

Measurement and Prediction of Time-independent and Time-dependent Rheological Behavior of Waxy Crude Oil

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Received: May 03, 2016; revised: November 02, 2016; accepted: December 13, 2016

Abstract

Wax deposition phenomenon changes the rheological behavior of waxy crude oil completely. In the current work, the rheological time-dependent and time-independent behaviors of waxy crude oil samples are studied and flow curve and compliance function are measured for the oil samples with various wax contents at different temperatures. A decrease in temperature and an increase in wax content lead to an increase in the viscosity and yield stress but a significant drop in compliance function. A modified Burger model is developed to predict the behavior of the compliance function and a modified Casson model is used to predict the flow curve of the waxy crude oil samples within a vast range of wax contents and temperatures. The proposed Burger and Casson models match with experimental results with R^2 of 99.7% and 97.33% respectively.

Keywords: Waxy Crude Oil, Viscoelastic Properties, Rheological Model, Flow Curve

1. Introduction

One of the severe problems in oil industry is wax crystal formation and deposition phenomenon. Crude oil with a wax content more than 5 wt.% is named waxy crude oil and it has a great potential of wax crystal formation (Zhang and Liu, 2008). Paraffins or waxes are hydrocarbons in the range of C_{10} to C_{70} (Kan  et al., 2003). The solubility of heavy components is high at very high temperature and pressure in reservoirs; however, after oil production and during transportation, the temperature and pressure drop significantly and a sharp decline in their solubility occurs; therefore, the solid phase, i.e. waxy crystal, appears. In the first place, the formation of this solid phase changes the rheological properties of waxy crude oil and converts its rheological nature from a Newtonian fluid to a non-Newtonian fluid. Since the design of pipelines and oil transmission equipment requires detailed rheological information (Adeyanju and Oyekunle, 2012), the rheological behavior of the fluid needs to be studied in different operational conditions. Sometimes emergency shutdowns happen for technical reasons such as maintenance and periodic inspections. In these situations, waxy crude oil is cooled statically, and then solid crystals interlock and build a waxy gel network. This viscoelastic gel has a yield stress which should be supplied adequately to restart the operation (Chang et al., 1999; Visintin et al., 2008). The calculation of the necessary pressure to break down the resistance of the gel

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network is a challenge that must be solved using the results of rheometry tests. The waxy gel behavior against the applied stress during the restart operation is divided into three regions. First region is the elastic deformation, the second region is creep phase and the third one is destruction of the waxy network. The second region i.e. the creep phase starts after a limit-elastic yield stress and continues to a static yield stress. The rheological behavior of waxy crude oil in the first and third region can be described with Hooke's law and rheological models like power law, Bingham plastic, Herschel-Bulkley and Casson models, respectively (Chang et al., 1998; Kané et al., 2004). The behavior description of the second zone (creep phase), which is dependent on time, requires the use of viscoelastic models.

The studies of the rheological behavior of waxy crude oil have started since about three decades ago. In all the shear-rotational tests studies, the non-Newtonian behavior of waxy crude oil samples has been reported at a temperature less than wax appearance temperatures (WAT). The viscosity and yield stress of these non-Newtonian fluids increase by decreasing the temperature and shear rate and increasing the wax content of oil samples (Agarwal et al., 1989; Alboudwarej et al., 2006; Chanda et al., 1998; El-Gamal, 1998; El-Gamal and Gad, 1998; Lorge et al., 1997). Several studies were performed to evaluate the effect of factors like temperature and wax content on the thixotropic behavior of waxy crude oil. The results showed that a decrease in temperature and an increase in wax content lead to an increase in hysteresis loop area of flow curve, which represents the increase in the thixotropic behavior of the waxy crude oil under these conditions (Guo et al., 2015; Japper-Jaafar et al., 2014; Van Der Geest et al., 2015). A few creep studies were conducted to achieve a better understanding of the creep phenomenon of waxy crude oil (Ghannam, 2004; Rønningsen, 1992). Ho and Zhang reported that an increase in the temperature of waxy crude oil leads to an increase in strain in an applied constant stress condition. The reduction in the internal resistance of crude oil and softening of gel structure at high temperatures were discussed as the reasons (Hou and Zhang, 2010). Many researchers have tried to propose some models to predict the rheological behavior of waxy crude oil in recent years. The studies in this area can be divided into four categories, including the studies in order to provide experimental and quasi-experimental models, the implementation of classical fluid mechanics models, the combined classical and theory-based models on the basis of thermodynamics and kinetics laws, and viscoelastic models. In some studies, the experimental rheological models such as models in (Al-Fariss et al., 1993; Al-Zahrani and Al-Fariss, 1998) were proposed to predict the rheological properties such as viscosity of waxy crude oil. The constant values of these models were determined through fitting experimental results (Iktisanov and Sakhabutdinov, 1999). The ability of the classical non-Newtonian fluid mechanical models like power law, Bingham plastic, and Casson models in predicting the rheological properties of waxy crude oil was compared (Hasan et al., 2010) and several models were combined to achieve a more comprehensive model (Rønningsen, 1992). Several classical rheological models were modified to increase the ability of the classical rheological models by introducing some parameters related to suspension rheology and considering the wax crystal formation phenomenon to the thermodynamic relationships (Adeyanju and Oyekunle, 2012; Li and Zhang, 2003; Matveenkova et al., 1995; Palermo and Tournis, 2015; Pederens and Rønningsen, 2000). Several studies have focused on the waxy gel formation phenomenon inside the pipelines in static conditions. The prediction of the rheological behavior of waxy gel is the important task for the determination of the necessary pressure to restart the flow. In (Li et al., 2015) a model was proposed to predict the yield stress. This model is based on the difference between the desired temperature and the gel point and density of the oil sample and agrees reasonably with experimental results (Li et al., 2015). To describe the complex behavior of a waxy

gel, one requires a model which consists of the elastic, viscoplastic, and thixotropic properties. Such models were developed to predict the minimum restarting pressure (Luthi, 2013; Van Der Geest et al., 2015). Some models were developed to describe the viscoelastic behavior of waxy crude oil. Dante et al. have proposed a model for predicting the behavior of waxy crude oil in terms of time and shear rate by combining Al-Zahrani empirical and Maxwell viscoelastic models (Dante et al., 2006). Moreover, some viscoelastic models based on suspension rheology theory was proposed for predicting the dynamic modulus of waxy crude oil (Dante et al., 2007).

The main aim of this study is to investigate the flow curve and the compliance function trends of the waxy crude oil samples, to propose a modified Casson model for predicting the flow curve, and to suggest a modified Burger model to describe the behavior of the compliance function of each types of waxy crude oil in terms of the amount of wax content and temperature.

