A DUAL MECHANISM OF THE DRAG REDUCTION BY RIGID POLYMERS AND CATIONIC SURFACTANT: COMPLEX AND NANOFLUIDS OF XANTHAN GUM AND HEXADECYL TRIMETHYL AMMONIUM CHLORIDE

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Abstract

Several approaches have been employed to reduce the high cost of energy associated with the way liquids are transported in pipelines. Polymers have been widely explored to replace the pumping stations and other high energy cost mechanisms, but degrade over a period of time due to the accompanying turbulent mode of such transportation. Surfactants which are better alternatives with the ability to reenact their lost efficiency, are less effective, there is therefore the need for an alternative mechanism for drag reduction. In this present work, drag reduction efficacy of dispersed silica nanoparticle additives with polar additives as complexes and nanofluid have been investigated as a new method to reduce drag. Thus the present work was carried out with Xanthan gum which is able to withstand degradation compared to the flexible polymers, hexadecyltrimethyl ammonium chloride as the surfactant and sodium salicylate as the counterion. In the study both complexes and nanofluid were able to reduce drag as well as withstand shear stresses, although at different concentration which could be as a result of the different approaches of working, about 60% drag reduction was observed. It could thus be concluded that, these materials are able to reduce drag both as complex or nanofluid, only that, they could do that at different concentrations.

Keywords: *Nanofluid, Polymers, Surfactants, Drag reduction, rotating disk apparatus, degradation*

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1. INTRODUCTION

The concept of frictional drag is not a new one, as it is a part of our daily activities. In air craft, liquid transportation or in the petroleum industries. Right from the earliest discovery in 1948 [1], numerous efforts have been made to explain the real mechanism associated with it as well as the best way to reduce such. The concept, otherwise referred to as drag reduction. As a result of this, many authors have contributed significantly to the study of drag reduction [2-6].

In the course of these investigations, many materials otherwise called "drag reduction agents" have as well been employed. Among these DRAs, Polymers, as discovered by Toms [1] have been the greatest explored and investigated. Nevertheless, they are prone to the challenge of mechanical degradation, especially under the influence of shear stress or temperature increase, which invariably reduce their efficiency [7]. Another set of material are the surfactants which have been investigated by many authors [8-11.], they offer an advantage of self-repair through micelles formation after degradation [12-14], but are less effective when compared to the polymers. Few other materials which have been investigated as drag reduction agents are fibers [15] bubbles [16] solid particles etc. which have been proven less effective as well as of different physical working mechanism and more prone to degradation compared to the polymers [17]. Thus, there is yet to be a universal acceptable material on this subject matter. This has initiated continuous efforts to research other materials.

In a study [15], suggests a combination of polymers and fibers as significant drag reduction with better stability against degradation compared to polymers alone. In view of this, Carbon nanotube nanofluid have been investigated to reduce drag and are mechanically stable as a result of their outstanding physical and chemical features [18]. In a recent study [19], carbon nanotube were as well used to form nanofluid which enhanced the drag reduction ability of polymeric additives. Nevertheless, CNT are very expensive and if cost it to be considered, then, alternative cheaper and cost effective materials should be explored.

As a result of this, a close substitute for CNT are the silica nanoparticles which have been confirmed of good stability in organic solvents, good dispersivity as well as lubrication additives [20-22]

This has been confirmed with the study by [23]. However, most of these studies were carried out in pipe flow system and with flexible polymer additives. Thus, there is need to investigate the role of these materials with rigid polymers which is the major motivation for this work.

In this present work, cost effective and efficient SiO2 nanoparticles were used for the first time, to modify rigid polar additives and to produce nanofluids which are investigated at various operating conditions in a rotating disk apparatus. Different operating parameters were as well experimented to verify their drag reduction efficacy.

1.1 Experimental Materials

Materials employed in this study were all supplied by Sigma Aldrich, Malaysia and used without further treatment. They are glycerine, Xanthan gum; 2.4 g/ cm^3 density, 20–30 nm length and 180–600 m2/g specific surface area (SSA) silica nanoparticle; hexadecyltrimethyl ammonium chloride (CTAC) of molecular weight 364 kg $kmol^{-1}$ and Sodium salicylate (NaSal) of molecular weight 160 kg $kmol^{-1}$ as counterion and sodium dodecyl sulfate (SDS) as dispersant

1.2 Experimental Procedure

The surfactant-counterion was prepared by accurately measuring both materials and dissolved in double deionzed water of about 5.07 kg, after which their mixture was mechanically agitated for a period of 15 min, this was carried out for a homogenous sample.

Polymers and Complexes were prepared by measuring the required concentrations of both polymers and surfactants, these were as well dissolved in double deionzed water of about 5.07 kg as stock concentration until the final concentration were prepared as the case may be for the experiment.

The Nanofluid was however prepared by dissolving the surfactant in the base liquid at 0.5 wt % and thereafter mixed with the silica nanoparticle in an ultrasonic bath for 12 h for the well dispersed homogenous suspension for this study. Detailed explanation is reported in Section 1.3.

