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Laboratory Study of the Application of a Novel Bio-Based Polymer to Synthesize Aphron Drilling Fluids

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Abstract

Aphron fluids are a special type of foam in which the gas bubble (air or any other gas) is surrounded by a double-walled layer consisting of surfactant and polymer. Therefore, it is more stable at high temperature and pressure conditions due to being preserved by three layers. These fluids are widely used in industry. Today, the industry uses various polymers such as acrylamides, polyacrylamides, and hydrolyzed acrylamides that are harmful to the environment. In this study, the possibility of using natural and biodegradable polymers such as Astragalus Gum and starch is investigated. The results showed that the Aphron fluid made from Astragalus Gum (extracted from a dessert plant) had a higher volumetric yield than industrial polymers. Stability over time and rheological properties for Astragalus Gum are also acceptable. Also, it is found that increasing the polymer concentration increases the stability and rheological properties, but in contrast, the volumetric yield decreases. The effect of salt and surfactant concentrations is also evaluated in this research. The results show that increasing the surfactant concentration increases the volumetric yield of the fluid. Increasing the surfactant concentration from 1 wt% to 2 wt% increases the volumetric efficiency of Aphron fluids by 5%. In general, according to the results obtained in this research work, Astragalus Gum's performance is better than synthetic polymers for making Aphron fluids.

Keywords: Biodegradable Polymer, Aphron Drilling Fluid, Rheological Properties.

Introduction

The concept of Aphron fluids was first introduced in 1971 by Sebba as the Colloidal Gas Aphron (CGA) [1, 2]. The scientist described the properties of the fluid in detail, as well as its possible applications. Sebba described Aphron as a fluid with sizes of bubbles from 10 to 100 micrometers [3-5]. The structure of an Aphron bubble is usually spherical and is made of gas or liquid covered by layers of polymer and surfactant [6-11].

Aphron fluids, due to their special properties and suitable rheological properties, are suitable for use as drilling fluids, and in recent years, their applications have expanded in the oil industry [2, 7, 10, 12, 13]. This fluid is used for drilling in low pressures or depleted formations. Aphron fluid differs from foam previously used in the drilling and oil industry. Bubbles are finer in Aphron fluids and are more robust and durable because they are coated with layers of surfactants and polymers [4, 14, 15]. A layer of surfactant covers the bottom of each bubble. Still, in the Aphron fluid, each bubble is covered by three layers of surfactant and polymer, the inner layer of which contains surfactant molecules that separate the air from the liquid and protect it [16]. The outermost layer is double-walled, the inner part is hydrophilic, and the outer part is hydrophobic.

The structure of an Aphron bubble is shown In Figure 1-a, and in Figure 1-b, the bubbles' dispersion [17]. As can be seen in the figure, the bottom of each bubble is covered by a thin layer of surfactant, which is hydrophilic, but in Aphron, in addition, there is a double-walled layer, the inner part of which is hydrophilic and the outer part is hydrophobic [18].

In 2002, Ramirez et al. [19] Evaluated the possibility of using Aphron fluids as a suitable fluid for drilling in relatively depleted formations, with significant results. In this paper, the mechanism of reducing the filtration of drilling fluid is described.

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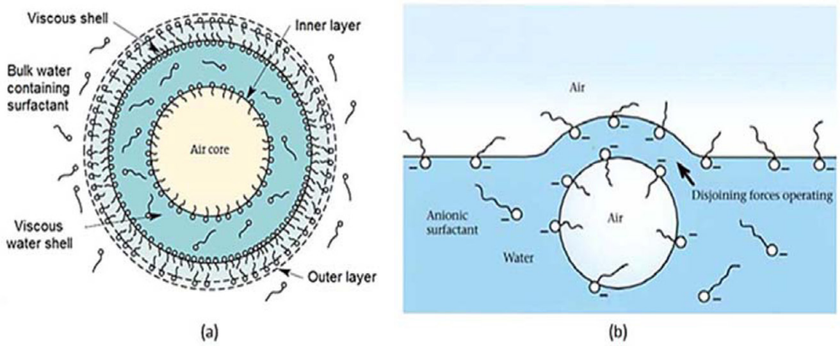

Fig. 1 schematically illustrates the structure of an Aphron bubble (a) individual aphron bubble (b) dispersion of bubbles in bulk fluid [16].