2. Materials and methods

The oil samples with different wax contents are provided by adding the desired amount of a raffinate sample provided from Sepahan Oil Company to the Isfahan refinery crude oil as the base oil fluid. The density, wax, and asphaltene content of the crude oil are 895.8 kg/m³, 11.68 and 0.6 wt.% respectively. The pour point and kinematic viscosity of raffinate are 51 °C and 37.71 mm²/s at 60 °C respectively. The wax contents of the oil samples are measured according to the modified UOP 46-64 method (Elsharkawya et al., 2000). Eight shear-rotational tests and eight creep and recovery tests are conducted to determine the flow curve and compliance function by means of a MCR 300 Anton-Paar rheometer with a cone and plate geometry. The diameters of plate and gap size are 25 mm and 0.05 mm respectively. The temperature control is provided by Peltier elements.

2.1. Flow curve measurement

The flow curve is a plot of shear stress against applied shear rate. This curve is the result of shear-rotational tests and can be used to evaluate the rheological properties such as viscosity and yield stress of materials. In this study, eight flow curves are determined by adopting a rheometer with the ability to control shear rate at different temperatures and wax contents. The shear rate is of 100 s⁻¹-1000 s⁻¹ range. The capability of the power law, Bingham plastic, and Casson models of describing the flow curves are assessed. The Casson model is modified in order to match better with experimental results

2.2. Compliance function determination

Compliance functions are measured as a function of time by conducting creep and recovery tests. The creep and recovery test is a subset of unsteady shear tests. A constant shear stress is applied to the sample and the resulted strain is calculated as a function of time. After achieving a maximum strain, the stress is suddenly removed and the resulted strain gradually decreases to achieve equilibrium constant. Elastic materials recover quickly after the removal of stress and viscous materials will never recover, while viscoelastic materials recover gradually. The linear viscoelastic region (LVR) had to be determined in order to conduct the creep and recovery test. The linear viscoelastic region (LVR) is a region in which dynamic modules do not depend on applied stress (Steffe, 1996). In fact, the behavior of the viscoelastic materials in the linear viscoelastic region is only a function of time and temperature and does not depend on the amount of applied stress or strain (Fecarotti et al., 2012). In order to measure the linear viscoelastic properties of the waxy crude oil, the creep and recovery test is conducted with small stress within the LVR. The stress sweep test is conducted to measure the LVR

at a frequency of 1 Hz. The creep phase results are fitted with the four-element mechanical viscoelastic Burger model.

3. Results and discussion

3.1. Flow curve results

Eight shear-rotational tests are performed in accordance with Table 1. The flow curves of the oil sample with a wax content of 22 wt.% are shown in Figure 1(a) at temperatures of 5, 15, 25, and 35 °C. The results show that with a decrease in the temperature, the shear stress values and viscosity of the oil samples increase (Figure 1(b)). It means that a decline in temperature strengthens the waxy network. The solubility of waxes drops by decreasing the temperature, and it causes more waxy crystals to form (Vignati et al., 2005).

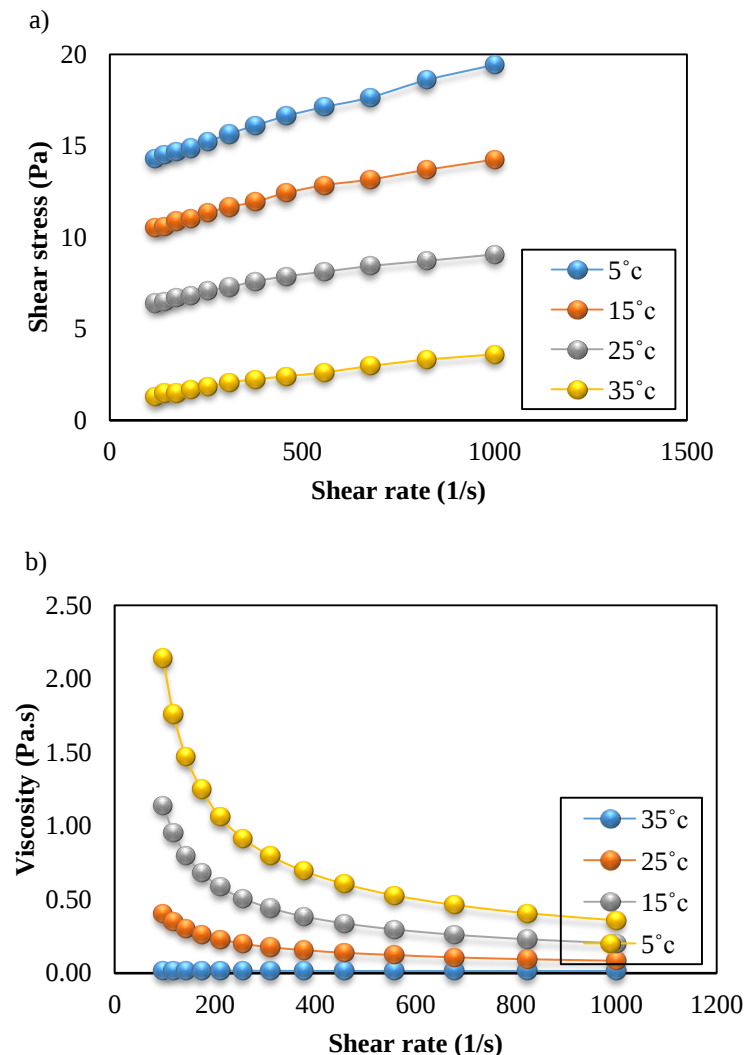


Figure 1

a) Flow curve and b) viscosity-shear rate curve at different temperatures.

The trend of viscosity reduction by increasing the shear rate represents a non-Newtonian rheological behavior of the waxy crude oil at temperatures of 5, 15, and 25 °C; however, the crude oil viscosity values do not change at the temperature of 35 °C, which means the fluid is Newtonian at this

temperature. An increase in the shear rate causes a decrease in the slope of viscosity-shear rate curve at high shear rates. It can be concluded that forces on the waxy network increase, break down the bonds between crystals, and reduce the network strength; therefore, the rheological behavior of the crude oil is described as a Newtonian fluid in this condition (El-Gamal and Gad, 1998).