1.3 Nano Fluid Preparation

In this present work, the first mixture to be prepared was a baseline which is a combination of glycerine and double deionized water in the ratio of 60wt% to 40wt% respectively, this was able to achieve our desired viscosity of approximately $8.10*10^{-3}$ Pa.s. This was followed by preparing a conventional polymer drag reducing fluid mixture by mechanically mixing the Xanthan gum of M_v = $2.0*10^6$ g/mol with water–glycerin solution baseline, we then prepared another mixture, comprising of the baseline and 20–30 nm silica nanoparticle of 2.4 g/ cm^3 density and specific surface area (SSA), 180–600 m^2/g, this was done to compare between these mixtures. Lastly Nano fluid was prepared by dissolving 70ppm of 20–30 nm silica nanoparticle of 2.4 g/ cm^3 density and specific surface area (SSA), 180–600 m^2/g and 100ppm of Xanthan gum of M_v = $2.0*10^6$ g/mol which were all mixed and magnetically stirred. But it is of interest to note that, these materials are prone to agglomeration, thus, we dispersed them before further investigations. In most of the literatures, Nano fluids have been well dispersed by (a) sonication in ultrasonic bath for a period of time, (b) Dispersed in distilled water containing other dispersant at known adjusted PH, (c) High shear homogenizer treatment for some time, all of these have been reported and according to [24], Nano fluids produced in this manner are stable for months without any form of sedimentations. But in this present work, a surfactant, sodium dodecyl sulfate (SDS) was used as the dispersant where it was initially dissolved in the base fluid, at 0.5 wt.% with magnetic stirrer followed by the introduction of other materials as initially explained in this section and further sonicated with 9 W of 30 kHz ultrasonic processor for a period of 12h. Nano fluids were then produced within the range of 0.4-1.0 wt. % nanoparticle concentrations

1.4 Rotating Disk Apparatus (RDA)

The schematic representation of the Rotating Disk Apparatus (RDA) used in this present study is denoted by Figure 1. It is used to stimulate external flow of the sample thereby recoding the influence of Torque against their respective rotational speed. The equipment consists of a stainless steel solution container and a lid of about 165 diameter and 88mm height and 60 mm thickness for the container and lid dimensions respectively, maximum solution capacity of about 1200mL, an accompanying disk of about 3mm thickness and 148mm in diameter. For data collection and recording, the RDA has a computer display system where the torque is taken supported by the inbuilt motor assembly which enable the disk to be operated, it consists of a servo driver DS2-20P7-AS of motor capacity 0.75 kW by Xin Jie Electronic Co. Ltd, Malaysia. The equipment is operated at a maximum operated rotational disk speed of 3000 rpm with excellent rotational acceleration.

There is direct connection between the servo motor and an interface which captures the torque values at every rotational speed of the motor thereby converting to readable form in the computer display system with a SCADA software.

