Propagation of Viscous Waves and Activation Energy of Hydrocarbon Fluids

Ram N. Singh, Abraham K. George, and Dawood N. Al-Namaani

Abstract—The Euler's equation of motion is extended to include the viscosity stress tensor leading to the formulation of Navier–Stokes type equation. The latter is linearized and applied to investigate the rotational motion or vorticity in a viscous fluid. Relations for the velocity of viscous waves and attenuation parameter are obtained in terms of viscosity (μ) and the density (ρ) of the fluid. μ and ρ are measured experimentally as a function of temperature for two different samples of light and heavy crude oil. These data facilitated to determine the activation energy, velocity of viscous wave and the attenuation parameter. Shear wave velocity in heavy oil is found to be much larger than the light oil, whereas the attenuation parameter in heavy oil is quite low in comparison to light one. The activation energy of heavy oil is three times larger than light oil.

Keywords—Activation Energy, Attenuation, Crude Oil, Navier-Stokes Equation, Viscosity.

I. INTRODUCTION

IT has always been a matter of great interest to formulate suitable relations which can readily be used to investigate the viscous properties of dense fluids in terms of variables that can be determined experimentally. From the fundamental point of view, a good amount of literature exists [1]-[4] based on the theory of continuous media which is an extension of the particle mechanics. In the present work we provide a formulation to generalize the Euler's equation of motion of perfect fluids to include the viscous stress tensor leading to the formation of Navier-Stokes (NS) type equation. Under acoustic approximation, NS equation is linearized and applied to investigate the rotational motion or vorticity of fluids. The latter gives rise to propagation of shear waves which are usually known as viscous wave. The transverse wave solution of linearized NS equation gives the desired relation connecting the propagation velocity (v_s) and the attenuation parameter (k) of the viscous wave to the viscosity (μ) and the density (ρ) of the fluid.

We have applied here our formulation to investigate the viscous properties of crude oils. Important ingredients are viscosity and density. We have experimentally measured the temperature dependence of viscosity of the two crude oil samples using *Haake-Viscometer*. The samples were procured directly from the two different oil fields of Oman which differs considerably in their API (American Petroleum Institute oil gravity number). Another important property which is required for our investigation is the density. It is measured accurately as a function of temperature using *Anton-Paar Density Meter*. These data facilitated to determine v_s, k, and the activation energy.

Viscous property of crude oil plays a very prominent role in the petroleum industry [5]-[9]. The viscosity of fluids affects our ability to pump the crude oil out of the reservoir; the viscosity and volatility of a fuel affect how easy it is to atomize in the fuel injector; it is the viscosity of a lubricant that affects its ability to protect an engine. It is a very important measurement and a small change can have a dramatic impact on the properties of petroleum fluids.

Necessary formulation is provided in section II. Experimental results of the temperature dependence of the viscosity (μ) and the density (ρ) are presented in section III. Computed values of v_s and k as a function of temperature are also given in this section. The measured values of the temperature dependence of viscosity are further expressed in the form of Arrhenius type equation to determine the activation energy. The results are provided in section III. It follows a short summary and conclusions in section IV.

II. THEORETICAL FORMULATION

Whenever fluids are deformed, motion is produced which in the course of time propagates through the medium in the form of elastic wave. It is convenient to describe the motion of continuous medium through a function v(x, t) [v – velocity, x – position, t – time] which is often called velocity flow function. Taking into account of the various contributions of forces acting on the elemental unit of the fluid, one writes:

$$\rho \frac{Dv_i}{Dt} = \sum_j \frac{\partial \sigma_{ji}}{\partial x_j} + \rho F_i \qquad (1)$$

where $\dfrac{D}{Dt}$ stands for material derivative, ρ is material density, F_i stands for external forces and σ_{ij} are local stress components. For inviscid and incompressible fluids, $\sigma_{ij} = -p\partial_{ij}$, therefore,

$$\rho \frac{Dv_i}{Dt} = -\frac{\partial p}{\partial x_i} + \rho F_i \qquad (2)$$

which is the celebrated Euler's equation of motion, one of the fundamental equations of fluid mechanics. Expanding the material derivative (see for example [3]), one arrives at:

Authors are with Department of Physics, College of Science, Sultan Qaboos University, P.O. Box 36, Al Khodh 123, Muscat, Sultanate of Oman (Corresponding Author Ram N. Singh e-mail: ram@squ.edu.om).