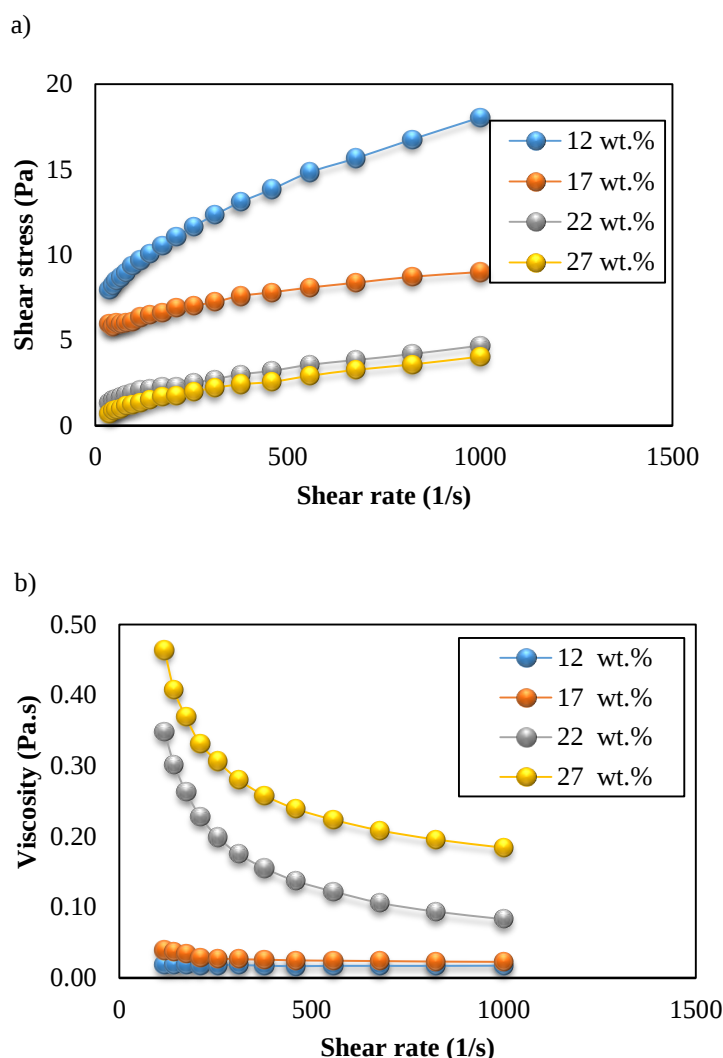


Figure 2

a) Flow curve and b) viscosity-shear rate curve for the samples with different wax contents.

Four flow curves are shown in Figure 2(a) for the oil samples with wax contents of 12, 17, 22, and 27 wt.% at 25 °C. The changing in the wax contents of the oil samples has a significant influence on the flow curves. An increase in the wax content causes the flow curves to move toward higher stress values.

The wax content increases the possibility of the formation of waxy crystals. The presence of a high amount of waxy crystals leads to forming a stronger waxy network. According to the above results, the shear stress and viscosity of the crude oil increase in this case. The increasing trend of the viscosity values with increasing wax content is clear as depicted in Figure 2(b). An increase in wax content causes the slope of viscosity-shear rate curve to increase, which represents a non-Newtonian behavior of the oil samples containing higher amounts of wax.

a. Rheological models

Waxy crude oil has been introduced as a non-Newtonian time-independent fluid (Matveenkova et al., 1995; Rønningsen, 1992). The shear-rotational test results are fitted with the power law, Bingham-plastic, and Casson models, and the results of the model parameters are reported in Table 1. According to this table, it is clear that all three models are successful in fitting the experimental results; however, the power law model is weaker than the Bingham-plastic and Casson models. The reason is that the power law model is for pseudoplastic fluids and cannot describe the rheological behavior of a waxy crude oil under different situations. The Bingham plastic model is a linear model and is usually applied to describing the behavior of Bingham-plastic fluids, while the Casson model has an ability to describe the curvature of the flow curve, and it is suitable to predict the rheological behavior of a viscoplastic fluid (Chhabra and Richardson, 2008).

Table 1
Comparing the rheological models.

Test number	Temperature (°C)	Wax content (wt.%)	Power Law			Bingham-plastic			Casson		
			$\tau_{yx} = m(\dot{\gamma}_{yx})^n$			$\tau_{yx} = \tau_0^B + \mu_B(\dot{\gamma})$			$(\tau_{yx})^{0.5} = (\tau_0^c)^{0.5} + (\mu_c \dot{\gamma}_{yx})^{0.5}$		
			m (Pa.s ⁿ)	n	R ²	τ_0^B (Pa)	μ_B (Pa.s)	R ²	τ_0^c (Pa)	μ_c (Pa.s)	R ²
1	5	22	63.02	0.2453	0.9526	189.8	0.1762	0.9912	145.6	0.04565	0.9955
2	15	22	33.53	0.2533	0.9491	104.1	0.1024	0.9784	77.80	0.02838	0.9854
3	25	22	10.46	0.2942	0.9739	35.29	0.05259	0.9752	25.38	0.01721	0.9943
4	35	22	0.02407	0.9909	0.9976	0.3837	0.01273	0.9986	0.1799	0.009211	0.9755
5	25	12	0.02063	0.9706	0.9993	0.1894	0.01669	0.9995	0.1099	0.01290	0.9871
6	25	17	0.1210	0.7497	0.9900	1.58	0.02116	0.9969	0.6168	0.01491	0.9975
7	25	22	10.46	0.2942	0.9739	35.29	0.05259	0.9752	25.38	0.01821	0.9943
8	25	27	9.323	0.5029	0.9742	55.80	0.2841	0.9925	34.30	0.1415	0.9960

By comparing the R^2 values for Bingham and Casson models in each test, it can be concluded that Bingham-plastic model is better than Casson model for the experiments No. 4 and 5, while Casson model matches better with the experimental results for the rest. The test No. 4 is performed at a temperature of 35 °C and the oil sample in test No. 5 has a low wax content of 12 wt.%; therefore, it is clear that the behavior of those oil samples are similar to a Bingham-plastic fluid under this condition. A decrease in temperature or an increase in wax content causes the waxy crude oil to become a viscoplastic fluid. The change of temperature and wax content changes the rheological nature of the waxy crude oil. At high temperatures or low wax content, there is a difficult condition to form waxy crystals and the waxy crystal formation rate is very low. Moreover, the rheological behavior of the crude oil has a linear relationship with the shear rate, while a strong waxy network exists within the oil at low temperatures or high wax content. This network changes the rheological behavior of the waxy crude oil. In this case, the dependency of the rheological behavior of the waxy crude oil to the shear stress is more complicated. In another similar study, which was performed to provide a model for the prediction of the flow curve of waxy crude oil, it was shown that the waxy crude oil had different rheological behaviors and its rheological nature was changed from a Newtonian to a viscoplastic fluid followed by a viscoelastic behavior (Iktisanov and Sakhabutdinov, 1999).

In this study, the Casson model is selected as the base model for providing a modified model to predict the flow curve of the oil samples with various wax amounts at different temperatures. In the following, the Casson model parameters changing trends are interpreted.

τ_0^c : This parameter is the Casson yield stress, which increases with a decrease in temperature and an increase in wax content. This parameter is a measure of yield strength of material, and by definition, yield stress is a minimum stress required to flow the fluid. The change of this parameter can be related to the changes in the internal structure of the materials. The solubility of waxes in the crude oil decreases with decreasing temperature and it leads to produce waxy crystals. The waxy crystals are linked together and form waxy agglomerates and network at low temperatures. As temperature is lowered, the links become stronger and the resulted network has a higher yield stress (Aiyejina et al., 2011). As the oil wax content increases, the waxy network grows and the Casson yield stress increases.