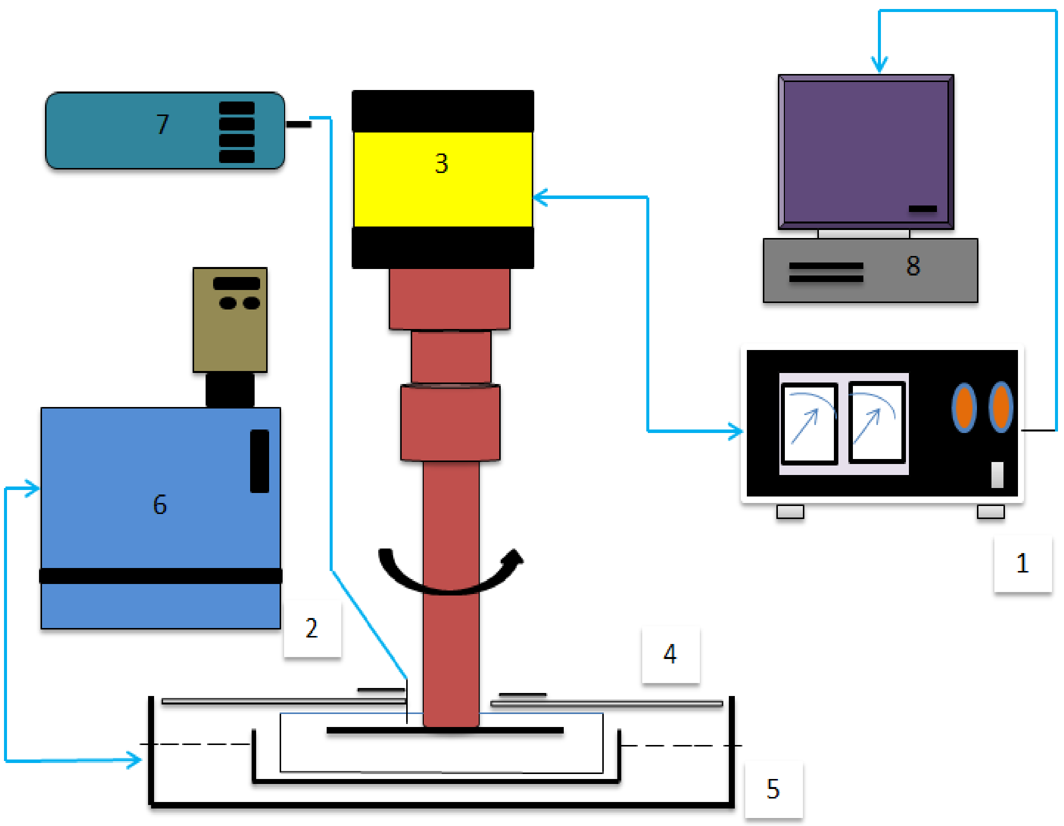

Fig 1: Graphical image of a rotating disk apparatus for the drag reduction measurement: (1) speed controller, (2) thermocouple, (3) motor, (4) solution container, (5) water bath, (6) water-circulating system, (7) thermometer, and (8) PC.

1.5 Calculations

For data acquisition, materials tested were fed into the chamber of approximately 1200Ml, as the disk were rotated from 50-3000rpm, data were taken and recorded while maintaining the temperature at 25^{0}C ±0.05^{0}C. Thus, the percentage drag reduction was calculated as:

$$\%DR = \frac{T_i - T_a}{T_i} \times 100$$

T_i and T_a denote torques reading before and after adding the polymeric additive respectively. Flow parameters are depicted by rotational Reynolds number N_{Re} obtained as:

$$N_{Re} = \frac{\rho R^2 \omega}{\mu}$$

From the equation above ω, μ, ρ, R represent disk rotational speed, fluid viscosity, fluid density and disk radius respectively.

2. RESULTS AND DISCUSSIONS

2.1 Effects of Additive Concentration

Figures 2, 3 and 4 depict the impact of additive concentration on Torque as the rotational speed increased, despite the effects of the torque which invariably exerts high shear forces on the additive molecules, increase in the concentration were able to withstand degradation in all these additives, from this observation, the concentration played important role in all. It could thus be opined that all these materials are effective drag reducers. In addition, their mechanism of working could be based on the increase in percentage drag reduction molecules which is favored by the increase in their respective concentrations. Therefore, any further increase in the additive concentrations has a direct drastic increase in the solution viscosity which decreases the turbulent strenght, other wise referred to as the reduction of Reynolds number, *N*re. As the process continued, the frictional drag increases. It could be clearly seen in these Figures that the energy dissipated due to friction by the rotation of the disk could be taken which indicate the rate of additives stability against degradation, owing to the fact that, rotational flow is a drag induced flow. From the Figures 1,2 and 3 there are no much difference in the Torque reading at lower *N*re, which are the initial readings from 50-400rpm, but as they move further, there are noticeable impact of the torque, yet, as a result of the concentration increase, they were observed to be stable.