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:6, No:12, 2012

$$\rho(\frac{\partial \mathbf{v}}{\partial t} - \mathbf{v} \times curl\ \mathbf{v}) + \tfrac{1}{2}\rho\ grad\ \mathbf{v}^2 + grad\ p = \rho\mathbf{F}. \quad (3)$$

This is a very convenient representation of Euler's equation of motion. It can easily be specialized in any curvilinear coordinate system just by substituting the respective values of *curl* and *grad* for a real fluid. For including the velocity gradient existing among the different layers of the fluid, as the case for viscous medium, the stress components are introduced as:

$$\sigma_{ij} = -p\delta_{ij} + \Pi_{ij} \quad (4)$$

where Π_{ij} represents the viscosity stress tensor and are identically zero if all $\partial v_i / \partial x_j = 0$. It is safer to assume the fluids as isotropic medium, therefore analogous to the stress-strain relation for elastic isotropic solids ($\sigma_{ij} = \lambda(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})\delta_{ij} + 2\eta_{ij}$; ε_{ij} are strain tensor, η and λ are Lame's constants), we express the relationship between Π_{ij} and v_{ij} as:

$$\Pi_{ij} = \mu'(v_{11} + v_{22} + v_{33})\delta_{ij} + 2\mu v_{ij} = \mu'\ divv\ \delta_{ij} + 2\mu v_{ij}. \quad (5)$$

Here μ and μ' are known as the first and second coefficients of viscosity and take the place of Lame's constants μ and λ respectively. Substituting equations (4) and (5) in equation (1), one has,

$$\rho\frac{Dv_i}{Dt} = \rho F_i + \sum_j \frac{\partial}{\partial x_j}(-p\delta_{ij} + \Pi_{ij}). \quad (6)$$

Substituting the vales of Π_{ij}, one writes in vector notation,

$$\rho\frac{D\mathbf{v}}{Dt} = \rho\mathbf{F} - grad\ p + (\mu + \mu')\ graddivv + \mu\nabla^2\mathbf{v} \quad (7)$$

After expanding the material derivative as we did in equations (2) and (3),

$$\rho\frac{\partial \mathbf{v}}{\partial t} = \rho\mathbf{F} - gradp - \tfrac{1}{2}\rho\ grad\mathbf{v}^2 + \rho(\mathbf{v} \times curl\mathbf{v})$$
$$+ (\mu + \mu')graddiv\mathbf{v} + \mu\nabla^2\mathbf{v} \quad (8)$$

Equation (8) is the most celebrated Navier-Stokes (NS) type equation of motion for real fluids. By deleting the viscosity containing terms from equation (8) one recovers equation (3) of motion for perfect fluids. Under acoustic approximation (neglecting non-linear term of equation (8)) and for zero body force ($\mathbf{F} = 0$), equation (8) is linearized to,

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -grad\ p + (\mu + \mu')grad\ div\ \mathbf{v} + \mu\nabla^2\mathbf{v}. \quad (9)$$

The rotational motion or vorticity in a fluid gives rise to shear waves which are usually known as viscous waves. By taking the *curl* of both sides and remembering that *curl grad* = 0, one gets,

$$\frac{\partial w}{\partial t} = \left(\frac{\mu}{\rho}\right)\nabla^2 w \quad (10)$$

where $w = \tfrac{1}{2}\ curl\ v$ is the vorticity. Consider a transverse wave solution such that the wave motion is directed along the x_1-axis and the particle motion is along the x_2-axis, i.e.,

$$v_2 = v_2^0 \exp[i(\omega t - kx_1]\ ; \quad v_1 = v_3 = 0. \quad (11)$$

Obviously *div* $\mathbf{v}$ = 0 and therefore we get:

$$\frac{\partial^2 v_2}{\partial t^2} = \frac{\mu}{\rho}\frac{\partial}{\partial t}\left(\frac{\partial^2 v_2}{\partial x_1^2}\right) \quad . \quad (12)$$

