Rheological and Fluid Loss Properties of Water Based Drilling Mud Containing HCl-Modified *Fufu* as a Fluid Loss Control Agent

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***Abstract*—Investigation on rheological and fluid loss properties of water based drilling mud containing acid modified *fufu* starch is presented. Hydrochloric acid at 8% and 16% was used, aiming at improving *fufu* performance as a fluid loss agent under extreme drilling temperature of 300 °F. Three formulations of mud weights of 75, 100 and 150 pcf were used, as proposed by the API and NISOC standards. Rheological properties, which are apparent viscosity, plastic viscosity, yield point and gel strength for the modified fufu showed significant improvement when 16% acid was employed. A significant amount of fluid loss reduction was obtained within light and average mud weights formulation (75pcf and 100pcf). Although none of the samples (modified and unmodified) meet the NISOC fluid loss standard requirement for the applied temperature, a great improvement was observed in ascending order of 16%HCl > 8%HCl > unmodified *fufu* WBMs, accordingly.**

***Index Terms*—Drilling mud, fluid loss, *fufu*, starch.**

I. Introduction

In the petroleum industry starch is mostly applied in water based drilling muds (WBMs) as a fluid loss control additive. This is in favor of its low cost and easy accessibility. Conversely, starch application has been confronted by some restrictions, such as extreme brittleness, poor resistance in moisture, low processing capability (due to high viscosity) and irreconcilability with a number of hydrophobic polymers. In view of that, to overcome these weakness numerous methods of modification have been proposed by different scientists thorough the years [1]-[5].

Modification of starch is defined as a procedure where starch configuration is changed by altering its hydrogen bond in a convenient manner. Typically, the degradation of starch may be made by numerous techniques like chemical modification, physical degradation, genetic alteration or enzymatic conversion. Chemical modification is by far the most

Starches which been chemically modified own major industrial importance, in their favor of glue manufacturing, chemical and industrial materials and also advancing practical properties of victuals and extra [6], [7]. There have been some studies based on physiochemical behaviors of numerous acid-alcohol modified starches such as potato, maize, wheat, sago and tapioca with some promising results. [7]-[12]. Various chemical techniques such as hydrolysis, oxidation and cross linking were used to generate carbohydrates. Method of acid hydrolysis which goes back to more than 150 years involves starch suspension in an aqueous solution (sulfuric or hydrochloric acid) at definite temperatures. When a strong acid and heat come together, it will result in cleaving of the glycosidic bonds that link monosaccharides molecules together in the starch structure [7].

The chemical treatment of the starch is the most applied modification method for starches. In that category the acid-modified starches have some significant properties compared to unmodified starches such as: Subordinate molecular weight, extra linear molecules, Low viscosity (capable of be consumed at higher solids), superior gelling affinity, amplified paste clearness and advanced gelatinization temperature. Acid modification of starch suitable for industrial applications is usually prepared by Hydrochloric acid treatment [13], [14].

Fufu is made by steeping cassava roots in water for fermentation for period of 3 to 5 days depending on ambient temperature. After fermentation the products is well crushed and sieved to dry [15], [16]-[18].

The rheological and fluid loss evaluation of *fufu* as a fluid loss control agent in WBMs, based on American Petroleum Institute (API) and National Iranian South Oil Company (NISOC) standards for starch, have been previously studied in our group and revealed the potential of *fufu* as additive for fluid loss control functionality in water based drilling muds. An acceptable and compatible amount of fluid loss was reported in all the mud weights applied (75pcf, 100pcf and 150pcf) within the temperature of 250 °F [19]. When the drilling operation temperature is challenge to extreme condition of 300 °F, all starches used in the WBM formulations (including potatoes, corn and cassava) were failed in their function as fluid loss agent [19].

With the visualization of improving the fluid loss control and thermal stability of cassava starch for WBMs formulation under extreme temperatures operation, we investigated the effect of acid modification on rheological and fluid loss properties of WBM samples containing treated *fufu* as a fluid loss agent.

II. Methodology

A. Materials

All the reagents applied in this research were analytical grade, purchased from Iran Kaolin and Barite Company (IKB Co.) in Tehran/Iran, whereas food grade *fufu* was precured

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from a local market Chow Kit in Kuala Lumpur, Malaysia. *fufu* starch was characterized using different techniques as presented in Table I below.