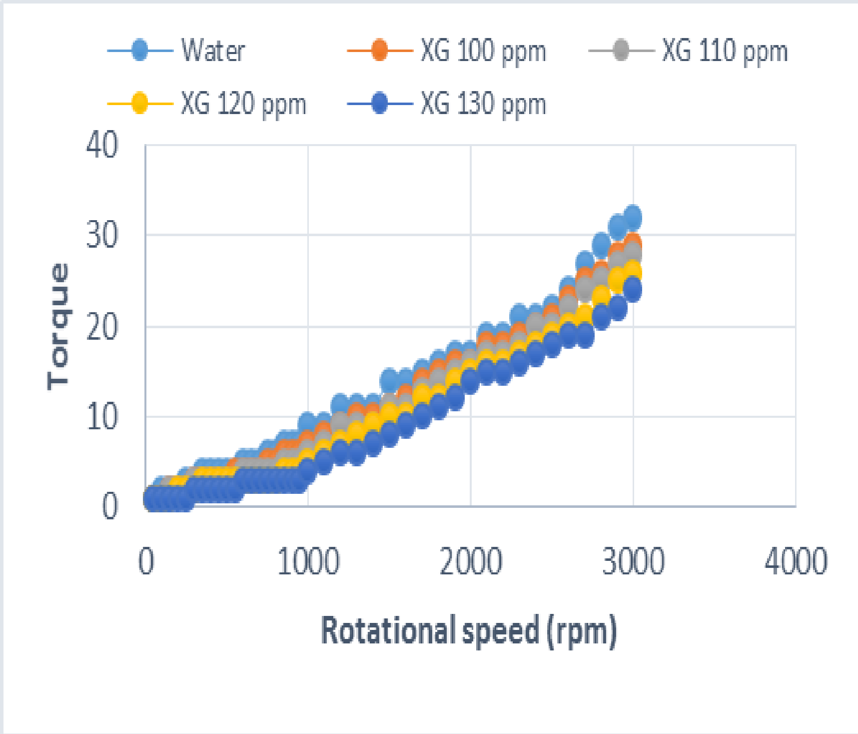

Fig 2: Torque effects on different concentrations of XG

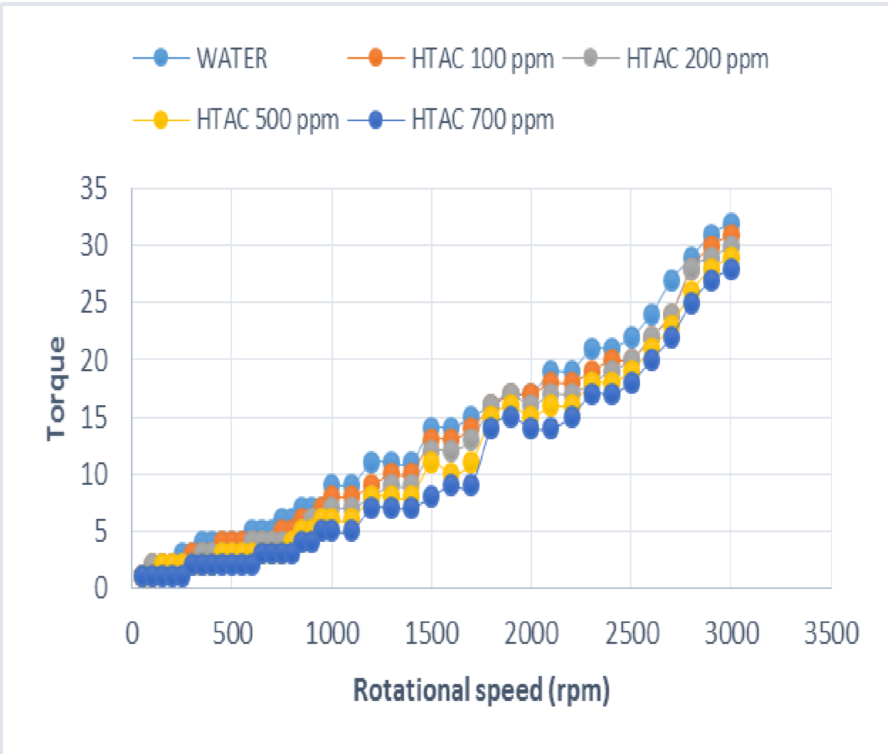

Fig 3: Torque effects on different concentrations of HTAC

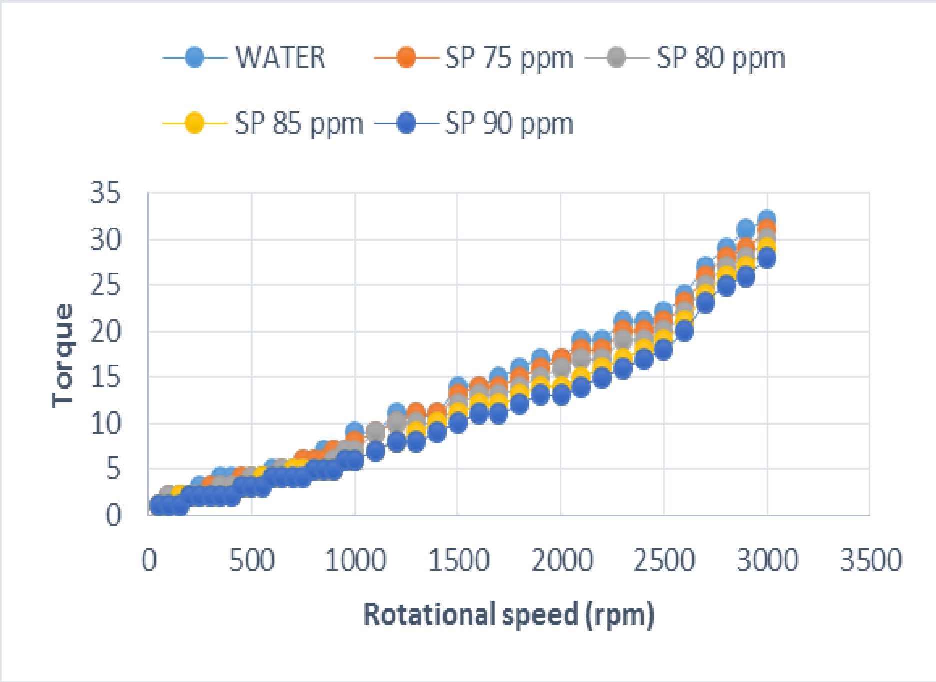

Fig 4: Torque effects on different concentrations of SP

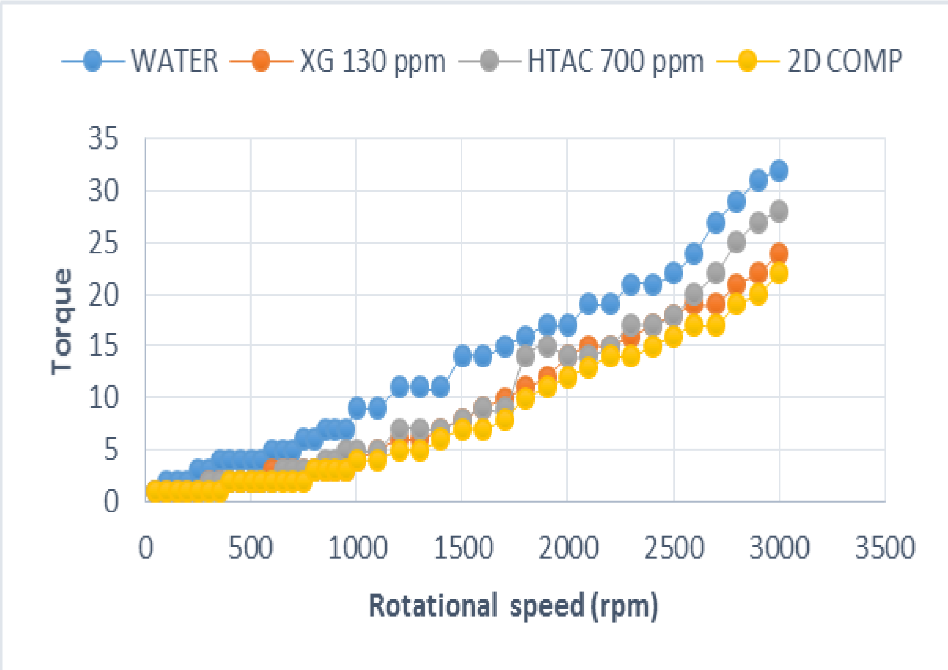

Fig 5: Torque effects on additives and 2D complex

2.2 Drag Reduction of all Samples

The Drag reduction ability of all samples is reported in Figures 2-8. This was achieved from the Torque reading, the data obtained from this investigation are the only prerequisite measurement required for fluid drag reduction calculations with repect to the pure solvent as explained in section 1.5. In all the additives, they all showed drag reduction capability, only that, their concentration, mechanism are not the same.

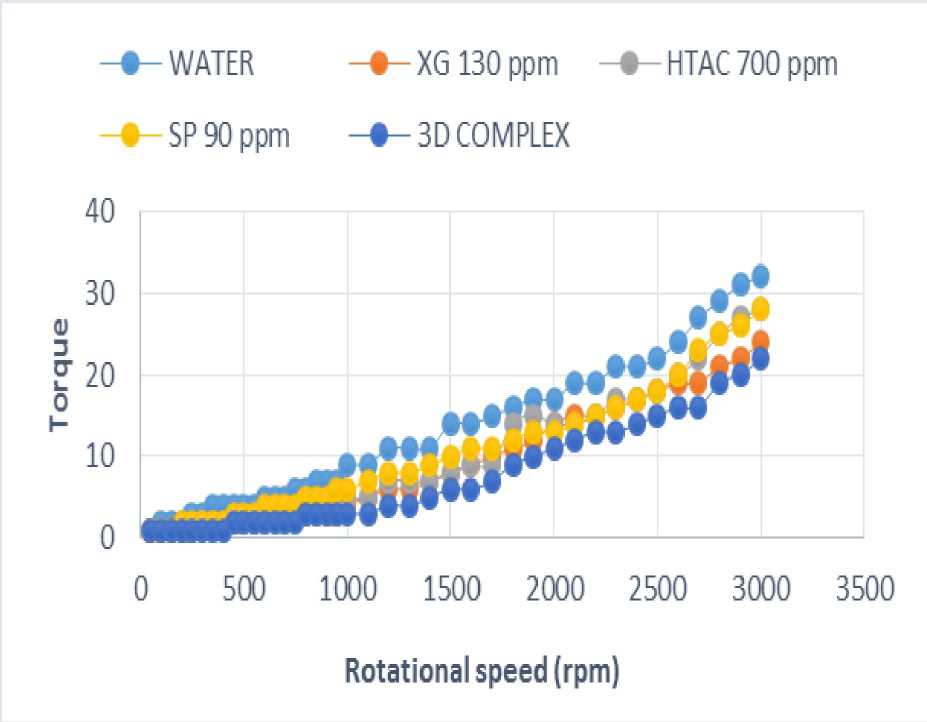

Fig 6: Torque effects on additives and 3D complex

2.3 Drag Reduction of the Polar Additives

Drag reduction efficacy of the polymer and the surfactant are clearly shown in figures 2 and 3 respectively, from the Figures, it could be seen that the two additives were able to reduce drag. Neverthless, the drag reduction by the polymer is more pronounced than in the surfactant, this could be as a result of the viscoelastic nature of the polymer which is less with the surfactant. However, the surfactant has ability to form micelles which is why they were able to withstand the degradation under the influence of shear stress, this could be seen in Figure 3 at 1750 rotaional speed, this is the major attribute which initiated their combination with polymer as complex mixture. Although it has been argued that, the mechanism of their drag reduction is different from that of the polymer as well as less effective to the polymer [17], nevertheless, the two materials were able to reduce drag to an extent.