The above two equations yield:

$$k^2 = -\frac{i\omega\rho}{\mu}. \quad (13)$$

By setting $k = k_1 - ik_2$, one has:

$$k_1^2 - k_2^2 - 2ik_1k_2 = -\frac{i\omega\rho}{\mu}. \quad (14)$$

The separation of real and imaginary parts gives:

$$k_1 = k_2, \quad k_1k_2 = \frac{\omega\rho}{2\mu} \quad (15)$$

The attenuation $k_2 = k$ (say) and the propagation velocity of the viscous wave becomes,

$$k = \left(\frac{\omega\rho}{2\mu}\right)^{\frac{1}{2}}, \quad (16)$$

and

$$v_s = \frac{\omega}{k} = \left(\frac{2\mu\omega}{\rho}\right)^{\frac{1}{2}} \quad (17)$$

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:6, No:12, 2012

In order to apply equations (16) and (17) to determine the velocity of viscous wave and the attenuation, we require experimental values for viscosity (μ) and density (ρ). Below we provide the details of experimental measurements.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Two different crude oil samples were procured from different oil fields located in the Sultanate of Oman. The two samples will be referred as sample I, sample II. Due to variation in chemical composition of crude oil from different regions, an accepted index number called API (American Petroleum Institute oil gravity number; API gravity is a measure of how heavy or light is petroleum liquid compared to water) has been used to classify the samples. The equation for finding the API is,

$$API = \frac{141.5}{\rho} - 131.5 \qquad (18)$$

where ρ is the density (g/cm^3) measured at 15.6^{o}C and at atmospheric pressure. We have used our density data (see Table I) to determine the API values for each sample :

Sample I: API = 21.93 (*Heavy oil*)
Sample II: API = 42.41 (*Light oil*)

The API number usually varies from 5 for very heavy oils to near 100 for light condensates. For the sake of brevity, hereafter we will designate Sample I as heavy oil and sample II as light oil.

A. Measurement of Density

The density of the samples was measured by using *Anton Paar Density Meter*. The unit consists of a U-shaped oscillating tube, a system for electronic excitation, frequency counting and a display. The injected sample volume was kept constant and vibrated. The density calculation was based on a measurement of the sample oscillation period at a given temperature. The temperature was controlled to ±0.01^{o}C using a built-in thermostat. The above instrument enables density to be measured to an accuracy of ±5 kg/m^3. The density measurements are performed at temperatures varying from 20°C and 60°C. Density values of the two samples are listed in Table I.

The experimentally determined density of the two samples is found to decrease linearly with increasing temperature. The density data can be fitted to the equation,

$$\rho(t) = \rho_o + m(t - t_r) \qquad (19)$$

where ρ_o is the density at room temperature, m stands for (dρ/dt) and t_r is the room temperature (20°C). After substituting the values of ρ_o and m, we have, in units of kg/m^3

$$\rho(t) = 0.93238 - (6.48468\text{E-}4)t \quad \text{(heavy oil)} \qquad (20)$$

$$\rho(t) = 0.82478 - (7.12586\text{E-}4)t \quad \text{(light oil)} \qquad (21)$$

TABLE I
MEASURED DENSITY OF CRYDE OIL SAMPLES

t ± 0.01 ^{o}C	Density (ρ ± 0.005) × 10^3 kg m^{-1}	
	Heavy oil	Light oil
20	0.919	0.811
25	0.916	0.807
30	0.913	0.803
35	0.910	0.800
40	0.906	0.796
45	0.903	0.793
50	0.900	0.789
55	0.897	0.786
60	0.893	0.782

The temperature gradients of density for both samples are negative and the magnitude for light oil is about 10% higher than the heavy oil. On the contrary, the density at room temperature of heavy oil is about 13% higher than light oil. The data of the temperature dependence of ρ are also very important to determine the thermo-elastic properties like, coefficient of volume expansion, adiabatic compressibility and the acoustic impedance [10].

B. Measurement of Viscosity

The viscosity of the crude oil samples is determined using a *Haake-viscometer* which is a Searle viscometer. The rotational speed was set and the flow resistance of the oil was measured. The values of viscosity in (Pa s) for the two samples are listed in Table II.

