Flow Behavior Comparison of Xanthan and Alcoflood Polymers Aqueous Solutions

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ABSTRACT:
The flow characteristics of some commonly used polymers in the enhanced oil recovery were investigated. Two different types of polymer were selected, Alcoflood and Xanthan gum. Rheostress RS100 was used for measuring and analyzing the experimental measurements. A cone and plate of RS100 rheometer under control shear rate was utilized for this investigation. During the shear rate sweep over the range of 0.1-1000 s⁻¹, the measurements of shear stress and viscosity of different solutions versus shear rate were investigated. The polymer concentration range of 0.05-1.0 wt % was examined. A detailed comparison of the flow behavior of Alcoflood polymers solutions and Xanthan gums solutions was completed. Two distinct profiles can be found from the flow behavior comparison. For shear rate higher than 10 s⁻¹, all polymer solutions showed similar flow behavior independent on the polymer type. For shear rate of less than 10 s⁻¹, the viscosity behavior of Xanthan solutions is significantly higher than the Alcoflood solutions for all the examined concentrations.

Keywords: Enhanced Oil Recovery, Alcoflood Polymer, Xanthan Gum, Shear Stress, Shear Rate, Viscosity.

1. Introduction
A new well of crude oil first produces spontaneously, then by a pumping system until the production rate becomes uneconomical. More oil can be produced by injecting water into the formation and pumping out a mixture of oil-water at other locations. Eventually, this injection process becomes uneconomical too. A large amount of crude oil, around 40 – 50 % of the original crude oil, remains or traps in an oil well and cannot be produced through the conventional techniques. Enhanced oil recovery is a recommended technique to extract this residual crude oil.

The application of polymer aqueous solutions in the enhanced oil recovery stage is very necessary to keep the crude oil production rate at the required economical level after the conventional methods have been exhausted. In several enhanced oil recovery applications, polymers are utilized as thickeners to alter the rheology of the aqueous phase in order to improve mobility ratio, sweep efficiency, and increase recovery and oil production rates. There are two principal types of polymers being used in the polymer flooding stage. These are hydrolyzed polyacrylamide and polysaccharides biopolymer or Xanthan gum [1-2]. One important application of such polymers is in the enhanced oil recovery processes, either to recover the oil remaining in the oil reservoir or to push surfactant solutions in the tertiary oil recovery stage [3].
The polyacrylamide is produced by the polymerization of the acrylamide monomer, through hydrolysis some of the acrylamide monomers are converted to carboxylate groups with a negative charge. Polyacrylamide is widely used in modern technologies as a thickening agent, suspending agent, turbulent reduction agent and in the enhanced oil recovery [4-5]. Xanthan gum is a high molecular weight extracellular polysaccharide produced by bacteria of the genus Xanthomonas campestris. Xanthan gum has enormous industrial importance with applications in the food, pharmaceutical and oil industries [6-7].

Many rheological studies have been carried out on polyacrylamide aqueous solutions [8-14]. Li and McCarthy [8] investigated the flow behavior of polyacrylamide aqueous solution in pipelines employing nuclear magnetic resonance imaging. Ghoniem et al. [9] and Chang et al. [10] reported mechanical degradation of polyacrylamide
aqueous solution. On the other hand, Chauveteau [11] and Durst et al. [4] studied the flow behavior of polyacrylamide aqueous solution in porous media. They reported significant pressure drops compared to Newtonian solutions. Dupuis et al. [12] studied the rheological behavior of polyacrylamide in aqueous solution of glycerol and water. They concluded that the viscosity of this solution showed time effect with strong instability followed by steady state behavior. Ait-Kadi et al. [13] investigated the effect of salt on the viscoelastic behavior of the polyacrylamide solution. They found that the salt provided a stability effect on the solution viscosity. Shin and Cho [14] studied the effect of temperature on the rheological behavior of polyacrylamide aqueous solution. They concluded that the viscosity showed temperature dependence at low shear rates and temperature independence at high shear rate.