TABLE I: THE CHARACTERIZATION ANALYSIS OF *FUFU*

Technique Applied	Samples Properties	*Fufu*
Oven-Direct Heat	Humidity (%)	12.73
pH meter	pH	5.43
Digestion& Distillation System	Protein (%)	3.85
Soxhlet Method	Fat (%)	0.4
Muffle Furnace	Ash (%)	0.4

B. Preparation of Acid-Alcohol Treated Fufu

Acid-alcohol treatment of fufu starch was conducted according to a method described by Robyt *et al.*, 1996 [10], [20]. Briefly, a suspension from 2.5% w/v of cassava derivative fufu was prepared in anhydrous alcohol and treated with concentrated acid within 1-16% v/v. The suspension was placed under isothermal condition in a water bath set at 68 ℉ to 69.8 ℉, for 2 hours. The acid modification was initiated adding appropriate volume of concentrated hydrochloric acid to the suspension under constant gentle mixing. In this study, we used two different volumes (8.0 and 16.0mL, which represent the medium and the maximum amount recommended by Robyt et al. 1996). Then, the starch suspension was left to dry for 7days at room temperature under gentle mixing. Then, the starch was filtered and washed with 70% ethanol for a couple of time until the pH drop to neutral. Then, the starch was air-dried prior ready to be used as mud additives.

C. Preparation of Mud Samples

Mud samples were prepared in 3 different mud weights (75, 100 and 150pcf representing light, average and heavy weight, respectively) and their formulations were according to Table II. The rheological and fluid loss properties of mud samples containing the acid-modified *fufu* were investigated using the same method and environmental conditions as the unmodified *fufu* by Samavati *et al.* [19]. The mud was subjected to extreme drilling temperature via placing it a hot rolling oven at 300 ° F for 8hr under constant heating and circulation. Then, the mud samples were ejected and analyzed for their rheological and fluid loss properties.

TABLE II: THE COMPOSITION OF MUD SAMPLES

Mud Composition	Light Weight	Average Weight	Heavy Weight
Saturated Salt Water (Mud base)	350 cc	350 cc	350 cc
Fufu starch (Fluid loss agent)	14 g	14 g	14 g
Barite (Viscofier)	-	226 g	900 g
Hematite (Viscofier)	-	-	70 g
Mud Weight	75 pcf	100 pcf	150 pcf

D. Rheological and Fluid Loss Analysis of Drilling Mud

The rheological characterization of the mud samples were carried out by measuring plastic viscosity (PV), yield point (YP), apparent viscosity (AV) and gel strength (GS) at 10sec and GS at 10min using OFITE viscometer (model 800, USA). The volume of fluid loss was evaluated using a High Pressure-High Temperature filter press (HPHT) manufactured by Fann (model 3878, USA).

III. RESULTS AND DISCUSSION

The influence of acid modification on fufu starch applied as a fluid loss control agent in WBMs towards rheological and fluid loss properties in different mud weights were investigated. The results on plastic viscosity (PV), yield point (YP), apparent viscosity (AV), Gel strength (Gs) and fluid loss were obtained for both the modified and unmodified fufu mud samples before and after being subjected to extreme temperature of 300°F.

The experiments were carried out in 3 different mud weights (75, 100 and 150 pcf), to represent NISOC standards applied for water based drilling muds in industrial formulations of exact on-shore drilling circumstances.

A. The Effect of Acid Modification on Rheological Properties of WBM

For better understanding on the influence of acid modification (HCl 8% and 16%) on drilling mud functional properties, the rheological evaluation of the modified samples was compared to the mud samples containing unmodified *fufu.* The analyses were conducted in the same laboratory circumstances for both samples and shown in Table III and Table IV for mud with acid modified (8%HCl and 16%HCl), respectively. These are compared with the rheological properties of the unmodified *fufu* in different mud weights (Table V).