The results of this study show that the most important factor that plays this important role is pore throat blockage by Aphron bubbles. Contrary to previously thought, this factor is much more important than weight loss and bubble stability. In fact, at high pressures (bottom of the well), the size of the Aphron bubbles is drastically reduced so that their compressibility is close to that of solids, allowing them to clog pores like solids. The results of this study also show that the presence of surfactants in Aphron drilling fluids reduces the swelling capability of clay layers and reduces drilling problems [20].
In 2003, Mr. White and colleagues introduced the use of Aphron fluids. They announced the best way to reduce the filtration of drilling fluids when drilling in the North Sea. The problem of drilling fluid filtration in the North Sea was finally solved by Aphron fluids, and it was proved that this type of fluids perform best to reduce the magnitude of filtration [21].
In 2005, Bordalan et al. worked on the rheological and mechanical margins of Aphron fluids. They stated that these properties directly affect the performance of Aphron fluids because the kinetic properties of the fluid and bubbles influence the stability of Aphron bubbles with time and pressure. One of the results of this research is the optimization of surfactant and polymer concentrations. Surfactant concentration directly increases the air entering the fluid system during mixing. As a result, to improve their stability, the polymer concentration must be increased to the same extent. However, it should be noted that the excessive addition of polymer to the drilling fluid system creates problems for drilling pumps like high pumping pressure, vibrations, and delayed charging that need to be optimized [8].
In 2012, Milad Arabloo et al. first investigated the possibility of using plant surfactants as an Aphron builders. Industrial examples of surfactants used for this purpose are CTAB and SDS, which are not biodegradable and harm the environment, thus imposing large costs on oil companies to dispose of these fluids in more suitable environments. However, in this research, it has been stated that the efficiency of plant surfactants is similar to these industrial materials and does not have environmental problems [9].
In 2015, Molayi et al. compiled the results of previous research in all fields, noting that Aphron fluids are used not only in the oil industry but also in other industries, such as water purification, protein separation, and so on. They also stated that the type, concentration, and electrical charge of surfactants are the most important factors affecting the properties of Aphron fluids [10].
In 2016, Alizadeh et al. examined the draining of Aphron fluids in porous media in the form of laboratory and mathematical modeling. They stated that the stability of bubbles and their number have the greatest effect on slowing this emission. Furthermore, it is evident that with increasing the concentration of bubbles, the mobility of the fluid at high pressures decreases, and the filtration of these fluids during drilling reaches its minimum value [5, 11].
In 2015, Amin Tabzar and Ghazanfari performed experiments on increasing the stability of Aphron's and their rheological properties. The results of this study showed that the presence of anionic or cationic surfactants as a critical additive plays a vital role in forming Aphron fluids and also introduced appropriate concentrations of the combination of xanthan gum and CMC for the preparation of these fluids [7]. In 2017, Hassani and Ghazanfari investigated the possibility of using silicate nanoparticles to prepare Aphron drilling fluids. Their results acknowledged that nanoparticles with a cation exchange mechanism strengthen the layers and increase their stability [12].
In 2016, Tabzar and Ghazanfari conducted a laboratory study on the filtration property of Aphron fluid against a porous medium. They found that at very high pressures, although the gas bubbles shrink to such an extent that they have little effect on fluid loss, These tiny bubbles act like solids for the Aphron fluid and strongly prevent its filtration [22]. In 2017, Hassani et al. examined the possibility of creating Aphron fluid from petroleum-based fluid to reduce its weight and filtration in porous formations. It is stated in the paper that all the necessary components to prepare the Aphron should be hydrophobic and use a combination of nanosilicates and petroleum surfactants [23].
This study intends to evaluate the possibility of using natural polymers to make Aphron fluids in a laboratory and compare the results with common industrial polymers used in industry. In this regard, Aphron fluids made from natural gum derived from Astragalus were examined for volumetric, rheological, and stability efficiency properties and compared with HPAM results.

Materials and Methods

In this section, the materials and methods used and the procedure for performing the experiments are fully discussed.

Materials

Astragalus Gum (AG)

In 2011, Balaghi et al. worked on the kinetic properties of this type of natural gum. It consists of water-soluble and water-insoluble parts. The insoluble part swells in the presence of water [24].

This property will cause the water-based drilling fluid to disperse well in the continuous phase and increase the carrying capacity of the particles by increasing the viscosity. Therefore, they reduce the filtration of drilling fluids.
Iranian gum tragacanth exuded by various species of Astragalus (Astragalus Gum) was collected from plants growing in different provinces of Iran, including Isfahan, Khorasan, Semnan, and Shiraz. The plants were tapped with a knife by making careful longitudinal incisions in the taproot and the bark of the branches. The gum readily exuded from these cuts in the form of ribbons that became brittle on drying [25].

Industrial Polymers

In this research, biopolymers called Hydrolyzed PolyAcryLamide (HPAM), and Starch have been used as industrial polymers. HPAM is a high molecular weight industrial polymer that is added to the fluid to increase the viscosity of the drilling fluid and to stabilize the Aphron bubbles suspended in the fluid system [26, 27]. This polymer is used in both water-based and oil-based mud as a filtration controller on the drilling fluid and as a viscosity enhancer. Starch is a member of the family of carbohydrates whose general formula is $C_6H_{10}0_5$. This polymer is a major part of the grains of corn, wheat, rice, etc. Starch is also added to the fluid system to control drilling fluid filtration [28, 29].

