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Comparative Analysis of Corrosion Inhibition: Between Jatrophacurcas, Palm and Diesel Oil based Emulsified Acids for Acid Stimulation Operations

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Abstract. The recent environmental concerns have raised the need for a green acidizing fluid, which is able to replace diesel oil as an oil phase in emulsion based acidizing fluids. In order to do so it must be able to provide not only retardation in acid reaction against the rock surface, but also provide suitable inhibition characteristic that can reduce the amount of corrosion which occurs due to acidizing. In this paper emulsified acids made from triglyceride oils namely; Jatropha curcas oil and Palm oil have been tested for corrosion inhibition in comparison with Diesel oil based emulsified acid and 15wt.% HCl. The emulsion made with Jatropha curcas oil showed capability to replace diesel oil as a viable and an environmental friendly substitute for oil phase in emulsified acids.

1. Introduction

Well acidizing is a process used for improving well productivity of a hydrocarbon reservoir suffering from lack of permeability either by restoring or increasing its permeability. This is done by injecting acidizing fluid into reservoir which reacts with the rock surface to create flow conduits and remove obstructions for formation fluid to pass through into the wellbore.

Type of acid used during any acidizing operation depends on various factors such as temperature, stability, lithology, dissolving power, reaction rate and the products that will be formed by the use of a certain acid, the acids are accordingly used either solely or by making mixtures while keeping the prior mentioned conditions under consideration, normally the mineral and organic acids utilized consist of : hydrochloric acid (HCl), hydrofluoric acid (HF), formic acid, acetic acid respectively, whereas industrial ones such chloroacetic acid and sulfamic acid have been employed [1]. The paper is limited to acid usage on carbonate reservoirs, therefore acids utilized for sandstone have been stated concisely. Generally acidizing done on carbonate rocks such as Limestone ($CaCO_3$) and Dolomite [$CaMg(CO_3)_2$] is with HCl. HF is not to be used on carbonate formations as with minerals consisting of calcium HF react in an unfavorable manner creating insoluble calcium fluoride. HCl, however, tends to react with carbonate rock in a favorable manner.

Acids although effective have a high reaction rate with the carbonate formations, especially limestone, which leads to rapid consumption of the acidizing fluid before reaching the targeted depth [2], along with creating other problems such as generating excess wide face flow paths which cave in due to closure stresses and do not cater to low permeable zones[3].

Acid are also a cause of corrosion to the metallic equipment being used, it causes weakening of the metal and propagation of Fe^{2+} precipitates in spent acids which generates formation damage. Thus causing a decrease in recovery from that production zone.

Emulsified acids, which are a mixture of acid (diluted) and oil, have been used as retarding fluids which minimize the contact of acid with the rock and metal surfaces. This allows better stimulation of the rock by reducing the consumption of acidizing fluid, which is then able to create long narrow flow zones and prevents corrosion of metal to a considerable extent.

Diesel oil has been used in synthesizing emulsified acids for a number of decades. Diesel oil based emulsified acids are effective but have a high toxicity load, the use of diesel oil and related products such as xylene, benzene and kerosene have all been banned under the Energy Policy Act of 2005 (Safe Drinking Water Act, Section 322)[4]. This is because of the severe carcinogenic health issues caused by it such as, elevation in cancer rates, clotting deficiency and skin damage. During well production phase the flowback fluid containing diesel oil when introduced to local water supply is hazardous even after treatment, similarly the acidizing fluid can contaminate the groundwater as it is flushed after the acidizing operation. Due to such issues in February 2014 EPA published Underground Injection Control program to provide regulators with guidelines when giving permits to operators [5]s, in order to prevent diesel fuel usage to ensure environmental security in exploration and production operations.

In this regard, plant oils have the potential of replacing diesel oil in emulsified acids, courtesy of being more environmental friendly. The fatty acid content is suitable for providing a viscous emulsion which can retard acid reaction and provide corrosion inhibition.
Considering the use of Jatropha curcas oil and Palm oil previously in drilling [6], [7] and EOR applications [8], [9],[10]. Especially Jatropha, due to it being long chain triglyceride oil and having a high fatty acid percentage. In order to compare their potential as acidizing fluids tests were conducted on emulsified acids based on Jatropha oil and Palm oil which were compared with Diesel oil based emulsion for various properties mentioned in table 1. Based on those results and due to these presence of a sufficient amount of oleic and linoleic acids mentioned in table 2, which are able to provide corrosion inhibition property. Further study was conducted on the two plant oil based emulsions, in order to find out which one can provide corrosion inhibition comparable to diesel oil based emulsified acid.