μ_c : In the Casson rheological model, this parameter is a measure of the apparent viscosity of fluid and is named as Casson viscosity. According to Table 1, the μ_c decreases inversely with temperature but directly with wax content. The solubility of waxy crystals in the crude oil increases by temperature but drops by wax content, which in turn causes the waxy network to become a weaker structure. The weakening of the structure of the network is followed by Casson viscosity reduction.

The Casson rheological model is able to match the experimental results successfully. The dependency of the model parameters on temperature and wax content are correlated by applying four different combinations of power and exponential functions through Equations 1-4. The fitting results and the statistical parameters are reported in Table 2. It should be noted that the experimental results of the test which is conducted for the oil sample with wax content of 22 wt.% at 5 °C is not included in the regression and it is used to validate the proposed modified Casson model prediction.

$$f(T, W) = a \cdot \exp(bT + cW) \quad (1)$$

$$f(T, W) = a \cdot T^b \cdot \exp(cW) \quad (2)$$

$$f(T, W) = a \cdot W^c \cdot \exp(bT) \quad (3)$$

$$f(T, W) = a \cdot T^b \cdot W^c \quad (4)$$

The statistical parameters such as the coefficient of determination (R^2), mean percent error (MPE), mean bias error (MBE), and standard error (RMSE) are evaluated to judge the mentioned functions. The above statistical parameters are calculated as the following equations (Toğrul and Arslan, 2004).

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_{exp,i} - y_{pre,i})^2}{\sum_{i=1}^N (y_{exp,i} - y_{exp,ave})^2} \quad (5)$$

$$MPE = \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{y_{exp,i} - y_{pre,i}}{y_{exp,i}} \right) \right] \times 100 \quad (6)$$

$$MBE = \frac{1}{N} \sum_{i=1}^N (y_{pre,i} - y_{exp,i}) \quad (7)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (y_{exp,i} - y_{pre,i})^2 \right]^{1/2} \quad (8)$$

where, $y_{exp,i}$ is the experimental result; $y_{pre,i}$ is the result predicted by the model; $y_{exp,ave}$ is the average of the experimental results, and N is the number of experimental results; k stands for the

number of independent variables in the model. In multiple regression, a greater R^2 value and lower absolute values of MPE, MBE, and standard error for each model mean that the model fits the experimental results reasonably (Toğrul and Arslan, 2004).

Table 2

The effect of temperature and wax content on the Casson model parameters.

	Parameters of the proposed model			Statistical parameters			
	a	b	c	R^2 (%)	MPE	MBE	RMSE
$\tau_0^c = a \cdot \exp(bT + cW)$	19.96	-0.0926	0.1126	95.96	-17.42	2.231	9.466
$\tau_0^c = a \cdot T^b \cdot \exp(cW)$	86.324	-1.103	0.1056	89.96	-24.77	2.336	14.61
$\tau_0^c = a \cdot W^c \cdot \exp(bT)$	0.09	-0.091	2.545	96.45	-14.83	2.142	8.88
$\tau_0^c = a \cdot T^b \cdot W^c$	0.5349	-1.086	2.386	90.57	-22.02	2.146	14.46
$\mu^c = a \cdot \exp(bT + cW)$	0.000007	-0.04665	0.4118	97.62	0.1362	-0.0025	0.000638
$\mu^c = a \cdot T^b \cdot \exp(cW)$	0.000014	-0.5876	0.4106	97.31	0.1519	-0.0026	0.00679
$\mu^c = a \cdot W^c \cdot \exp(bT)$	3×10^{-14}	-0.0367	8.783	18.35	0.6882	-0.0245	0.0388
$\mu^c = a \cdot T^b \cdot W^c$	1.6×10^{-14}	-0.515	9.21	22.15	0.6806	-0.0241	0.0365

The best model for describing τ_0^c and μ^c parameters are Equations 3 and 1 respectively. These relations have the highest R^2 and the lowest absolute values of MPE, MBE, and standard error, which reflects the high ability of these equations to match with the experimental results. The final form of the modified Casson model is reported in Table 3.

Table 3

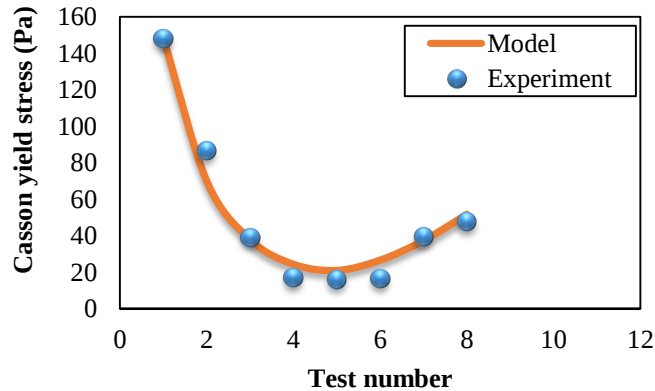
Modified Casson model.

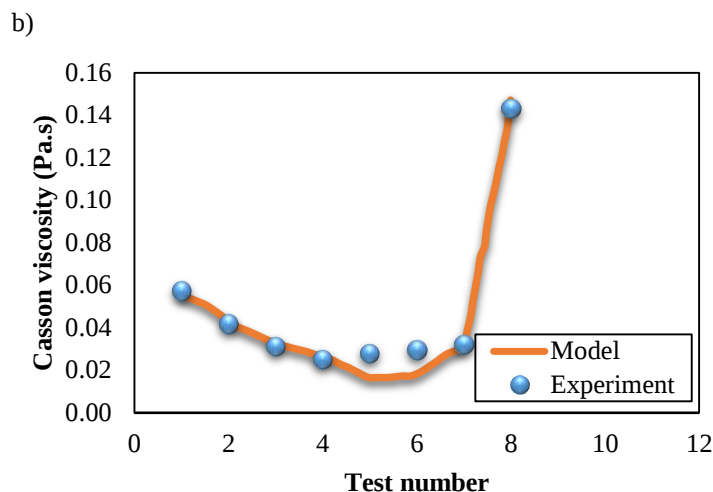
$(\tau_{yx})^{0.5} = (\tau_0^c)^{0.5} + (\mu^c \dot{\gamma}_{yx})^{0.5}$	R^2 (%)
$\tau_0^c = 0.09 \times W^{2.545} \exp(-0.091 T)$	96.45
$\mu^c = 7 \times 10^{-6} \exp(-0.04665 T + 0.4118 W)$	97.62

b. Model validation

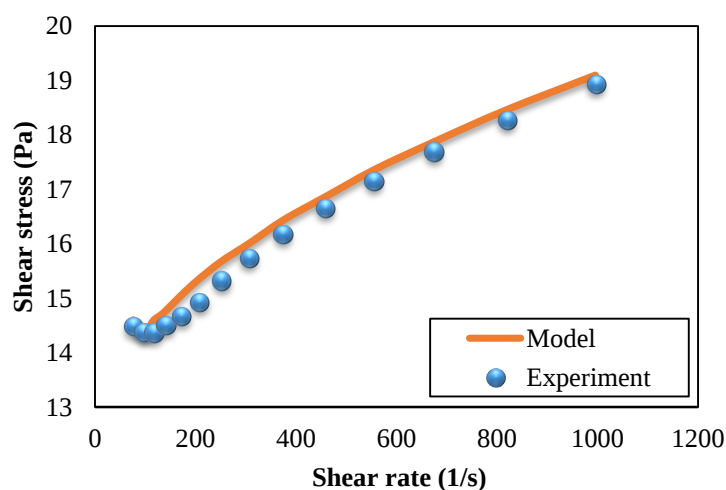
The predictions of the proposed model are validated through the experimental results of the Casson model parameters for all the eight tests and the flow curve of the sample with wax content of 22 wt.% at a temperature of 5 °C. These comparisons are shown in Figures 3 and 4.

a)



**Figure 3**

Comparing the experimental and predicted results for a) Casson yield stress and b) Casson viscosity.