Surfactants

To create an Aphron fluid, we first need a surfactant that reduces the surface tension to allow air to enter the fluid. These Surfactants are called Aphron surfactants [30]. The surfactant used in this study is CTAB.
CTAB, which stands for Cetyl Trimethyl Ammonium Bromide, is a cationic surfactant with a molecular weight of 364.45 grams. The chemical structure is shown in Figure 2. This cationic surfactant is also known as HDTMABr, which stands for Hexa Decyl Tri Methyl Ammonium Bromide.

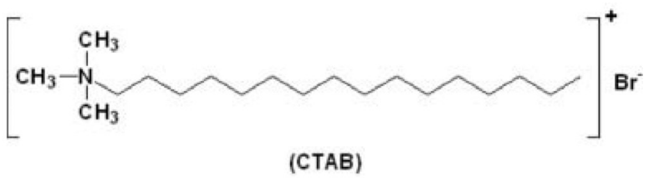

Fig. 2 Chemical structure of CTAB [31].

Methods

This section explains the laboratory procedures performed to assess the performance of AG polymers to make Aphron fluids and compare them with other polymers.

Preparation of Aphron Fluid

To create an Aphron fluid, we need a surfactant to make way for air to enter the water body and a polymer to increase the stability of the bubble.

Laboratory Process of Fluid Preparation

1- 350 grams of distilled water is poured into a stirrer glass (equivalent to 350 ml and eliminates eye errors from the tests)
2- Add a certain amount of polymer while the mixer is spinning at 8000 rpm and stir the polymer for 20 minutes (the polymer is slowly added to the water while the mixer is spinning; otherwise, it will cause the polymer to accumulate and it does not spread evenly in the fluid system.)
3- A certain amount of salt is added to the system, and after adding the fluid, it is mixed for ten minutes in the same cycle.
4- A certain amount of surfactant is added to the fluid system. After adding the surfactant, the stirrer mixes the fluid system for three minutes at 12,000 rpm. (The high speed of the stirrer at this stage causes air to enter the fluid system and creates Aphron bubbles.)

Measuring the Yield of Aphron

The obtained volume ratio of Aphron drilling fluid to the volume of water used in its preparation is called Aphron yield. As mentioned before, 350 ml of water was used to prepare each Aphron sample in the laboratory. However, its volume increased by stirring at high speed, resulting in air bubble formation. Therefore, this ratio is defined as the yield of Aphron.

Yield measurement procedure

1- Aphron fluid preparation (detailed in previous sections)
2- The prepared drilling fluid is poured into a one-liter graduated cylinder.
3- The volume of Aphron drilling fluid obtained is recorded and divided by 350.
It is expected that the higher the surfactant concentration, the higher the amount of air entering the fluid system, and therefore higher the Aphron yield.

Measurement of rheological properties

The rheological properties of the drilling fluid, including viscosity, apparent viscosity, yield point, and gelation strength of 10 seconds and ten minutes, were measured by a rotation VG-meter. All these parameters can be inferred by drawing torque in terms of rotational speed. This experiment is conducted under atmospheric pressure and 800C temperature.

Rheology measurement procedure

1- Pour 350 ml of Aphron drilling fluid into the viscometer glass.
2- Place the rotor and stator of the viscometer in the fluid up to the marked line above the stator.
3- Rotate the viscometer at 600 rpm for 60 seconds to homogenize the fluid.
4- Record the values of torques at 3, 6, 100, 200, 300, and 600 rpm.
5- Turn off the viscometer for 10 seconds to allow the fluid to settle, and then record the amount of dial reading at 3 rpm as the gelatinous force of 10 seconds of fluid. (Note that dial reading increases to the maximum size and then decreases, and the maximum amount must be recorded).
6- Rotate the viscometer at 600 rpm for one minute.
7- Turn off the viscometer for ten minutes, then measure the gelation strength of the fluid for ten minutes according to step 5 above.

Filtration measurement

This experiment is used as a characteristic to predict the amount of filtration of the drilling fluid inside the formation using an API filter paper.

Test procedure
1- Pour 350 ml of drilling fluid into the chamber.
2- Connect the top of the chamber to a 100 psi compressor and ensure it is tightened and has no leakage.
3- Record the amount of water output against time.
It should be noted that this experiment was conducted under 100 psi pressure and 800F temperature.

Aphron fluid stability test
The stability of Aphron bubbles is one of the most important factors in their performance. Due to the buoyant force, air density is less than water. Therefore, over time, the Aphron bubbles migrate upward and accumulate at the top of the container, so the bottom becomes bubble-free, and the fluid becomes two-phase, which is called drainage. Therefore, the lower the Aphron fluid discharge rate, the more stable it is.