Several biopolymers can be utilized in oil recovery processes, while Xanthan gum has been the most employed biopolymer. [15] Xanthan gum is a polysaccharide produced by fermentation of the microbe Xanthomonas compestris, and has been investigated by both chemical and physical techniques [16]. Solutions of Xanthan are highly pseudoplastic and show very good suspending properties. This makes Xanthan very useful as a suspending, stabilizing, thickening and emulsifying agent for food, cosmetics, pharmaceuticals and oil recovery among other applications [17]. Rodd et al. [18] reported that the Xanthan gum solutions are one of the most intensively studied polysaccharide systems both in terms of physical chemistry and rheological properties. Whistler and BeMiller [19] found greater pseudoplasticity results from Xanthan gum solutions due to the formation of high molecular weight aggregates of stiff rod molecules. Milas and Rinaudo [20] reported that the Xanthan macromolecules in the ordered helical structure would stiffen the polysaccharide solution, and this makes Xanthan one of the stiffest natural biopolymers [21]. Morris [22] and Sato et al. [23] reported that the Xanthan molecules behave as a rigid rod at low molecular weights whereas the shape would be a stiff wormlike coil at high molecular weight. Therefore, the shape of the Xanthan molecules in solution depends on the molecular weight of the polysaccharide.

From the above discussion, it is important to compare the flow behavior of the well known utilized polymers in the enhanced oil recovery. This study will be focused on the flow behavior of the actual commercial polyacrylamide polymer (i.e. Alcoflood polymer) which is widely employed in the enhanced oil recovery techniques and polysaccharides biopolymer. Knowledge of the polymer flow behavior is necessary for the design, selection, and operation of the equipments employed in mixing, storage, pumping, and transportation of polymer solution.

The objective of the current investigation is to study the comparison between the flow behavior of Alcoflood polymer and Xanthan gum using RheoStress RS 100 rheometer. This investigation examined a wide range of concentrations of polymer 0.05-1.0 weight %, different types of polymer, and wide range of shear rate.

2. Experimental work

2.1. Alcoflood polymers

Two Alcoflood polymers AF1235 and AF1285 supplied by Ciba Specialty Chemicals (Bradford, West Yorks, England) were employed for this study. Alcoflood materials are high molecular weight polyacrylamide copolymers. AF1235 is recommended for low–medium permeability reservoirs, whereas AF1285 is applied for high permeability reservoirs. Water-soluble Alcoflood materials are supplied in a white granular powder form. The bulk density of the Alcoflood materials is 800 kg / m³ with intrinsic viscosity equal to 12 and 24 for AF1235 and AF1285, respectively. The tested solutions were prepared by adding a certain weight of polymer material to 0.25 liter of warm distilled water. Enough time was given to achieve complete polymer dissolution without external mixing to avoid any mechanical degradation on the polymer network.

2.2. Xanthan gums

Two Xanthan gums were used for this investigation. The first one is a chemical grade from Sigma-Aldrich Canada Ltd (Oakville, Ontario L6H 6J8, Canada) with product # G1253 under the product name of Sigma. The other one is an industrial grade of Xanthan gum from CP Kelco (Atlanta-GA 30339, USA) with product # 10040282 under the product name of Kelzan. Both products are white to tan color powders and they are intended for use in non-food applications as a thickener and rheology control agents. The tested solutions were prepared by dispersing the
Xanthan gum powder slowly to 0.25 liter of warm distilled water to the required concentration. The solutions were gently stirred until all the Xanthan gum dissolved completely. To avoid bacterial growth, since Xanthan solution is biodegradable, 5.0 gm formaldehyde / liter was added and the solutions were stored at 4°C until use.