Table III showed rheological profile of *fufu* starch added to the 3 mud weight formulations (75,100 and 150pcf). The *fufu* was treated with 8% HCl prior to the mud formulation. The AV and PV value in all mud samples was increased significantly after 8hrs hot rolls conditions at 300 °F. The YP values in 75 and 150 pcf was dropped after the hot roll treatment, however, this was not observed in the 100pcf sample. For the GS at 1s and 10min, the value remained unchanged after the 8hrs hot roll for the 75pcf sample. However, for the 100pcf and 150pcf samples, the GS values were found to increase and reduce, respectively. Meanwhile, the pH values in all the samples dropped to mild acidic after 8hrs hot rolls treatment.

TABLE III: THE RHEOLOGICAL EVALUATION OF WBM CONTAINING MODIFIED FUFU (8%-HCL) BEFORE HOT-ROLL (BHR) AND AFTER HOT-ROLL (AHR) AT TEMPERATURE OF 300 ° F IN DIFFERENT MUD WEIGHTS

	75 pcf		100pcf		150pcf	
Rheology	BHR	**AHR**	BHR	**AHR**	BHR	**AHR**
AV	2	**2.5**	6	**24**	37	**70.5**
PV	1	**2**	6	**18**	27	**65**
YP	2	**1**	0	**12**	20	**11**
GS (10 s)	1	**1**	1	**3**	18	**11**
GS (10min)	1	**1**	2	**4**	20	**12**
pH	9.5	**5**	6.9	**5.9**	8.5	**6**

When a higher strength of acid (16% HCl) was used in the starch treatment, the rheological properties exhibited slight deviation in some of the mud formulations, than that observed in the 8% HCl. Table IV showed the overall rheological properties of three mud weight containing *fufu* that was pre-treated with 16% HCl. The AV value showed a significant increment after the hot roll. A linear trend in the AV property was observed as the mud weight composition is increased from 75 to 100 and 150pcf. PV remained constant in 75pcf, but significantly increased in the 100 and 150pcf samples, after the hot roll. YP for all the mud weight showed a consistent increment in its value while the GSs of 10s and 10min remained constant after they are subjected to hot roll. Similar to the 8%HCL formulation, the pH drop to mild acidic in all the formulations in the 16%HCL-treated sample

TABLE IV: THE RHEOLOGICAL EVALUATION OF WBM CONTAINING MODIFIED FUFU (16%-HCL) BEFORE HOT-ROLL (BHR) AND AFTER HOT-ROLL (AHR) AT TEMPERATURE OF 300 ° F IN DIFFERENT MUD WEIGHTS

	75 pcf		**100pcf**		**150pcf**	
Rheology	BHR	**AHR**	BHR	**AHR**	BHR	**AHR**
AV	1.5	**2**	5.5	**8**	21.5	**25**
PV	1	**1**	5	**7**	18	**23**
YP	1	**2**	1	**2**	7	**4**
GS (10 s)	1	**1**	1	**1**	8	**8**
GS (10min)	1	**1**	1	**1**	9	**9**
pH	8.9	**5.5**	8.1	**6.4**	9.1	**7.1**

To make a fair comparison, a rheological performance of the untreated *fufu* starch was performed as well. This was presented in Table V. Here, it showed that a reduction in the AV value after the hot rolls for both 75 and 100 pcf samples. In contrast, the value was found to increase in the 150pcf sample. As for the PV, reduction in its values in 75pcf samples was observed, while increment in the 100 and 150pcf sample, accordingly. The YP in 75pcf and 150pcf samples showed an increment, however not in the 100pcf sample (reduced it value). The GSs remained unchanged upon hot roll treatment for the 75pcf and 100pcf, but not in the 150pcf (showed a significant increment). Similar to all acid treated *fufu* formulations, the pHs of the untreated *fufu* formulations were dropped to mild acidic range.

TABLE V: THE RHEOLOGICAL EVALUATION OF WBM CONTAINING UNMODIFIED FUFU BEFORE HOT-ROLL (BHR) AND AFTER HOT-ROLL (AHR) AT TEMPERATURE OF 300 ° F IN DIFFERENT MUD WEIGHTS

	75 pcf		**100pcf**		**150pcf**	
Rheology	BHR	**AHR**	BHR	**AHR**	BHR	**AHR**
AV	2.5	**2**	11.5	**7.5**	-	**40.5**
PV	2	**1**	7	**8**	-	**36**
YP	1	**2**	7	**1**	-	**9**
GS (10 s)	1	**1**	1	**1**	-	**10**
GS (10min)	1	**1**	1	**1**	-	**11**
pH	7.6	**6.5**	7.6	**6.4**	7.4	**6.3**

B. Comparison of PV, AV, YP and GS Properties between Unmodified and Modified-Fufu Containing WBMs Formulation

The four rheological properties evaluated for both treated and untreated *fufu* starch are PV, AV, YP and GS. These values were measured after 8hrs hot-rolling condition at 300 ^{o}F, which simulate the extreme drilling operation condition. In other word, the following discussions are made based on AHR data from the Table III-Table V.