Test procedure
1- Pour 200 ml of Aphron drilling fluid into a 250 ml graduated cylinder
2- Record and draw the ratio of the height of the emptied area to the height of the whole fluid.
3- Plot the measured values against time.

Results and Discussion
In this section, the experiment's results are illustrated and explained comprehensively.

Volumetric yield experiment
The first step in studying the effect of different materials on Aphron fluid properties is to measure volumetric efficiency and fluid density.
Figure 3 shows the laboratory data obtained from measuring the volumetric yield of different fluids. In the following sections, the results will be discussed.

The effect of salt concentration
As seen from the diagram in Figure 3, increasing the salt concentration reduces the volumetric efficiency of the Aphron fluid. It should be noted that this can occur due to increased interfacial stress with increasing salt concentration, so air bubbles need more force and energy to be trapped and persist in the continuous phase of the Aphron fluid.

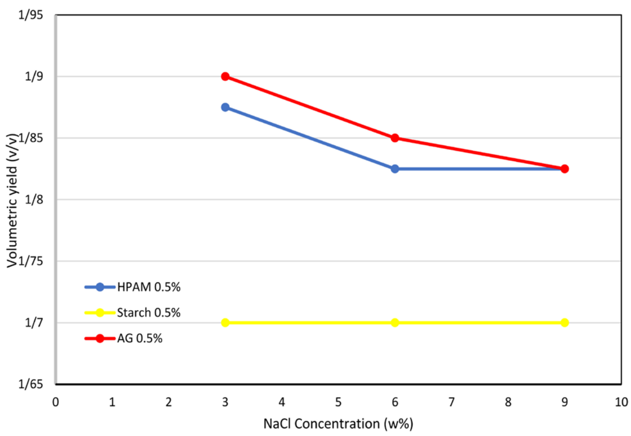

Fig. 3 Volumetric yield of different fluids.

Effect of Polymer Type
As shown in Figure 3, the fluid containing AG polymer has a higher efficiency than HPAM and Starch. It could be due to the two-part structure of natural gum, which consists of hydrophobic and hydrophilic parts. The hydrophobic part of this polymer facilitates the entry of air bubbles into the Aphron fluid system, resulting in higher volumetric efficiency.

Effect of Polymer Concentration
Increasing the polymer concentration in the Aphron fluid composition makes the fluid more viscous and prevents air from entering the fluid space. Therefore, based on this theory, it can be predicted that by increasing the polymer concentration, less air can enter the fluid, decreasing the Aphron fluid's volumetric efficiency.
The data illustrated in Figure 4 shows that the volumetric yield of the fluid is inversely related to the concentration of polymers in the Aphron fluid. This reduction in yield is the minimum for AG polymer and decreases the volumetric yield from 1.9 to 1.85. In contrast, the efficiency of HPAM polymer is much higher, and the efficiency decreases from 1.87 to 1.55.

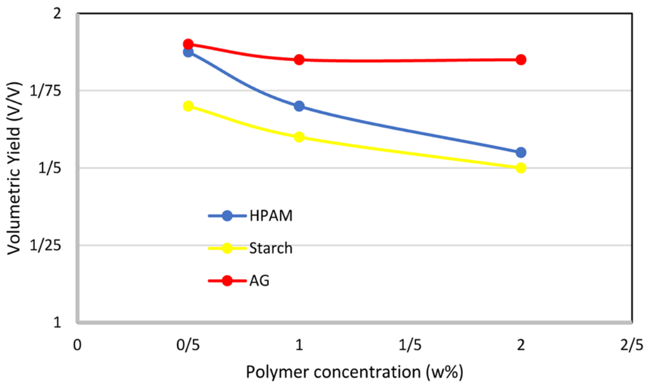

Fig. 4 Effect of concentration and type of polymer on the volumetric yield.

Effect of Surfactant Concentration
Surfactants reduce the interfacial stress of insoluble phases and cause phases to mix more and dissolve. Therefore, it is expected that by increasing the concentration of surfactant in the Aphron fluid, more air enters the fluid, and as a result, the volumetric yield of the fluid increases.
In Figure 5, it is clear that for the Aphron fluid made by all three polymers, increasing the surfactant concentration increases the volumetric yield. This is due to the reduction of air-water surface tension. The increase in volumetric yield is almost the same for all three types of polymers and is independent of the type of polymer.

Rheological Properties of Aphron Fluid
This section describes the rheological behavior of the synthesized Aphron fluids. It should be noted that various rheological models have been proposed to predict fluid behavior at different stresses and shear rates. Therefore, the first step in studying the rheological properties of these fluids is to find the best model to describe the fluid.