Table 1. Properties of Jatropha oil, Diesel oil and Palm Oil based Emulsified Acids

Tests	Jatropha curcas Oil based Emulsion	Diesel Oil based Emulsion	Palm Oil based Emulsion	Test Standard
Droplet size Distribution median size, (μm)	2.17886	2.38166	2.24068	ISO 13320
Acid Solubility, (%)	57.22	66.95	66.68	API RP 40
Toxicity, (ppm)	86.5	12	85	LC50, OECD 203

Table 2. Fatty Acid Composition Percentage of Jatropha oil and Palm Oil

Name of the oil	% of oil in seed of Kernel	Myristic (Tetradecanoic)	Palmitic (Hexadecanoic)	Stearic (n-Octadecanoic)	Oleic	Linoleic
		C14	C16	C18	C18:1	C18:2
Palm Oil	30-60	0.5-2.0	32.0-45.0	2.0-7.0	38.0-52.0	5.0-11.0
Jatropha Curcas	30-40	0.5-1.4	12.0-17.0	5.0-9.5	37-63	19-41

2. Methodology

2.1. Materials

Diesel and Palm oil were purchased from a local supplier and Jatropha Oil was ordered from BATC Development BHD. 15 weight% hydrochloric acid, nonionic surfactants: Span80 and Tween80 were obtained from Benua Sains SDN BHD. A Linear alcohol based nonionic surfactant with an ethoxylation grade of 9 was obtained from a proprietary company. Steel samples were purchased from a local metal supplier.

2.2. Synthesis

A Water in Oil type emulsified acid was made [11], having acid to oil ratio of 70:30, as this ratio gives ample mobility and retardation along with reducing the amount of oil cost, thus has been used in many research studies [12], [13], [14]. A surfactant blend was prepared using a highly hydrophilic surfactant (15 HLB) and a lipophilic surfactant (4.3 HLB) in order to create an emulsifier which provides a strong bond between the acid and oil phases [15], the surfactant mixture is mixed with the oil phase for 10 minutes. Hydrochloric acid is introduced into the oil and surfactant mixture which is being continuously stirred, the acid is sprayed in order to obtain fine droplet size [16]. After adding the acid, emulsion mixture is stirred at a speed of 1000 RPM for additional 20 minutes to obtain a stable Water in Oil emulsion.

2.3. Electrical Conductivity

The emulsions were tested for near zero electrical conductivity to ensure a Water in Oil emulsion [17], [18], [19]. In case of conductivity the emulsion was mixed for another 30 minutes and was tested again after which the emulsion exhibited no indication of conduction [20].

2.4. Corrosion Testing

Corrosion tests were using the weight loss analysis for Jatropha, Diesel, Palm oil based emulsified acids and 15wt. % HCl conducted at temperatures of 25ºC and 70ºC. Weight loss analysis is a gravimetric method to determine corrosion rate or metal loss. A coupon of metal sample for which the weight loss was to be determined was immersed in the corrosive sample fluid and was removed after a considerable amount of time. The coupon was then cleaned of all corrosion products and reweighed [21], [22]. Metal loss was determined using the following equation:

$$\text{Metal Loss} = \frac{\text{W (g)} \times \text{K}}{\text{D (g/cm}^3) \times \text{A (cm}^2)} \quad (1)$$

Where,
W= Weight Loss, K = K- Factor (constant=8.76 x 10^4), D= Alloy Density, A= Exposed Area

3. Results and Discussion

3.1. Weight loss Analysis at 25ºC

The three emulsified acid samples and 15wt% HCl were measured for weight loss after a period of 24 hours. Figure 1 shows the lowest amount of metal loss was from the metal immersed in Jatropha curcas oil based emulsified acid, followed by metal taken out from Diesel oil based emulsion. These two emulsions had relatively close corrosion inhibition performance possibly because Diesel oil and Jatropha oil have long carbon chain lengths, which provide a highly viscous emulsion, keeping the acid reaction retarded with the metal surface to a certain extent more in comparison to the metal loss of Palm oil based emulsified acid which was higher than the other two emulsified acids. In order to evaluate the effect of acid in absence of a retarding medium the 15wt. % HCl solution was used as a reference which yielded a great amount of metal loss.