The AV value was set at 72 ±2cp for 150pcf mud weight by the NISOC standard. Note that, for the 75pcf and 100pcf mud weight, AV value is not available by this standard. The AV value increases as the mud weight increase (from 75 to 100 to 150pcf) in all the samples (treated and untreated). None of the sample exhibited an acceptable AV values at the extreme 300 ^{o}F condition, set by the NISOC standard.

The PV value after hot-roll treatment for 8hrs under 300 ^{o}F for light mud weight formulations (75pcf) containing 8%HCL-treated, 16%-HCL treat and untreated *fufu* starch showed very low value at 2, 1 and 1cp, respectively. With reference to the PV recommended under NISOC, value in the range of 15 ±2cp and 65±2cp for 100 pcf and 150pcf mud weight must be met, respectively. However, no set value was made available for the 75pcf mud weight. The PV value increase as the mud weight increased. This is judged by the elevation of the PV from 2 to 18 to 65 cp for 75pcf, 100pcf and 150pcf mud weight treated with the same strength of 8% HCl acid. Similar trend was also observed when dosage of acid used was doubled at 16%, however the value was not as high as the 8% acid treated, which measured at 1 to 7 to 23 for 75pcf, 100pcf and 150pcf samples, respectively. The PV profile of 16% acid treated *fufu* was similar to the untreated fufu.

YP for 100pcf and 150 pcf was set at 12 ±2cp and 18 ±2cp, respectively. While, no YP value was available for the 75pcf mud weight. Unlike AV and PV, no increment trend was observed between YP and mud weight employed. The YP value was also outside acceptable range set by NISOC. However, some of them are acceptable under API standard (set value at 2cp), such as the mud weight of 75 and 100pcf that were acid-treated (16%) and in the unmodified *fufu* (at 75 pcf mud weight).

Under NISOC standard, acceptable value for GS (10s and 10min) is set at 3 lb/100ft^2 and 4 lb/100ft^2 for 100pcf and 150pcf mud weight formulation, respectively. Whereas there was no set value for GS of 75 pcf mud weight in the NISOC standard. In this study, only one formulation is acceptable under NISOC regulation, which is the 8% acid modified *fufu* in 100pcf mud weight. The GS 10s and 10min in all treated and untreated *fufu* with light (75pcf) mud weight remained constant at 1 lb/100ft^2. In the heavy (150pcf) mud formulation, all the sample was rejected since the GS values are higher than 4 lb/100 ft^2 (set by NISOC).

pH is another important criteria in the drilling operation. It is desirable to have mild-alkaline pH value (8.0 -9.5). Usually, this is achieved by adding limestone (if needed) to the mud formulation. The initial pH in the unmodified fufu in all the mud weight was around neutral pH. This was observed consistently with other type of starch used in our laboratory (results unpublished). When the starch was treated with acid, the pH of the formulations increase to mild alkaline range, which was desirable by drilling practice. After 8hrs hot roll operation at 300 ^{o}F, the pHs in all the samples dropped to mild acidic-neutral value (pH5-7). Thus, requiring pH adjustment (preferably via lime addition), if further use of the mud is required.

C. The Effect Acid Modification of Fufu on Fluid Loss

Investigation on the fluid loss properties were carried out using an API proved High Pressure-High Temperature Filter Press (HPHT) manufactured by Fann (model 3878, USA). The NISOC standard requires acceptable amount of fluid loss for WBMs to not exceed 2mL. Fig. 1- Fig. 3 present the fluid loss evaluation of modified and unmodified *fufu* in different mud weights at the temperature of 300 °F. All the mud samples containing modified and unmodified *fufu* failed to function as a fluid loss control additive, because their values exceeded the acceptable fluid loss limit (more than 2 mL).