**Figure 4**

Comparing the experimental and predicted flow curve of the oil sample with wax content of 22 wt.% at 5 °C.

There is reasonable agreement between the experimental results and the predictions of the model. This model matches with the experimental results with $R^2 = 97.33\%$ as shown in Figure 4.

3.2 Viscoelastic properties

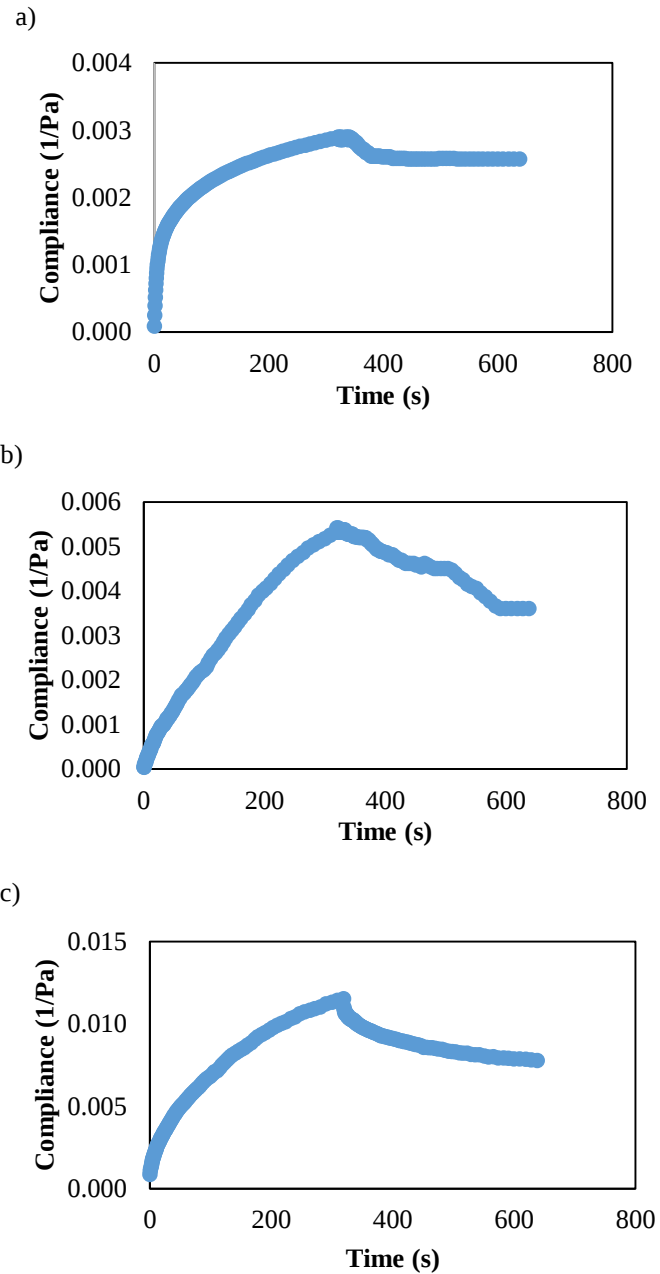
a. Linear viscoelastic region (LVR)

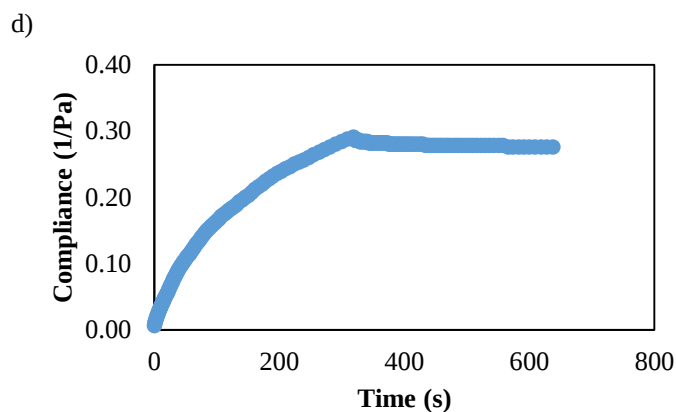
In this study, four different waxy crude oil samples with different wax amounts are prepared and used to perform creep and recovery tests at four different temperatures. The linear viscoelastic region should be valid for all the samples within the test temperature range; therefore, the LVR should be measured under a condition that the crude oil has the weakest waxy structure. Therefore, the sample with the lowest wax content (12 wt.%) is selected to perform the stress sweep test at the highest temperature (35 °C). The stress sweep test is performed at a frequency of 1 Hz and 0.01 and in stress range of 50 Pa; the results show that G'' and G' moduli are independent of the stress up to stress

values of 35 Pa and 8 Pa respectively. To ensure that the selected stress is within the linear viscoelastic region, the stress should be less than 8 Pa; herein, the stress of 0.5 Pa is considered.

b. Creep and recovery test results

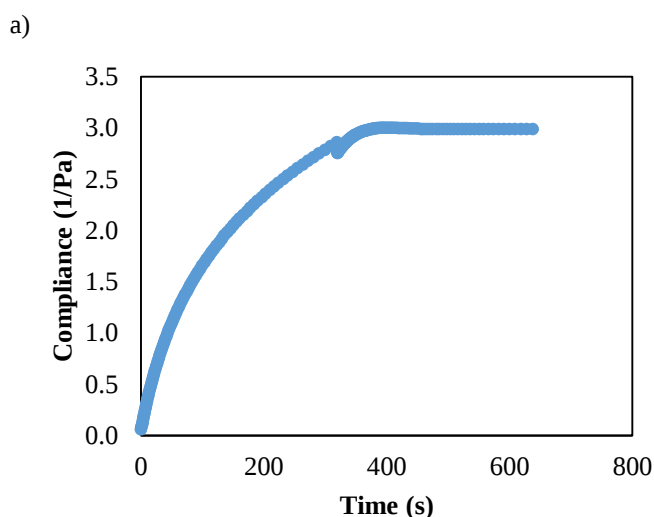
In the creep phase, a constant stress of 0.5 Pa is applied to the oil samples for 319 seconds and then it is suddenly removed. Next, the recovery phase continues for 319 seconds. The compliance functions in terms of time are shown in Figures 5 and 6.