2.4 Drag Reduction Effects of Nano Silica

Figure 4 shows the drag reduction investigation of the silica nanoparticle, it is also observed that these materials were able to reduce drag as well as influence the drag reduction capability of the other materials, although they exhibit a slight behavior than the water alone, the slightest drag reduction behavior noticed with them could have been as a result of the present of the baseline in the sample. These materials were tested on preparing different concentrations and investigated in the rotating disk apparatus. In addition, combining these materials with other drag reduction additives yielded better impact on their drag reducing efficacy, moreover they greatly influence the drag reduction ability in the Nano fluid. All these could have been made possible due to the role of the baseline, polymer and the surfactants. From this, it could be opined that silica nanoparticles could augment the drag reducing ability of xanthan gum and Nano fluids.

2.5 Drag Reduction Effects of Complex and Nano Fluid

Figures 5 and 6 show drag reduction capability of the complex mixtures produced from the individual additives without and with the introduction of nanosilica particles respectively. It is of interest that both complexes were able to reduce drag as well as great stability, this is as a result of the data from the Torque reading with respect to the rotational speed of the disk in each case. However, the introduction of the silica nanoparticle in Figure 6 enhanced greater stability than in the two dimensional complex of Figure 5, this could be as a result of the great attributes of the materials as enumerated by [20-22]. On the other hand, Figures 7 and 8 depict the results of the\ Nano fluids prepared from the baseline, polymer and the silica nanoparticles where the Torque percent is related to the respective rotational speed, overall, the materials were able to reduce drag, despite the fact that there are different types prepared, from these Figures, at very low concentration of the silica nanoparticle, there was no much impact on the drag reduction as all the material exhibit almost same characteristic like the water, from this behavior, one could opine that the inability of the disk wall to be well by the presence of the nano-SiO_2 could have resulted into such, in contrast, an entirely different observation was noticed when there was increase in the concentration as there was effective drag reduction. This observation suggests the availability of reasonable quantity of nano-SiO_2 available to smoothen the disk surface, a similar study was reported by

[23], which was investigated in pipe while this is the first time such will be investigated in a rotating disk apparatus. From this behavior, it could be said that surface modification is one of the most important mechanism through which these materials reduce drag with Nano fluid of nano-SiO_2, initiated by their rigid nature. In addition to this, presence of well dispersed nano-SiO_2 in the complex mixture could have initiated their ability to influence these materials whereas their rigidity might have prevented them from reducing drag when solely applied but were able to interact with other DRAs to give structures which could influence them and also enhance their mechanical degradation while maintaining some flexibility, in a similar study by [19] with CNT and PEO in pipes, same was reported, but for the first time, similar study is undertaken in a RDA.