Even so, within the light WBM formulation (Fig. 1), a significant drop in fluid loss value was observed in modified *fufu* sample as compared to the unmodified, from 250ml (unmodified) to 130ml (8%HCl) and 100ml (in 16% HCl).

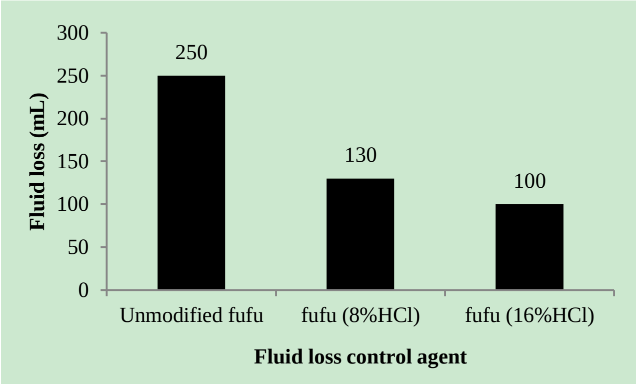

Fig. 1. The fluid loss evaluation of unmodified and acid modified fufu (8%HCl and 16%HCl) after hot-roll at 300°F in mud weight of 75pcf.

In the average weight mud (Fig. 2), there was no improvement observed in a fluid loss value between untreated and 8% acid treated fufu. Doubling the acid strength (16% HCl) resulted in a notable reduction in fluid loss by ~66%, however the value is still rejected by the NISOC standard.

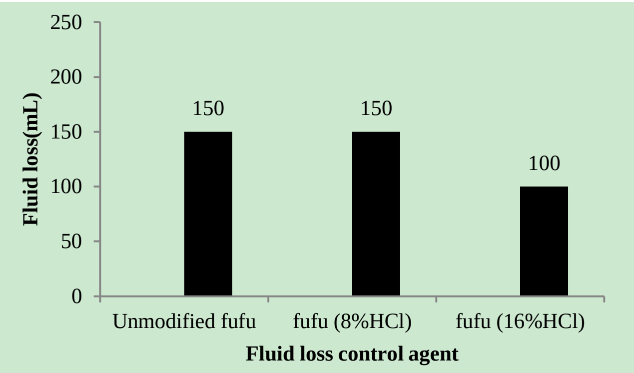

Fig. 2. The fluid loss evaluation of unmodified and acid modified fufu (8%HCl and 16%HCl) after hot-roll at 300 ° F in mud weight of 100pcf.

Contradict to the fluid loss profile observed in light and average mud, the heavy mud formulation (Fig. 3) showed augmentation in the fluid loss when subjected to HCLmodification.This probably due to the increment in the mud composition in the formulation.

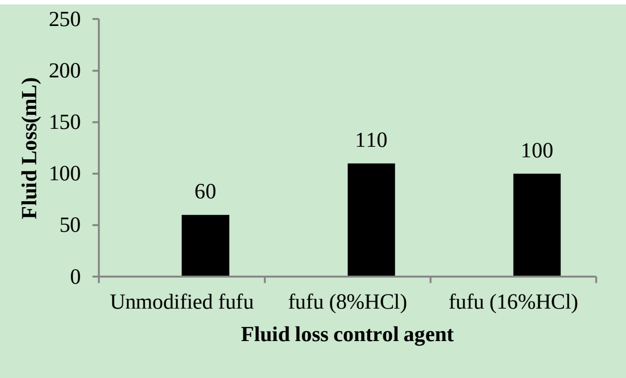

Fig. 3. The fluid loss evaluation of unmodified and acid modified fufu (8%HCl and 16%HCl) after hot-roll at 300 ° F in mud weight of 150pcf.

IV. Conclusion

HCl-modified *fufu* (cassava derivative) applied as an additive in WBMs formulation for use under the temperature of 300 ° F has shown a significant improvement as compared to that without acid-modification. A significant amount of fluid loss reduction was obtained within light and average mud weights formulation (75pcf and 100pcf). Although none of the samples (modified and unmodified) meet the NISOC fluid loss standard requirement (up to 2mL of fluid loss) for the applied temperature, a great improvement was observed in ascending order of 16%HCl > 8%HCl > unmodified *fufu* WBMs, accordingly.

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