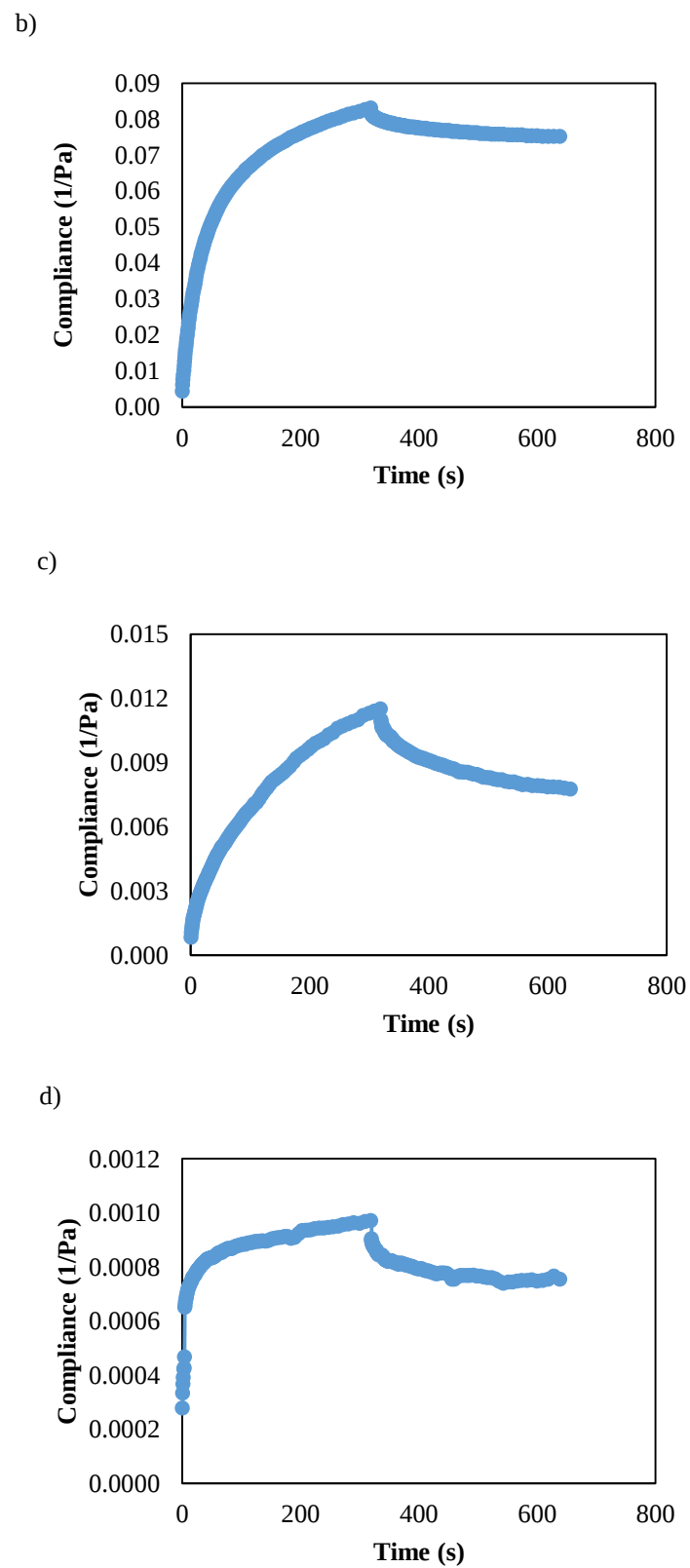


**Figure 5**

Compliance function of the oil sample with wax content of 22 wt.% at a) 5 °C, b) 15 °C, c) 25 °C, and d) 35 °C.

The general trend of the results in Figure 5 represents a viscoelastic nature and time-dependent rheological behavior of the waxy crude oil. The compliance function value at 35 °C is much higher than the others because of the high solubility of waxes at high temperatures. The internal structure is weak at high temperatures due to the lack of waxy crystals to form a strong waxy network. This weak structure is deformed quickly, and its deformation is large. As the recovery phase starts, the compliance function drops to an equilibrium value, and, at the end of the recovery phase, a full recovery is not observed at all four temperatures. Since viscoelastic materials have a partial recovery and reach their full recovery at a long time, it can be concluded that the waxy crude oil samples have viscoelastic behavior (Steffe, 1996). After the removal of the stress, as shown in Figure 5, at 5 °C the waxy crude oil achieves the 99% of its final recovery suddenly; however, the compliance functions decline gradually at the other temperatures. It represents that the rheological behavior of the waxy crude oil is similar to an ideal elastic material at 5 °C. A very little recovery can be observed at 35 °C because the absence of the waxy crystal network has caused the crude oil to behave like a viscous fluid.



**Figure 6**

Compliance functions of the oil samples with wax content of a) 12 wt.%, b) 17 wt.%, c) 22 wt.%, and d) 27 wt.% at 25 °C.

The compliance function for the oil sample with wax content of 12 wt.% has a higher value compared to the other samples as shown in Figure 6. Increasing the wax content, the compliance decreases since the compliance function depends on the strain and the strain depends on the strength of the internal structure of the material directly. As the wax content of the oil samples increases, according to the results of this research, a crystal network is formed; therefore, the internal strength of the crude oil increases.

Moreover, the wax content has a significant influence on the recovery phase. The sample with a wax content of 12 wt.% does not recover, which represents a viscous fluid. An increase in wax content leads to higher recovery levels of the waxy crude oil, so its behavior tends to a solid viscoelastic solid.

In order to evaluate the performance of the viscoelastic Burger model, the creep test experimental results are fitted with this model. The results are presented in Table 4. The Burger model has a good accuracy in predicting the compliance function according to the reported R^2 values. However, this model has the lowest accuracy in runs No. 4 and 5, where temperature is at the lowest level and wax content is in the highest level respectively. It can be explained that a favorable condition is provided for the formation of waxy crystals at either low temperatures or high wax content. In this situations, many waxy crystals form and a waxy network propagates in the whole crude oil medium. It changes the rheological behavior of the crude oil from a viscoelastic material to a Hookean solid. It is not surprising that the viscoelastic Burger model cannot predict the behavior of a Hookean solid very well.

Table 4
The Burger model parameters.