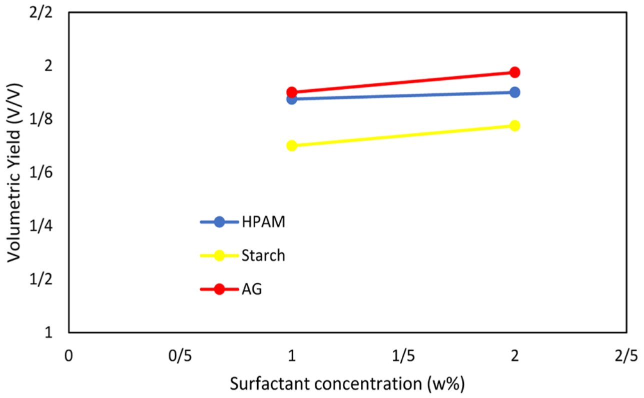

Fig. 5 Effect of surfactant concentration on the volumetric efficiency of Aphron fluid.

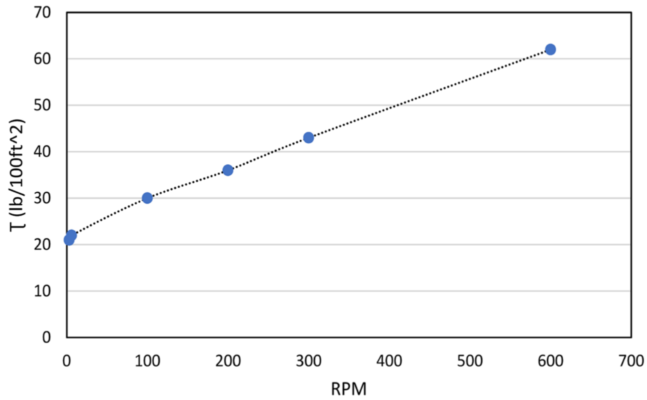

Fig. 6 Shear stress data at different shear rates.

Selecting the Best Rheological Model

To find the best model describing the rheological behavior of Aphron fluids, 400 ml of the base fluid was made. Then the shear stress of the fluid was plotted at different shear rates and tested against various models. Figure 6 shows the shear stress of the base fluid in terms of shear rate.

After measuring the rheological data, it was tested with well-known rheological models. The models used and the result of the adaptation performed are shown in Table 1.

According to the results in Table 1, the Bingham plastic model can best describe the rheological behavior of the base Aphron fluid. Therefore, for better and more realistic comparison, the rheological data of other fluids have also been calculated through this model (Bingham Plastic).

Table 1 Correlation of the rheological behavior of Aphron fluid with different models.

R^2	Best Equation	Overall formula	model
0.266	Y=0.121*X	Ʈ=μ * ẏ	Newtonian
0.8751	$Y=15.92*X^{0.1769}$	$Ʈ=μ*ẏ^n$	Pseudo plastic
0.7495	Y=6.0915*ln(X)+10.392	Ʈ=μ*ln(ẏ)+YP	logarithmic
0.9965	Y=0.0678*X+22.014	Ʈ=YP+μ*ẏ	Bingham plastic

Measurement of Rheological Properties

In this section, rheological parameters for all fluids are measured and shown. The laboratory data obtained from this activity are illustrated in Figure 7.

In addition to viscosity, the magnitude of the yield point is one of the important rheological properties in the oil and gas industry, especially in the drilling section. This parameter indicates the ability of the fluid to hold the suspended particles. The measured data for this parameter is shown in Figure 8.

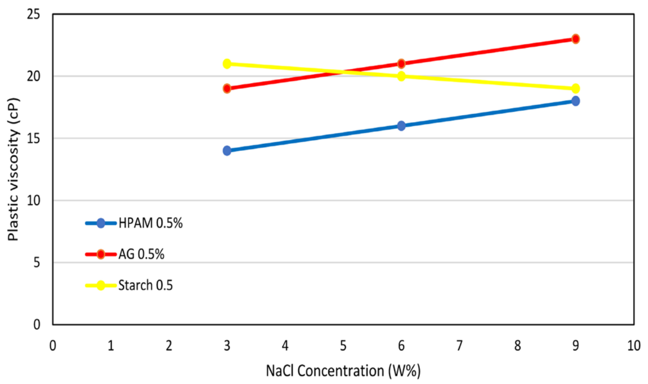

Fig. 7 Measured viscosity data for different fluids.