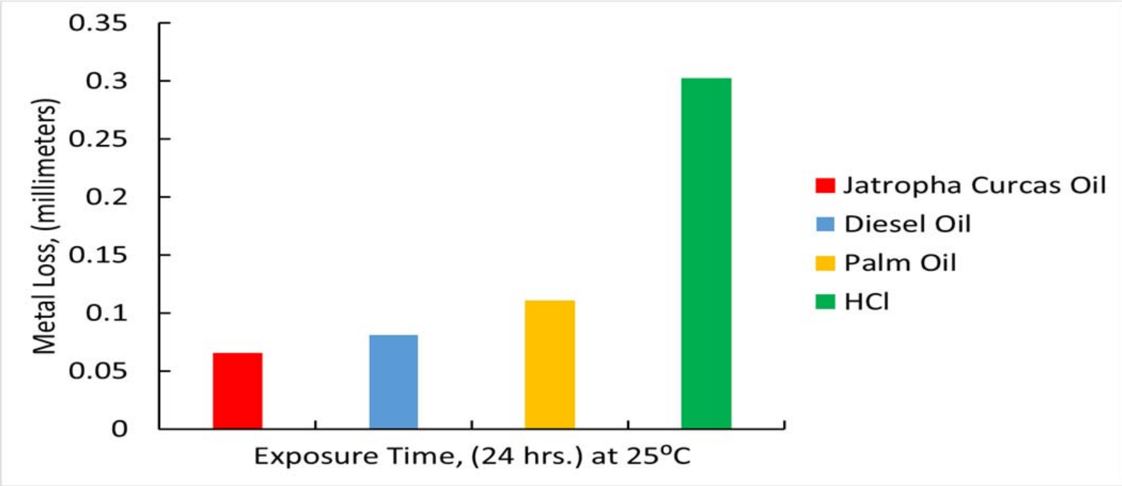

Figure 1: Weight loss Analysis at 25ºC

3.2. Weight loss Analysis at 70ºC

Following the weight loss analysis at temperature of 25ºC, the weight loss test was conducted at a temperature of 70ºC for the three emulsified acid samples and 15wt. % HCl solution. In this case the corrosion inhibition provided by Diesel oil emulsified acid was the highest followed closely by that of Jatropha oil based emulsion. When comparing the three emulsified acids Palm oil showed the lowest ability to inhibit the metal from corroding. As for the 15wt. % HCl solution, it completely dissolved the metal sample hence it was not mentioned in figure 2. At higher temperatures, acid reactivity increases, this is because the reactant particles get more energized causing them to move more quickly, resulting in an increment in particle collision rate [23]. Triglyceride oil based emulsions of Jatropha and Palm oil due to having a high fatty acid content, have a greater total acid value than that of Diesel oil based emulsified acid. Petrodiesel based rarely has olefin content and if present is normally less than 0.5mg of KOH/g, while Jatropha oil has total acid value of 32.8 mg of KOH/g [24]and around 6mg of KOH/g for Palm oil [25], [26] because of which the corrosion rate is found to be more. Jatropha oil based emulsion to its high viscosity compensates for its high acid value by giving a corrosion rate close to that of Diesel oil based emulsified acid.

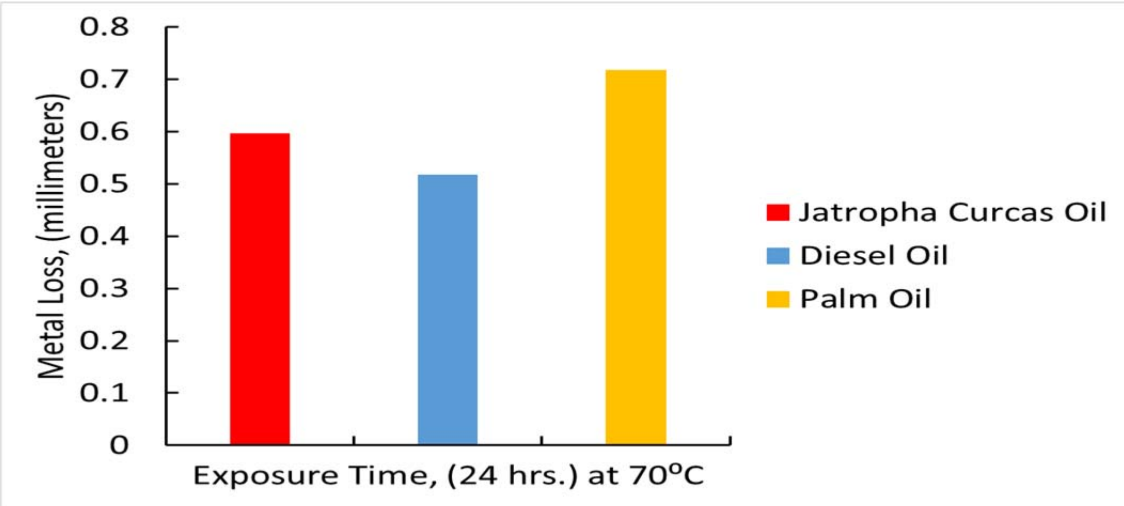

Figure 2: Weight loss Analysis at 70ºC

4. Conclusion

As the environmental concerns arise the need for a green acidizing fluid, it is necessary that such fluid fulfils rest of the requirements for being a stable medium for acidizing wells. Corrosion inhibition is an important parameter to consider during an acidizing operation, it is crucial that the stimulating fluid causes minimum corrosion to metallic equipment. Based on the results obtained, it is safe to say that Jatropha curcas oil has the potential to replace Diesel oil as the oil phase in emulsified acids, giving corrosion inhibition performance relatively close to that of Diesel oil based emulsion courtesy of having large carbon chain and high fatty percentage in comparison to Palm oil based emulsion which due to being a medium chain triglyceride is unable to provide the same inhibition capability.

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