TABLE II
MEASURED VISCOSITY OF CRUDE OIL SAMPLES

t ± 0.1 ^{o}C	Viscosity (μ ± 0.01) Pa s	
	Heavy oil	Light oil
20	0.500	0.0210
25	0.404	0.0198
30	0.291	0.0160
35	0.225	0.0154
40	0.180	0.0135
45	0.146	0.0127
50	0.117	0.0124
55	0.096	0.0122
60	0.074	0.0114

The viscosity decreases exponentially as the temperature increases. A contrasting feature is the large difference in the values of the viscosity of the two samples. The viscosity of heavy oil is about 25 times larger than the light oil at room temperature, $t = 20.0^o$C. This difference decreases sharply as the temperature increases to 60.0^o C at which μ of heavy oil is only 6.5 times larger than the light oil. We may recall that their API values only differ by a factor of 2 but μ's are quite different. Further, we observe that viscosity exhibits strong

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:6, No:12, 2012

temperature dependence in the region closer and above the room temperature. μ for both samples are considerably large in comparison with water (μ_w =1.002 x 10^{-3} Pa s) at t=20.0^{o} C. Recently Singh and Sommer [11] have discussed the different forms of empirical relations for viscosity in terms of Debye temperature for liquids. We intend to pursue such connections in the impending investigation.

C. Activation Energy

The formation of crude oil within the Earth's reservoir involves complex chemical reactions and phase changes under the influence of high temperatures and pressures. The processing of crude oil, in a major way, also depends on chemical reactions. The activation energy is a measure of the minimum energy necessary for a specific chemical reaction to occur.

Our measured data of μ with respect to temperature can be very well fitted to Arrhenius type equation. This has been used here to determine the activation energy. The activation energy (E_a) and the viscosity μ are related to,

$$\mu = A \exp(E_a / RT) \quad (22)$$

where A is constant, R is the gas constant and T is absolute temperature. Equation (22) has been very successful in explaining the temperature dependence of viscosity and hence in the determination of activation energy. We have used our experimentally determined values of μ as a function of temperature in equation (22) to determine E_a. Taking the natural logarithm of equation (22), we get,
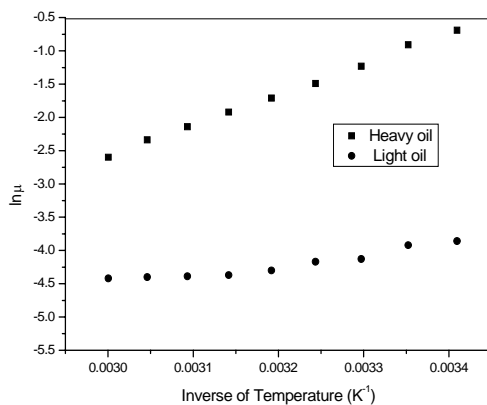

Fig. 1 ln μ versus inverse of temperature

$$\ln \mu = \ln A + (E_a / R)\frac{1}{T} \quad (23)$$

A plot of lnμ against T^{-1}, shown in Fig. 1, yields straight line behavior for both samples.

The activation energies determined from the slopes are:

$E_a = (38.5 \pm 0.6)$ kJ/mol   (*Heavy oil*)

$E_a = (13.5 \pm 1.0)$ kJ/mol   (*Light oil*)

The Arrhenius activation energy determined from the Arrhenius equation is best regarded as an experimentally

determined parameter that indicates the sensitivity of the reaction rate to temperature. The activation energy of two oil samples differs considerably from one another. Sample having lower API exhibits higher E_a which is about 2.9 times larger in magnitude to the oil sample with higher API.

D. Velocity of Viscous Wave and Attenuation Parameter

The measured values of viscosity and density have been used in equations (16) and (17) to determine the shear wave velocity and the attenuation parameter for 20 kHz frequency. The computed values of shear wave velocity are plotted in Fig. 2. v_s falls rapidly with increasing temperature for heavy oil. However, the variation of v_s for light oil with temperature is not as prominent as in the heavy oil. At room temperature, v_s in heavy oil are about 4.6 times larger than the light oil sample.