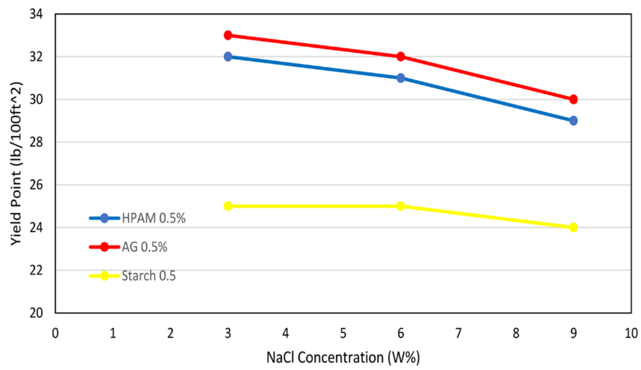

Fig. 8 Yield point measured for different fluids.

Effect of Salt Concentration

As shown in Figure 7, the viscosity of the resulting fluid increased with salt concentration. This action can occur due to Einstein's law of viscosity. This law states that the higher the number of particles dissolved and dispersed in a fluid, the higher the viscosity. However, in the case of starch additives, it is observed that increasing the salt concentration has the opposite effect on the rheological properties and reduces the viscosity. It can be related to the molecular structure of starch, which increases the salt to prevent swelling and play a negative role in increasing the viscosity of the polymer.

It is clear from Figure 8 that the salt concentration has little effect on the magnitude of the yield point of the Aphron fluid and, at very high concentrations, reduces this parameter by a tiny amount. This action is due to the neutralization of the surface charge of suspended particles and thus reducing the yield point of the fluid.

Polymer Type Effect

The viscosity data of Figure 7 shows that AG has a higher ability to increase rheological properties than the other two polymers. Aphron fluid synthesized by AG, especially at high salt concentrations, has a higher viscosity and yield point. It should be noted that this shows that AG has no sensitivity to high concentrations of salt, and even to some extent, its rheological properties are improved in the presence of salt, which can be an important advantage.

Polymer Concentration

Polymers are molecules composed of repeating units, and with increasing concentration in the aqueous phase, the viscosity of those fluids increases sharply. Therefore, the primary use of polymers in the industry is to control and increase viscosity.

Based on the data shown in Figure 9, it is clear that the viscosity of Aphron fluid has a direct relationship with the concentration of polymers in them. Therefore, the laboratory results obtained are completely in line with the published materials.

The yield point of the Aphron fluid is also one of the important properties of these fluids that need to be measured in a laboratory.

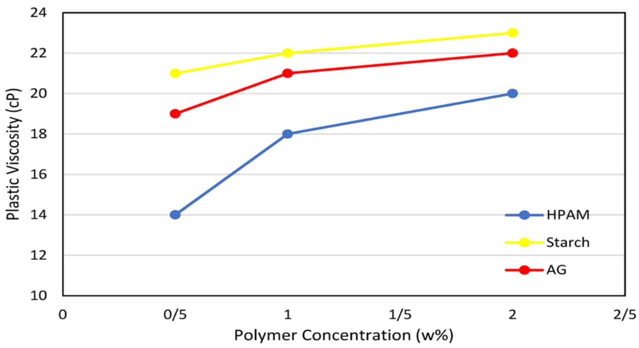

Fig. 9 Effect of polymer concentration on the viscosity of Aphron fluids.

It is clear from Figure 10 that the yield point of Aphron fluids, as well as their viscosity, increases with an increase in polymer concentration.

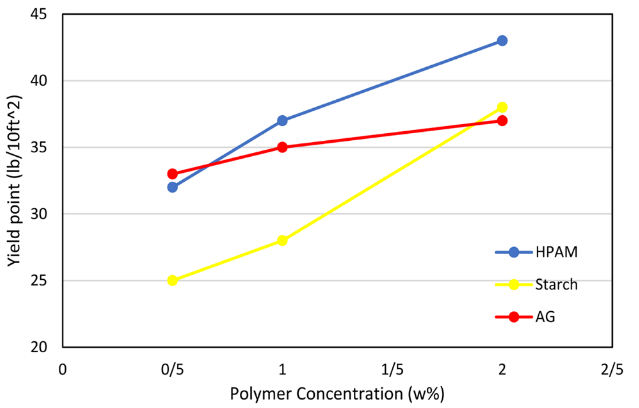

Fig. 10 Effect of concentration and type of polymers on the point of inversion of Aphron fluids.

Surfactant Concentration

Previously, based on the data obtained from experiments, it was explained that increasing the surfactant concentration causes more air to enter the Aphron fluid. As a result, the volumetric yield increased. Furthermore, it is known that increasing the amount of air entering the fluid increases the number of air bubbles. As a result, one can expect an increase in rheological properties.

It can be seen from Figure 11 that surfactant concentration increment raises viscosity of aphron fluid.

