. Paraffin is mixture of hydrocarbons constituted of linear/normal chains, comprising mainly from 20 to 40 carbon atoms, in addition to alkanes with branched and cyclic chains. The solubility of waxes with high molecular weight decreases by decreasing in temperature. Therefore, the wax fraction precipitate and phase separation occurs by wax crystallization. In the transportation of waxy crude oil in a cold environment (at temperatures below the oil pour point), the temperature gradient in the oil creates a concentration gradient in the dissolved waxes due to their difference in solubility. The driving force, created by the concentration gradient, transfers the waxes from the oil toward the pipe wall where they precipitate and form a solid phase. The solid phase reduces the available area for the oil flow, which in turn causes a drop in the pipe flow capacity. In order to predict the wax precipitation conditions a reliable thermodynamic model is necessary. Several thermodynamic models for wax precipitation estimation have been published in literature which is not in good agreement with experimental data. They usually overestimate the amount of precipitated wax and wax appearance temperature (WAT). A literature review indicates that models of wax precipitation can be classified into two different approaches. The first important approach in modeling of wax precipitation uses a cubic EOS for vapor—liquid

equilibrium and an activity coefficient model for solid–liquid equilibrium. These models are based on solid solution (SS) theory which assumes that all the components in the solid phase are miscible in all proportions. This category includes [1–10], models. Chen et al. [11,12] proposed the new correlations for the melting points and solid–solid transition temperatures of treated paraffins based on the experimental results by differential scanning calorimeter (DSC). The required thermodynamic properties of pure n-paraffins are first estimated, and then a new approach based on the UNIQUAC equation is described. Finally, the impact of pressure on wax phase equilibrium is addressed. The second approach based on multi-solid (MS) phase model uses only an EOS for all phases in equilibrium; in fact an EOS is used directly for vapor–liquid equilibrium, and solid phase nonideality is described indirectly from the EOS by fugacity ratio which assumes that each pure or pseudo component that precipitates constitutes a separate solid phase which is not miscible with other solid phases. This category includes [12–16]. Pan and Firoozabadi [16] developed the Lira-Galeana model [14] by dividing each heavy fraction into paraffin, naphthene and aromatics (PNA). They used their own experimental data with PNA analysis and considered the effect of composition on WAT. Nichita et al [15] accounted both the Pointing factor and solid-state phase transition for MS model and used the model for gas condensate mixtures. They have also considered the effect of pressure on WAT. Escobar-Remolina [13] suggested the new correlations for the fusion temperature, the enthalpy of fusion and heat capacity difference. In our previous work, the effect of wax inhibitors on pour point and rheological properties of waxy crude oils were investigated (2008, 2011, 2013). These thermodynamic models are based on the complex properties such as interaction coefficient, critical properties, acentric factor, solubility parameter and molecular weight which are not specified for long chain of wax in crude oil. In order to develop modeling of wax phase behavior in crude oils a powerful method is necessary. Artificial neural network methods (ANN) are especially useful for modeling highly nonlinear systems such as wax precipitation in crude oil. In this work, an Artificial Neural Network model has been proposed to account the wax appearance temperature and the amount of precipitated wax. Also the performance of the Artificial Neural Network model, solid solution (SS) model, and multi-solid (MS) phase model using the wax precipitation experimental data reported in the literature was studied. Also, a series of experiments was carried to investigation of rheological behavior of crude oil using waxy crude oil sample in the absence/presence of flow improver such as ethylene-vinyl acetate copolymer.

2. Experimental section

2.1. Materials

An Iranian waxy crude oil was used for investigation of rheological behavior of waxy crude oil in the absence/presence of flow improver such as ethylene-vinyl acetate copolymer. Two types of flow improver with different properties were selected. The characteristics of used flow improvers and the studied crude oil are shown in Tables 1 and 2.

2.2. Experimental apparatus and tests procedure

An appropriate quantity of flow improver was added to the crude oils and heated in a thermostatic bath maintained at 50 °C. Results show that polymer #1 has high molecular weight and polymer #2 has low molecular weight. Flow improvers were

Table 1
Characteristics of used polymers.

Specifications	Test method	Polymer #1	Polymer #2
N content	ASTM D-5291	<0.5	<0.5
C content	ASTM D-5291	86.5	85.5
H content	ASTM D-5291	13.1	13.1
Molecular weight	GPC	816,896	725,981

Table 2
Characterization of studied crude oil.

Specifications		Test method	Value
Specific gravity @15.56/15.56 °C		ASTM D-4052	0.8599
API		ASTM D-287	33.05
Sulfur content	WT%	ASTM D-2622	0.223
H2S content	ppm	FIP	Trace <5
Nitrogen, total	WT%	ASTM D-3228	1400
Base sediment & water	VOL%	ASTM D-96	1.0
Salt content	P.T.B	ASTM D-3230	140
Kinematic viscosity @10 °C	cSt	ASTM D-445	Solid
Kinematic viscosity @20 °C	cSt	ASTM D-445	Too viscos
Kinematic viscosity @40 °C	cSt	ASTM D-445	10.65
Pour point	°C	ASTM D-97	18
R.V.P.	PSI	ASTM D-323	3.5
Asphaltenes	WT%	IP-143	0.13
Wax content	WT%	BP-327	13
Drop melting point of wax	°C	IP-31	60
Carbon residue (Conradson)	WT%	IP-13	4.0
Ash content	WT%	ASTM D-482	0.05
Acidity, total	mgKOH/gr	ASTM D-664	0.0126
Molecular weight	Calculated		328.4
Nickel	ppm	A.A.S	9.1
Vanadium	ppm	A.A.S	Trace<0.3
Iron	ppm	A.A.S	9.9
Lead	ppm	A.A.S	1.1
Sodium	ppm	A.A.S	193.0

dissolved in cyclohexane (1:2 ratios) and then added to crude oil. Pour points were measured by ASTM D-97 method [17].

Apparent viscosity as a function of temperature was measured with a Haake RV12 concentric cylinder viscometer equipped with double gap geometry. Viscosity was measured at different shear rates in the range of 20–200 s^{-1}. Molecular weights of polymers were determined by a waters gel permeation chromatography (GPC) in a Shimadzu LC10AD system equipped with a refractive index detector and ultrastyragel columns of 106,105,104 and 500 A connected in series. Tetrahydrofuran as the mobile phase, at a flow rate of 1 ml/min was used. Composition of polymer was measured by an elemental analyzer. Wax and asphaltene contents were determined according to BP-327, IP-143, respectively.

3. Theoretical section

In existing works, several thermodynamic models for prediction of wax precipitation condition have been published in literature. A literature review shows that these models can be classified into two different categories including an equation of state (EOS) plus activity coefficient (EOS + GE) approach and an EOS approach. The first category in modeling wax precipitation uses a cubic EOS for vapor–liquid equilibrium and an activity coefficient model for solid–liquid equilibrium. These models are based on solid solution (SS) theory which assumes that all the components in the solid phase are miscible in all proportions. The second approach uses only an EOS for all phases in equilibrium; in fact an EOS is used directly for vapor–liquid equilibrium, and solid phase nonideality is described indirectly from the EOS by fugacity ratio based on multi-solid (MS) phase model which