The computed values of attenuation parameter (k) are plotted in Fig. 3. The results suggest that k increases with increasing temperature. The attenuation in heavy oil is small in comparison to light oil. k for light sample is about 4.6 times larger than the heavy oil near the room temperature.
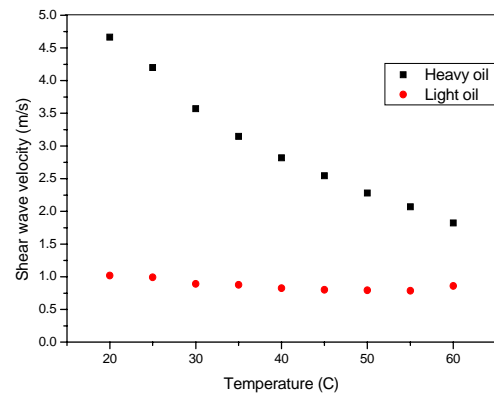

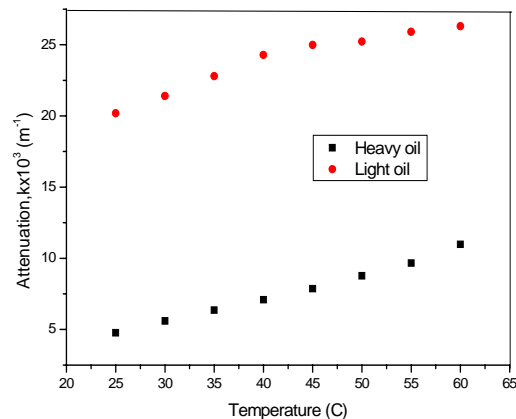Fig. 2 Plot of shear wave velocity versus temperature

Fig. 3 Plot of attenuation parameter versus temperature

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:6, No:12, 2012

IV. Summary and Conclusion

Density and viscosity for light (API = 42.41) and heavy (API = 21.93) crude oil samples were measured experimentally as a function of temperature ranging from 20°C up to 60.0° C. The density is found to decrease linearly with increasing temperature whereas the viscosity decreases exponentially (Arrhenius type) with increasing temperature. From the graph of $\ln\mu$ versus the inverse of temperature (T^{-1}), the slope has been used to estimate the activation energy E_a of the two samples; [38.5± 0.6] kJ/mol and [13.5 ± 1.0] kJ/mol for heavy and light oil samples respectively. Crude oil with larger API was found to have smaller activation energy. The values of viscosity and density are further used in visco-elastic equations that are derived by linearizing the Navier- Stokes equation to determine the shear wave velocity and the attenuation factor. At room temperature, the shear wave velocity of heavy oil is about 4.6 times larger than the light sample. But the attenuation for the light oil is about 4.6 times larger than the heavy oil near the room temperature. The effect of temperature on velocity of viscous wave and on the attenuation is prominent in heavy oil.

References

[1] S. Witaker, "Introduction to Fluid Mechanics'" New Jersey: Prentice Hall, 1968.

[2] L.D. Landau and E.M. Lifsitz, "Fluid Mechanics" London: Pergamon Press, 1959.

[3] A.B. Bhatia and R.N. Singh, "Mechanics of Deformable Media" Bristol: Adam Hilger, 1986.

[4] M. Fank White "Fluid Mechanics (7th Ed)" Mc Graw Hill Series, 2011.

[5] J. Bryan, A. Kautzas and C. Bellehumeur "Viscosity predictions for crude oils and crude oil emulsions using low field NMR" SPE Annual Tech Conf , San Antonio, Texas 2002.

[6] Mobil "Petroleum Manufacturing Orientation Course" New Jersey: Mobil Research and Engineering; 1997.

[7] K. Stephan and K. D. Lucas "Viscosity of Dense Fluids" New York: Plenum Press, 1979.

[8] R. N. Singh, A. K. George and S. Arafin , "Specific heat ratio, Grüneisen parameter and Debye temperature of crude oil", J Phy. D: Appl. Phys., vol 39 , 2006, pp 1-6.

[9] A. Hannisdal, R. Orr and Johan Sjoblom, 2007, "Viscoelastic Properties of crude oil components at oil-water interfaces: comparison of 30 oils" Journal of Dispersion Science and Technology, 2007, pp361-268.

[10] A.K. George, N. Al Majrafi, R. N. Singh and S. Arafin "Thermo-elastic and thermodynamic properties of light and heavy crude oil", Physics and Chemistry of Liquids, vol 46, 2008, pp328-341.

[11] R. N. Singh and F. Sommer "Viscosity of liquid alloys; generalization of Andrede's equation", Monatshefte Für Chemie – Chemical Monthly, vol 143, No 9, 2012,pp1235-1242.