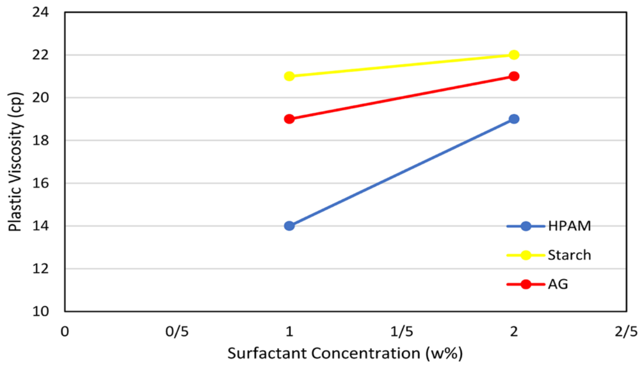

Fig. 11 Effect of surfactant concentration on the viscosity of Aphron fluids.

Stability of Different Aphron Fluids

As previously described, in Aphron fluids, gas bubbles are trapped by a bilayer of surfactant and polymer, increasing the volume and decreasing the fluid density. These gas bubbles coalesce over time and leave the liquid. This action is also called Aphron fluid drainage. The later and less the Aphron fluid is drained, the higher the stability and the more suitable it is. The stability and drainage rate of the samples were also measured, and the results are shown in Figure 12.

As shown in Figure 12, the Aphron fluid obtained from AG is more stable than other Aphron fluids, and a smaller volume of fluid is drained from the Aphron fluid after 24 hours. In contrast, the Aphron fluid from starch is unstable, drains very quickly, and is unsuitable.

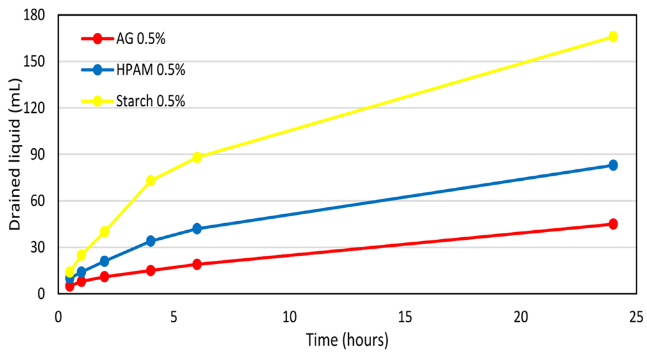

Fig. 12 Data obtained from stability tests.

Figure 13 illustrates that as the concentration of polymers increases, the stability of Aphron fluids increases, and less of those fluids are drained over time. It could be related to the structure of Aphron fluids in which air bubbles have double-walled layers protected by polymers and surfactants. As a result, with an increase in polymer concentration, the strength of these layers increases, and the resistance of the Aphron fluid increases over time.

As a whole, it is clear that for Aphron fluids made by all three polymers, the stability of the Aphron fluid increases with increasing polymer concentration.

It can also be seen that the stability of this fluid for AG is the highest value that approves that it can be a suitable aphronizer polymer for the oil and gas industries.

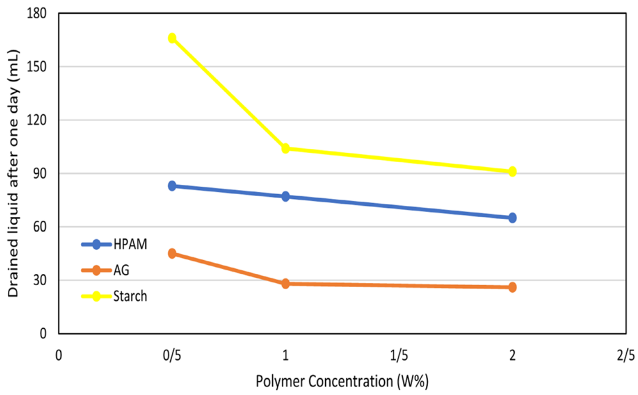

Fig. 13 The effect of polymer concentration on the stability of Aphron fluid.

In Figure 14, shown below, the volume of liquid discharged from the Aphron fluid after 24 hours is plotted.
As seen in the figure above, increasing the salt concentration reduces the stability of Aphron fluids. This action can be due to the acceleration of the osmotic process and, as a result, to drain of the liquid from the bubble fabric as quickly as possible.

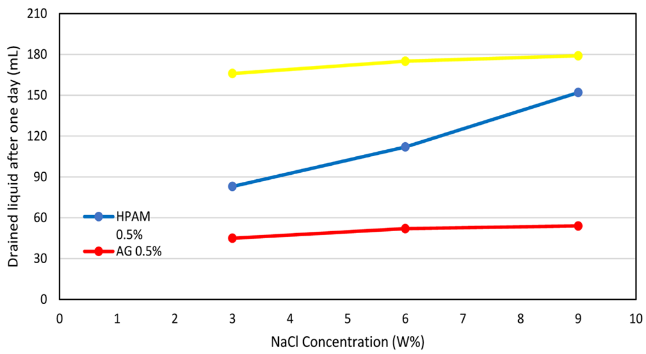

Fig. 14 Laboratory data for measuring the stability of Aphron fluids.