2.3. Rheometer
Rheostress RS100 rheometer from Haake was employed to study the flow behavior of various concentrations of polymer solutions. All measurements were carried out at a room temperature of 22 °C. A water bath was employed to control the applied temperature in the RS100 system. The control rate, CR-Mode, of RS100 was applied for all the rheological measurements. Cone-plate sensor was used with a cone angle of 4°. The cone diameter is 35 mm with gap of 0.137 mm at the cone tip. A controlled variable lift speed was used to locate the cone in the right position over the plate. All operation procedures, rheological measurements, and data analysis were controlled and carried out by Haake software package.

2.4. Rheological measurements
The flow behaviors of Alcoflood polymers and Xanthan gums solutions were investigated in terms of viscosity-shear rate and shear stress-shear rate behaviors. Rheostress RS100 was used in all the experimental measurements. A wide range of shear rate (0.1 to 1000 s⁻¹), polymer concentration (0.05-1.0 wt %), and different types of polymer were covered. A sample solution of 1 cm³ was placed first on the cone-plate sensor and then the sensor was driven automatically to the right position. After the measurement data was collected, the RS100 software package was utilized to carry out the data analysis required.

3. Results and discussion
The flow properties of different types of Alcoflood polymers and Xanthan gums solutions were investigated in the shear rate range of 0.1 to 1000 s⁻¹ and polymer concentration of 0.05-1.0 wt %.

3.1. Flow behavior of Alcoflood and Xanthan solutions
The flow behavior of the Alcoflood and Xanthan gum solutions in terms of shear stress in Pa versus shear rates in s⁻¹ are displayed in Figures 1A and 1B for low concentration of 0.05 wt%. These measurements covered the shear rate range from 0.1 to 1000 s⁻¹. Figure 1A shows the comparison of the rheogram behavior for low concentration of AF1235 and Sigma Xanthan solutions, while Figure 1B displays similar behavior for the low concentration of AF1285 and Kelzan Xanthan solutions. Figure 1 shows a non-Newtonian flow behavior in nature for the examined solutions. The rheogram behaviors of the Xanthan solutions are slightly above the Alcoflood response for shear rate of less than 100 s⁻¹. After the experimental measurements were collected, the Rheostress RS100 software package was utilized to carry out the data analysis of all the experimental data. The objective of this analysis is to obtain the more relevant model that predicts the rheogram behavior. This analysis revealed that two models can be found to sufficiently fit all the measurements depending upon the type of solution. These models are Power-law and Casson models respectively [24].

\[ \tau = m \dot{\gamma}^n \]  
\[ \tau = (\tau_0^{0.5} + (\dot{\gamma} \eta_c^{0.5})^2 \]  

Power-law model of equation 1 sufficiently fits the flow behavior of AF1235 solution, whereas, Casson model of equation 2 fits the flow behavior of AF1285 and both of Xanthan solutions. The solid curves shown in Figures 1 are plots of the Power-law and Casson models. Figure 1 shows that the Power-law and Casson models (i.e. solid curves) very adequately fit the flow curves of the above mentioned solutions over the entire range of the examined shear rate.
Similar behaviors are reported for the medium concentration of 0.1 wt% (Figure 2) and high concentration of 0.5 wt% (Figure 3). For medium and high concentrations, the rheogram behaviors of the Xanthan solutions are placed slightly above the response of the Alcoflood behaviors till limited shear rate. For Figures 2A and 3A, the cross over occurred around 6 s$^{-1}$ however for the other two Figures of 2B and 3B the cross over occurred around 11 s$^{-1}$.
Figure 2. Rheogram behaviors for medium concentration.
Tables 1-4 show the modeling analysis for AF1235, AF1285, Sigma and Kelzan solutions with different concentrations, respectively. The Power-law model parameters of m and n for AF1235 are reported in Table 1. As can be noticed from Table 1, the flow behavior index, n, gradually decreases with polymer concentration indicating strong shear thinning behavior for AF1235 aqueous solutions. The smaller the value of n, the greater is the degree of shear thinning. Table 1 shows that the flow consistency coefficient, m, for the polymer solutions increases gradually with Alcoflood polymer concentration.