$J(t) = J_0 + J_1 \left(1 - \exp \left(-\frac{t}{\lambda} \right) \right) + \frac{t}{\mu_0}$						
Temperature (°C)	Wax content (wt.%)	J_0 (Pa ⁻¹)	J_1 (Pa ⁻¹)	λ (s)	μ_0 (Pa.s)	R^2
5	22	0.0003108	0.001479	12.37	254653	0.9854
15	22	0.0003196	0.002799	39.18	131268	0.9988
25	22	0.001317	0.004679	58.28	54678	0.9981
35	22	0.008769	0.1462	68.95	2272	0.9998
25	12	0.05895	1.463	61.23	232.5	0.9999
25	17	0.004547	0.1336	59.81	2840	0.9999
25	22	0.001317	0.004679	58.28	54678	0.9981
25	27	0.0004321	0.001163	5.049	795213	0.9720

The Burger model parameters have particular physical interpretations. The functionality of these four parameters with temperature and wax content are studied.

The J_0 is instantaneous compliance, and J_1 represents retardation compliance; λ and μ_0 are retardation time and zero shear viscosity respectively. J_0 is the reverse of the Young's modulus of Maxwell spring (G_0), and J_1 is the reverse of the Young's modulus of Kelvin portion (G_1) in Burger model (Steffe, 1996). The Young's modulus is the slope of shear stress-strain curve. This modulus is a measure of the hardness of the internal structure of materials (Morrison, 2001). The λ is a measure of the response delay of materials to stress. In other words, as the value of this parameter is low, the system responds to the applied force quickly and deforms very fast. The value of this parameter relates to the

viscoelastic nature of the material. Ideal elastic materials have a low λ , whereas ideal viscous fluids have a high λ (Steffe, 1996). The μ_0 is the viscosity of Maxwell dashpot in Burger model and represents the viscous properties of materials in a long time. It is the inverse of creep phase curve slope at the end of this phase. It is infinite for the ideal elastic solids and is very low for ideal viscous fluids (Steffe, 1996). Therefore, the values of J_0 , J_1 , λ , and μ_0 relate to the strength of waxy network and the viscoelastic nature of waxy crude oil in different conditions. According to Table 4, a decrease in temperature or an increase in wax content causes J_0 , J_1 , and λ to decrease but μ_0 to increase. It shows that a strong waxy network is formed under these conditions and the rheological behavior of the crude oil approaches viscoelastic solids with decreasing temperature or increasing wax content.

c. Modified viscoelastic Burger model

In order to determine the best model for Burger model parameters predictions, four different combinations of exponential and power functions (Equations 1-4) are applied. The results are reported in Table 5. It should be noted that the experimental results of a test which is conducted by the oil sample with wax content of 12 wt.% at 25 °C is not included in the regression and it is used to evaluate the validity of the proposed Burger model.

Table 5
The effect of temperature and wax content on the Burger model parameters.

Proposed models	Parameters of proposed model				Statistical parameters		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>R</i> ² (%)	MPE	MBE	RMSE
$J_0 = a \cdot \exp(bT + cW)$	0.01051	0.3085	-0.4990	99.96	52.31	-0.000317	0.000512
$J_0 = a \cdot T^b \cdot \exp(cW)$	0.00003	3.5692	-0.3943	-0.3943	45.05	74.71	-0.00635
$J_0 = a \cdot W^c \cdot \exp(bT)$	0.014	7078.77	-7.1512	99.92	58.84	-0.000397	0.000535
$J_0 = a \cdot T^b \cdot W^c$	1.308	4.1428	-6.7258	91.33	51.28	-0.002818	0.00556
$J_1 = a \cdot \exp(bT + cW)$	0.8759	0.2521	-0.2424	99.94	-16.22	0.00105	0.003734
$J_1 = a \cdot T^b \cdot \exp(cW)$	0.001	3.583	-0.39	84.80	-33.62	-0.0266	0.1846
$J_1 = a \cdot W^c \cdot \exp(bT)$	44.732	0.1983	-7.0718	99.74	-110.74	0.0031	0.00845
$J_1 = a \cdot T^b \cdot W^c$	0.3631	5.8916	-7.071	99.73	-99.64	0.00283	0.00848
$\lambda = a \cdot \exp(bT + cW)$	19.144	0.057	-0.0197	62.17	-72.55	0.3034	13.9
$\lambda = a \cdot T^b \cdot \exp(cW)$	7.717	0.845	-0.0419	61.68	-73.11	0.712	14.02
$\lambda = a \cdot W^c \cdot \exp(bT)$	149.56	0.043	-0.742	57.71	-78.87	0.3307	14.72
$\lambda = a \cdot T^b \cdot W^c$	23.96	0.8456	-0.6652	57.02	-79.46	0.56	14.84
$\mu_0 = a \cdot \exp(bT + cW)$	2.786	-0.0783	0.538	99.86	-1.267	1632.87	9291.35
$\mu_0 = a \cdot T^b \cdot \exp(cW)$	11.501	-0.9345	0.242	99.39	-2.28	1927.75	19767.9
$\mu_0 = a \cdot T^b \cdot W^c$	$7.8 \cdot 10^{-12}$	-0.934	12.8	99.39	2.04	1662.37	19672.6

According to the results of Table 5 and comparing the statistical parameter values, it can be concluded that the best model for describing the behavior of J_0 , J_1 , and μ_0 is Equation 1; however, none of the equations are appropriate to predict λ . For this reason, more terms need to be included to this equation in order to comply with the experimental results of λ . A complex term as a function of wax content is included to Equation 1. The best relations with reasonable predictions are reported in Table 6.

Table 6
Modified Burger model.

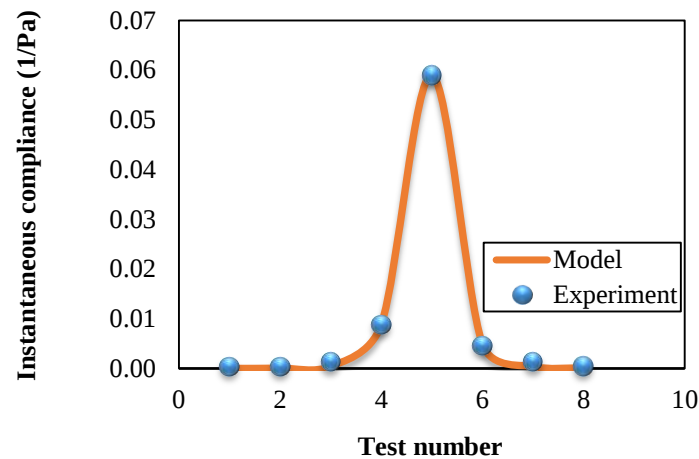
$J(t) = J_0 + J_1 \left(1 - \exp\left(-\frac{t}{\lambda}\right)\right) + \frac{t}{\mu_0}$	R^2 (%)
$J_0 = 0.01051 \times \exp(0.3085 T - 0.499 W)$	99.96
$J_1 = 0.8759 \times \exp(0.2521 T - 0.4824 W)$	99.94
$\lambda = \left[-6597 + \frac{6620.3}{1 + \left(\frac{W}{39.04}\right)^{15.55}} \right] \exp(0.0383 T)$	87.9
$\mu_0 = 2.786 \times \exp(-0.0783 T + 0.538 W)$	99.86

In these equations, T and W are temperature ($^{\circ}\text{C}$) and wax content (wt.%) respectively.