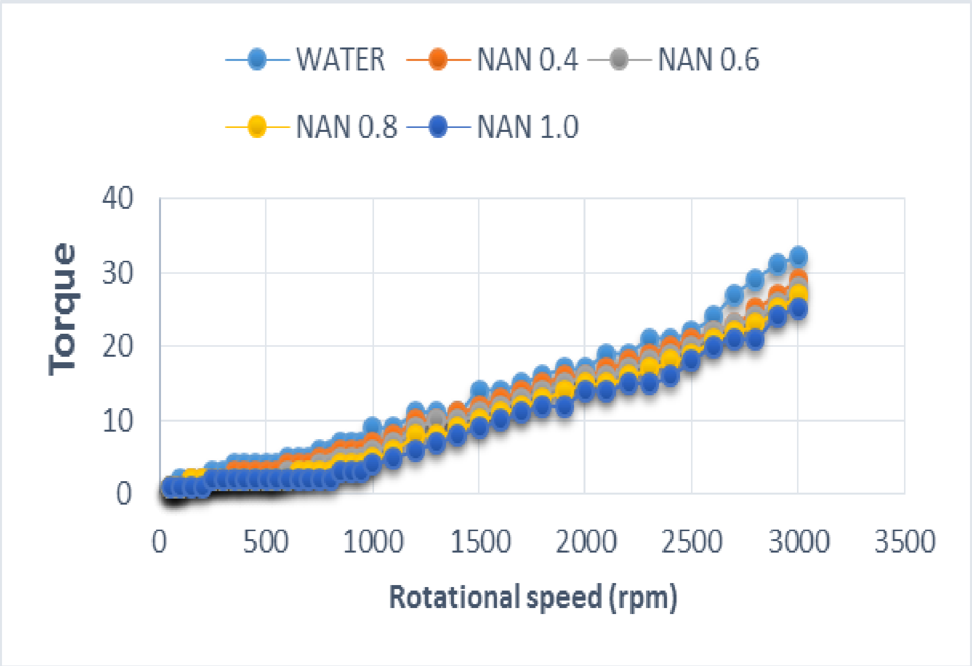

Fig 7: Torque effects on the nanofluid without counterion

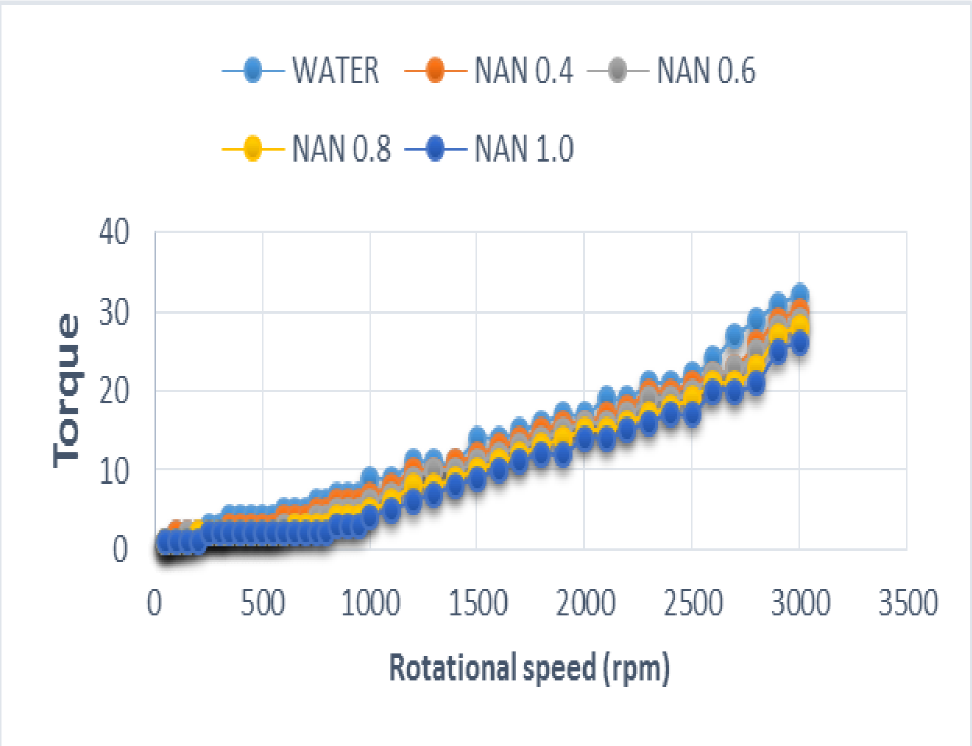

Fig 8: Torque effects on the nanofluid with counterion

2.6 Degradation Effects of Complex and Nano Fluid

Xanthan gum are able to reduce drag as well as withstand mechanical degradation than the flexible polymers, nevertheless, when a complex mixture was prepared with the surfactant, they improve greatly the drag reduction capability and they tend to perform better than the individual drag reducing agents, this could have been made possible due to the presence of the surfactants owing to the fact that they are able to realign after degradation, thus, introducing them into the polymer, they exhibit such characteristics whereby they withstand degradation over a period of time. Apart from this, introducing the silica nanoparticle has greatly improved such drag reducing ability. Moreover, Nano fluids produced from these combination were able to reduce drag, while comparing the complex and the Nano fluid, it is interesting to observe that the duo were able to reduce drag accordingly, one important observation to note here is that the micelles formed in the complex and Nano fluids with noticeable volume increase in larger assemblies of wormlike micelles observed in these mixtures could have been as a result of the counterion used with this surfactant, it could be opined that the counterion modified the packing parameter which reduce distances between surfactant molecules head groups and the effective surface area of the head group at micelle interface. Similar observation have been observed in the study by [10, 25, 26]

2.7 Comparing the Complex with Nano Fluids

The ability of nano-sio$_2$ to influence the drag reduction capability of both polymer and complex mixture could be confirmed while comparing their complex mixtures and the nano fluid, the ability of these materials enhance such mixtures in the dual nature has proven beyond reasonable doubts that they play a role in their host fluids, nevertheless, they were able to perform at different concentration and efficacy. Direct comparison of the influence of counterion on the drag reduction effectiveness in these mixtures shows a diminish drag reduction effectiveness in the absence of counterion in the complex mixture while it was the opposite when counterion was introduced, in similar study, the nano fluid behavior was opposite to the behavior with the complex, this is because there was improved drag reduction when counterion was absent in the nano fluid and opposite without.

2.8 Drag Reduction With Respect To Reynolds Number

Figures 9 and 10 show the roles of Reynolds number on the drag reduction percent of the naofluid prepared without and with counterion respectively, in both, drag reduction were observed, but their mechanical stability were different. It is a well known that there is a critical point and maximum point where drag reduction is observed with additives. From the Figures, the maximum drag reduction were observed at $N\text{re}=5*10^6$. From the two Figures, increase in the nanofluid concentration affected their respect stability. Since the best stability was noticed with the nanofluid prepared without counterions, thus, it could be realized that the counterion has little or no effects on the nanofluid, especially when they are preapared from rigid polymers. Virk [27] has been able to classify gross flow of polymeric additives solution in pipe as laminar, transitional, turbulent flow with or without drag reduction, decrease in the DR% behaviour of these nanofluids could be as a response to these flow behaviour until the final collapse. Thus, such classification couldd be applicable with rotating disk flow systems.