Table 1. Power-law model data analysis for AF1235 solutions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m [Pa.s^n]</td>
</tr>
<tr>
<td>wt% 0.05</td>
<td>0.022</td>
</tr>
<tr>
<td>0.10</td>
<td>0.083</td>
</tr>
<tr>
<td>0.50</td>
<td>2.0</td>
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<tr>
<td>1.00</td>
<td>6.2</td>
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</table>
Table 2 shows that the yield stress value, $\tau_o$, for AF1285 increases gradually with polymer concentration from 0.013 Pa to 9.2 Pa for concentration range of 0.05-1.0 wt%. The presence of yield stress indicates that a three-dimensional network is formed at no shear conditions. Under the effect of shear stress, the three-dimensional network is broken down. Thus, the flow behavior of these Alcoflood solutions exhibit shear thinning behavior.

Table 2. Casson model data analysis for AF1285 solutions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\tau_o$ [Pa]</th>
<th>$\eta_c$ [Pa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.013</td>
<td>0.0058</td>
</tr>
<tr>
<td>0.10</td>
<td>0.051</td>
<td>0.011</td>
</tr>
<tr>
<td>0.50</td>
<td>1.6</td>
<td>0.031</td>
</tr>
<tr>
<td>1.00</td>
<td>9.2</td>
<td>0.08</td>
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</table>

Tables 3-4 show that the predicted value of the yield stress increases gradually with Xanthan gum concentration for both types of Sigma and Kelzan.

Table 3. Casson model data analysis for Xanthan Sigma solutions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\tau_o$ [Pa]</th>
<th>$\eta_c$ [Pa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.044</td>
<td>0.0033</td>
</tr>
<tr>
<td>0.10</td>
<td>0.110</td>
<td>0.0042</td>
</tr>
<tr>
<td>0.50</td>
<td>2.900</td>
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</tr>
<tr>
<td>1.00</td>
<td>9.600</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

Table 4. Casson model data analysis for Xanthan Kelzan solutions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\tau_o$ [Pa]</th>
<th>$\eta_c$ [Pa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.085</td>
<td>0.0033</td>
</tr>
<tr>
<td>0.10</td>
<td>0.200</td>
<td>0.0039</td>
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<td>0.50</td>
<td>2.700</td>
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<tr>
<td>1.00</td>
<td>7.5</td>
<td>0.0097</td>
</tr>
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</table>

3.3. Viscosity behavior of Alcoflood and Xanthan solutions

After the discussion presented in the previous section for the flow behavior of the Alcoflood and Xanthan gums solutions, it will be useful to investigate the viscosity comparison of the examined aqueous solutions. Figures 4-6 display the flow behavior of the examined solutions in terms of viscosity, mPas, versus shear rate, s$^{-1}$, on semi-logarithmic scale for 0.05, 0.1 and 0.5 wt% respectively to cover low, medium, and high concentrations of the used materials. Figures 4-6 show that the viscosity is a strong function of polymer concentration and shear rate. Viscosity gradually increases with polymer concentration and decreases by shear rate. All solutions presented in Figures 4-6 showed a non-Newtonian shear thinning in which the measured apparent viscosity decreases with shear rate, for example, the apparent viscosity of the 1.0 wt% Sigma Xanthan solutions records 36,235 mPas at shear rate of 0.3 s$^{-1}$ and it decreases significantly to 38 at 750 s$^{-1}$. Similar behaviors were reported by other researchers such as Lopez et al. [25] Martinez-Padilla et al. [26] and Kayacier and Dogan [27].