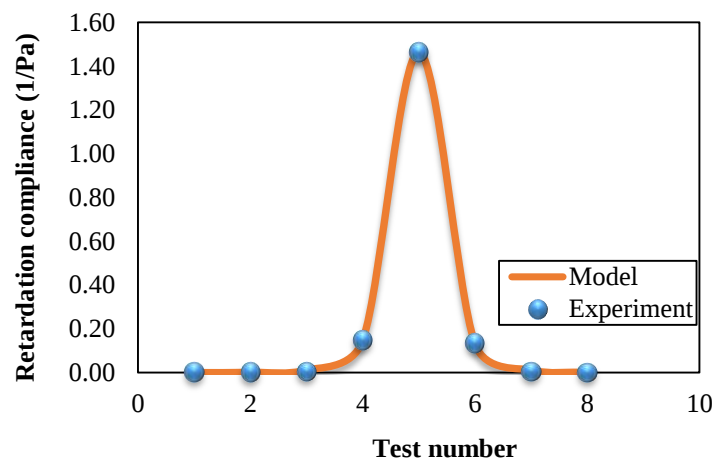
d. Model validation

The proposed model is validated by the comparison of the experimental and predicted results of Burger parameters and the compliance function of oil sample with wax content of 12 wt.% at temperature 25°C . The comparison results are shown in Figures 7 and 8.

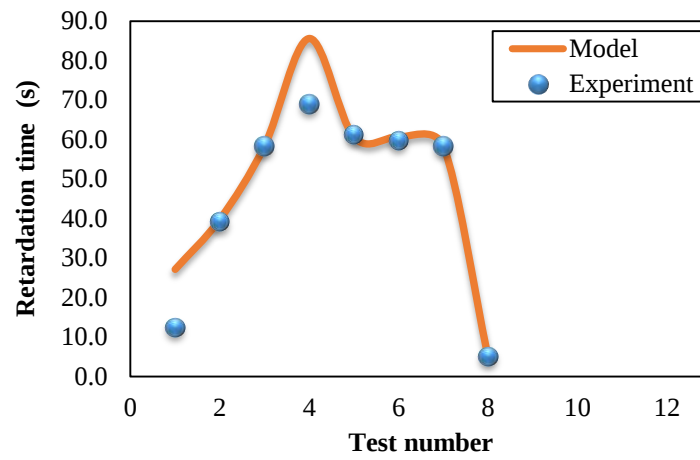
a)



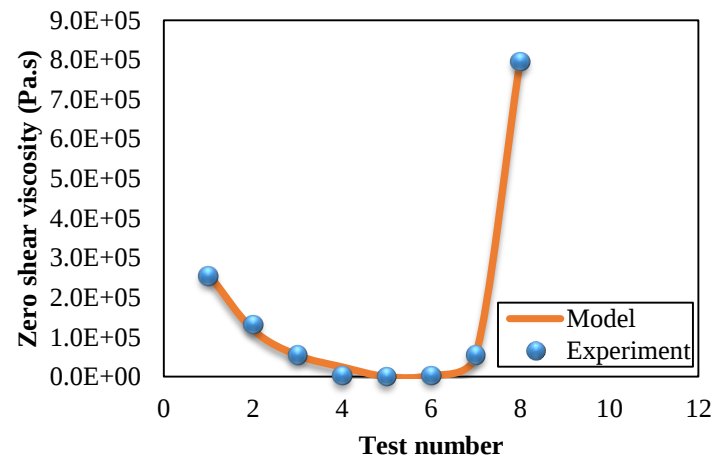
b)



c)

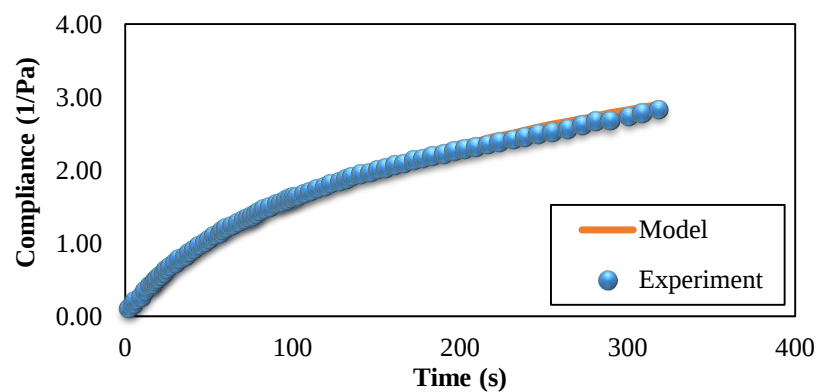


d)

**Figure 7**

Comparing the experimental and predicted results of a) instantaneous compliance, b) retardation compliance, c) retardation time, and d) zero shear viscosity of the Burger model.

There is reasonable agreement between the experimental results and the predictions of the model. The model matches with the experimental results with $R^2 = 99.7\%$ as shown in Figure 8.

**Figure 8**

Comparing the experimental and predicted compliance of the oil sample with 12 wt.% wax content at 25 °C.

4. Conclusions

In this study, several shear-rotational tests are conducted to investigate the time-independent rheological behavior of an Iranian waxy crude oil sample. The flow and the viscosity-shear rate curves show that a decrease in temperature or an increase in wax content raises the viscosity. The power law and Bingham-plastic models cannot predict the flow curves in all the wax amounts and temperature ranges since the rheological behavior of the waxy crude oil changes from a Newtonian to a viscoplastic fluid when temperature decreases or wax content increases. The Casson model is the best model for predicting the rheological behavior of the waxy crude oil. This model has two parameters τ_0^c and μ^c , which are increased as temperature decreases or wax content increases. It is concluded that a decrease in temperature or an increase in wax content causes the internal structure of the waxy crude oil to strengthen, and as a result, viscosity and yield stress increase. A modified model, based on Casson model, is developed to predict the flow curves of the waxy crude oil samples. The viscoelastic behavior of the waxy crude oil is studied using creep and recovery test. The Burger model can fit with compliance function results adequately. The functionality of the four parameters of this model is determined, and it is shown that a decrease in temperature or an increase in wax content leads to a decrease in the J_0 , J_1 , and λ but an increase in the μ_0 . It means that a strong waxy network forms in the crude oil, and the viscoelastic nature of the fluid tends to a viscoelastic solid in these conditions. A modified model, based on Burger model, is proposed, which reasonably predicts the compliance function of the waxy crude oil in a vast range of temperatures and wax content.

Nomenclature

J	: Compliance function
J_0	: Instantaneous compliance
J_1	: Retardation compliance
LVR	: Linear viscoelastic region
t	: Time
UOP	: Universal oil products (standards)
WAT	: Wax appearance temperature
Greek letters	
$\dot{\gamma}$	: Shear rate
λ	: Retardation time
μ	: Viscosity
τ	: Shear stress
Superscripts	
B	: Bingham
C	: Casson

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