Filtration Properties of Aphron Fluids

In this subsection, the filtration properties of different Aphron fluids are displayed and discussed. As previously explained, the filtration properties show the stability of the Aphron fluid against pressure differences.
According to Figure 15, it is clear that the Aphron fluid consisting of AG is more stable against pressure differences. This is due to the stability of Aphron bubbles, which are the strongest and the most stable for AG and the weakest and most unstable for starch.

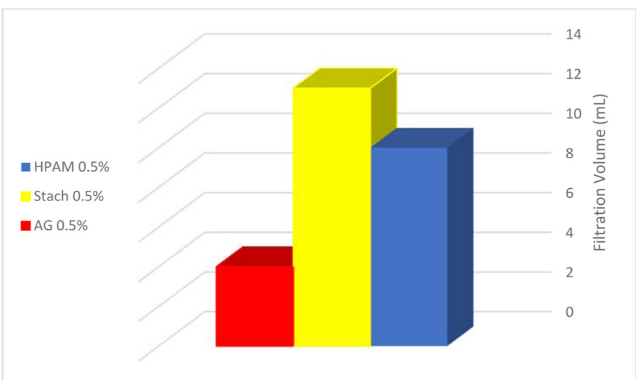

Fig. 15 Filtration volume of different Aphron fluids.

The effect of the concentration of polymers in Aphron fluids on the filtration properties was also investigated. Based on the experimental results, the kinetic and rheological properties of Aphron fluids, which were found to increase the viscosity of polymer Aphron fluids, were also expected to improve the filtration properties and reduce their amount.
According to the data shown in Figure 16, increasing the polymer concentration reduces the filtered volume of Aphron fluids, which can be due to the increase in continuous phase viscosity and the greater strength of Aphron bubbles. It is also clear that AG polymer is more efficient than other polymers in controlling Aphron fluid filtration.

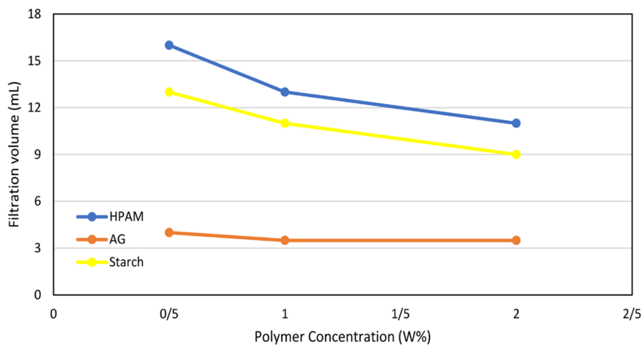

Fig. 16 Effect of concentration and type of polymer on the filtration properties of Aphron fluids.

Conclusions

The following conclusions can be made from the results obtained in this research:
1- The formation of solid Aphron bubbles in the fabricated fluid increases its volume by almost twice the original volume.
2- Increasing the salt concentration reduces the volumetric yield of Aphron fluids. Based on sources and references, it can be claimed that the increase in liquid-water interfacial tension prevents air molecules from entering the liquid bulk and thus reduces the volumetric yield.
3- Among the polymers tested, Aphron fluid made with AG has the highest, and fluid made with starch has the lowest volumetric yield.
4- Increasing the surfactant concentration increases the volumetric efficiency. It is related to the reduction of interfacial climate stress by surfactants.
5- Aphron fluid follows Bingham plastic's rheological model.
6- Aphron fluid has higher rheological properties (viscosity and yield point) due to the presence of solid bubbles coated with polymer and surfactant.
7- Salt increases the viscosity of the Aphron fluid because the particles dispersed in the aqueous medium increase with increasing salt concentration. However, in the case of the Aphron fluid made by starch, the opposite is true. The viscosity decreased with increasing salt concentration, which could be due to the adverse effect of salt on Starch performance, indicating the sensitivity of this polymer to high salt concentrations.
8- AG can increase the rheological properties of Aphron fluid more and better than other polymers.
9- Increasing the polymer concentration increases the stability of Aphron bubbles. It has also been observed that

natural gum polymers increase the stability of Aphron fluid more than other polymers.

10- Aphron fluids showed less filtration rate with increasing polymer concentration. It should be noted that the natural gum polymer controlled the filtration rate of Aphron fluids better than other polymers.

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Abbreviations

AG: Astragalus Gum
HPAM: Hydrolyzed PolyAcryLamide
CGA: Colloidal Gas Aphron
YP: Yield Point
cP: Centi Poise

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