Figures 4-6 for low, medium, and high concentrations show two distinct behaviors. The first behavior covers the lower shear rate up to 10 s$^{-1}$, whereas the second behavior covers the higher shear rate from 10 s$^{-1}$ to 1000 s$^{-1}$. Over the higher shear rate range, 10-1000 s$^{-1}$, Figures 4-6 show similar flow behaviors for all the tested polymer solutions independently on the polymer type. However, over the lower shear rate of < 10 s$^{-1}$, the viscosity behavior will be dictated by the type of the examined material. For low and medium polymer concentration of 0.05 and 0.1 wt%, the viscosity increases significantly in the order of AF1235, AF1285, Sigma Xanthan, and Kelzan Xanthan. For the higher polymer concentration of 0.5 wt %, the difference among each group diminishes and the Xanthan group provides higher viscosity measurements than the Alcoflood group.
Figure 4. Viscosity flow behavior for low concentration of different polymers.

Figure 5. Viscosity flow behavior for medium concentration of different polymers.
Table 5 reports the yield stress values predicted from the Casson model for the aqueous solutions of Alcoflood AF1285 and Xanthan gums. Yield stress directly influences the initiation of aqueous solutions flow from a container, pumping into a transportation pipeline, or spreading aqueous solutions over solid surfaces. Therefore it is necessary to investigate the flow behavior in terms of yield stress. Figure 7 shows that the yield stress increases gradually with concentration for all examined solutions. For concentrations lower than 0.5 wt %, no significant differences were noticed between the yield stresses of the three materials. For concentrations ≥ 0.5 wt %, Sigma Xanthan gum solutions reported slightly higher yield stresses than the other two solutions of Kelzan and AF1285.

<table>
<thead>
<tr>
<th>Concentration, wt%</th>
<th>AF1285 Sigma</th>
<th>Sigma Xanthan</th>
<th>Kelzan</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.013</td>
<td>0.044</td>
<td>0.085</td>
</tr>
<tr>
<td>0.10</td>
<td>0.051</td>
<td>0.110</td>
<td>0.200</td>
</tr>
<tr>
<td>0.50</td>
<td>1.6</td>
<td>2.900</td>
<td>2.700</td>
</tr>
<tr>
<td>1.00</td>
<td>9.2</td>
<td>9.600</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Figure 6. Viscosity flow behavior for high concentration of different polymers.

Figure 7. Yield stress comparison.
4. Conclusions

The current study was carried out to investigate the flow behaviors of two different groups of polymers commonly employed in enhanced oil recovery. These polymers were Alcoflood and Xanthan gums solutions. The following conclusions can be made:

1. The apparent viscosity of Alcoflood aqueous solutions are strong functions of shear rate and polymer concentration.
2. Alcoflood polymer aqueous solutions displayed strong shear thinning non-Newtonian behavior. Different degrees of shear thinning were reported for different polymer concentrations. The smaller the value of flow behavior index, the greater is the degree of shear thinning.
3. Modeling analysis showed that the power-law model fits well the AF1235 aqueous solutions, whereas, the Casson model adequately fits the aqueous solutions of AF1285.
4. Both Xanthans solutions of Sigma and Kelzan exhibited a non-Newtonian shear thinning behavior in which the apparent viscosity of 1.0 wt% Sigma solution decreased significantly from 36,235 mPas at 0.3 s\(^{-1}\) to 38 mPas at 750 s\(^{-1}\).
5. Casson model sufficiently fits both Xanthan gums solutions of Sigma and Kelzan.
6. Modeling analysis shows that the yield stress values increase gradually with Xanthan gum concentration.
7. From the flow behavior comparison of all tested solutions, two distinct profiles can be found. Over shear rate of higher than 10 s\(^{-1}\), all polymer solutions provided similar flow behavior independent on the polymer type.
8. Over shear rate of less than 10 s\(^{-1}\), the viscosity behavior will be dictated by the polymer type.
9. For concentrations \(\geq 0.5\) wt %, Sigma solutions reported slightly higher yield stresses than the other two solutions of Kelzan and AF1285.

References