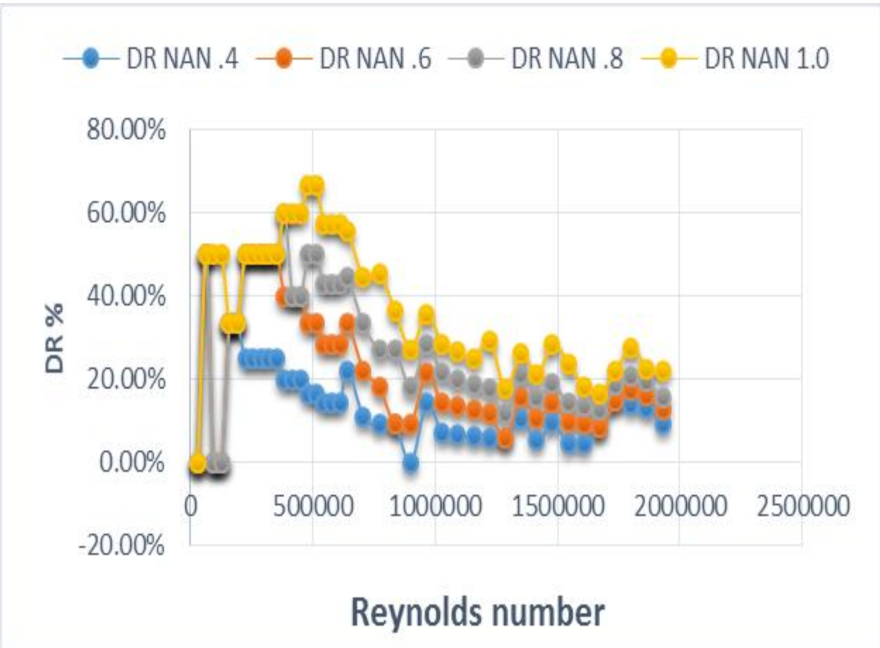

Fig 9: %DR at various Reynolds number of nanofluids

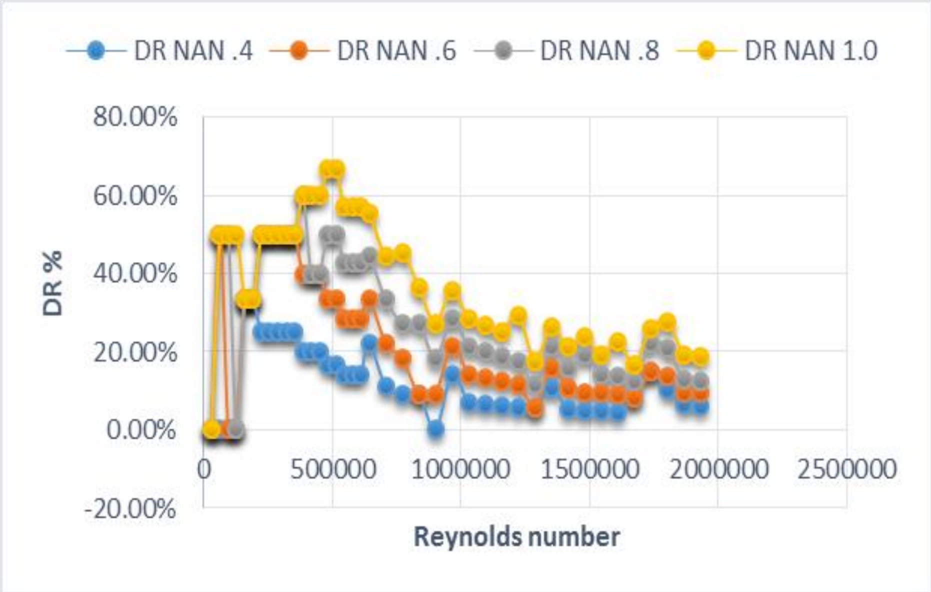

Fig 10: %DR at various Reynolds number of nanofluids with counterion

3. CONCLUSION

Several work as reported in this study, were undertakenin a rotating disk apparatus using rigid polymers and surfactants as complex mixtures and nanofluid. There was good agreement between the dual nature of the mixtures produced from these additives, although with different concentrations and materials substitutions. Major observation was the availability of reasonable quantity of nano-SiO_2 available to smoothen the disk surface in either of the cases. Moreover, the increase in drag reduction is enhanced with additive concentration.

Drag reduction and mechanical stability was more with the three dimensional complex which is augmented with silica nanoparticles and less with the two dimensional without nanoparticles.

Moreover, the impact of counterion in each case also has a role to play where it favored the complex mixtures and the opposite with the nanofluid.

Lastly, the silica nanoparticle has a major role in the stability of these materials as they augment them, thereby preventing their degradation over a period of time.

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