The Study of Mass Diffusion in Cold-Finger Equipment During Wax Deposition Analysis.

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***Abstract*— An investigation has been made to study the effect of inhibitors on the mass diffusion in cold-finger equipment during wax deposition analysis. Wax deposition occurs at many stages in the production of crude oil along pipelines. Most of petroleum productions of every oil field exist in the form of water in oil emulsion. The present of interfacial barrier prevent coalescence of the dispersed water droplets. This is due to present of asphaltenes and wax in crude oil. Wax deposition in surface and subsurface pipelines reduces the oil flow area, increases the friction loss and power costs. This situation may lead to higher pressure in the case of a re-start after transmission stop, and can even lead to wax solidification in the pipeline, resulting in great economy losses. The effective way to predict the amount of wax deposition in pipeline is chemical method. This study had two types of inhibitors, three variations of temperature, three different time and three variations of concentration of the inhibitors.**

Keywords*— Inhibitors, Cold-Finger, Wax deposition, Crude Oil, Asphaltenes, and Pipe lines.

I. INTRODUCTION

The deposition of wax from crude oil in subsea can occur along pipelines usually pipelines that connected from the offshore [1]. Production, transportation and storage of crude oil and petroleum in cold environments especially from deep water subsea flow lines, may cause solid waxy oil deposits to precipitate on the pipe wall [2]. Waxes are linear hydrocarbons with more than 16 carbons atoms and n-paraffin chains will crystalize and adhere to each other inside the pipelines to form wax [3]. During the transportation of crude oil along pipelines in cold ambient temperature well below wax appearance temperature (WAT), wax deposition or wax crystal may appear and deposit on the inner cooler wall pie and form a layer of wax oil gel deposit [4]. The crude oil contains solids such as sand particles and muds that can accumulate and cause fouling or wax deposition along pipelines to occur. During petroleum production, asphaltene particles can precipitate from the crude oil due to pressure, temperature and composition changes along the fluid path from the reservoir to the surface [5]. Under reservoir condition, asphaltene tend to remain dispersed in the oil as a colloidal suspension [5]. The deposition of large asphaltene can be readily diminished by reducing the production rates because both diffusion and particles inertia are minimized by that preventive measure. During transportation of oil along pipelines, the wax precipitation can be divided into three stages; crystal growth, nucleation, and agglomeration [6].

The formation of wax gives many problems in oil industry such as reduction in pipe diameter and also can lead to block pipes. Accumulated deposition of the material on the inner wall of pipe lines may lead to increase pumping power, a flow rate reduction or total blockage of pipe lines [7]. These problems can cause billions of dollars yearly to the petroleum industry [8]. The wax deposited will completely plug the flow or cause the whole pipeline to be stopped and cause economic loss in worst condition [9]. The problems of wax deposition become more complex especially for long subsea pipe lines as drilling moves further offshore where the temperature of the water is very cold and about 4℃ below wax appearance temperature (WAT) [10]. The wax deposition along the pipelines changes the flow behavior of the crude oil from Newtonian to non-Newtonian and the wax deposition lead to higher viscosity of the water flow and increase the energy consumption for pumping the fluid along the pipelines [11].

Many techniques have been introduced through removal and prevention of wax deposition such as thermal, chemical and mechanical methods. In this study, chemical method was chosen to reduce the rate of solid deposition. From this study the effectiveness of two inhibitors were tested and two different types of inhibitors were used which are diethanolamine (DEA) and maleic anhydride copolymer (MAC). DEA compromise of hydroxyl group and MAC is the acid anhydride of maleic acid. It is proved that the addition of inhibitor in a crude sample can weaken solid deposit through van der Waals bonding, which results in an easy removal of the deposit by shear forces flow streams [12]. We use laboratory devices names cold finger equipment. It is a thermally controllable device that stimulates wax deposition in pipelines [13]. Chemical additives also known as wax inhibitors are one of the well-known wax controlling strategy being implemented by petroleum production industries to reduce the frequency of pigging. Wax inhibitors were used to chemically modify the wax solid structure thus reducing the tendency of the wax crystal to interlock and form three dimensional network growths. DEA from hydroxyl group can acts as surfactant which is good oil-in-water emulsifier. It can avoid gelling problem in crude oil and act as inhibitor. Polymer inhibitors consist of wax-like portions that allow the molecules to integrate into wax deposit structure and it structural features can modify and interrupt wax deposition along pipelines. For the hydroxyl group, it can act as a surfactant. It is good oil-in-water emulsifier that can prevent gelling problem in crude oil. From many studies of inhibitors effect on wax deposition problem, it is found that different inhibitors will give different effect on wax deposition rate problem along pipe lines [14].

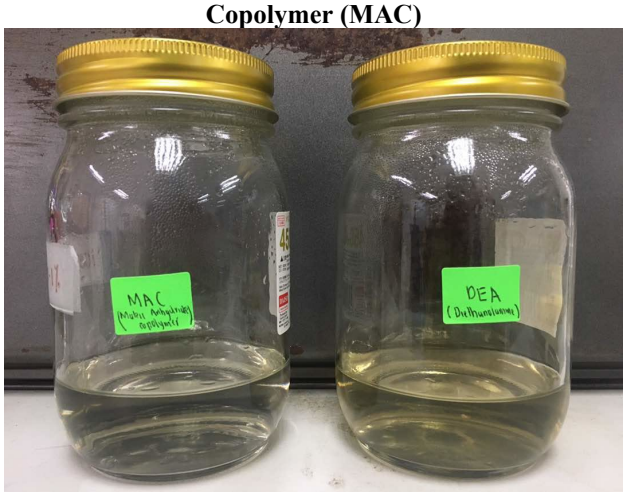
II. METHODOLOGY

A. Materials

The material used in this research project are diethanolamine (DEA) with melt range from 25 to 28 and maleic anhydride copolymer (MAC) with melt index range from 51 to 54

obtained from Sigma-Aldrich. The concentration of diethanolamine (DEA) and maleic anhydride copolymer (MAC) needed are 500ppm, 2750ppm, 5000ppm rescpectively. Cyclohexane also needed in order to mix it with maleic anhydride copolymer (MAC) to run the experiments. Raw crude oil was kindly supplied by PETRONAS Refinery from Kerteh, Terengganu, Malaysia.

Figure 1: Diethanolamine (DEA) and Maleic Anhydride Copolymer (MAC)



Preparation of inhibitors

DEA and MAC solution with concentration 500ppm, 2750ppm, 5000ppm were supplied by Sigma-Aldrich, and used at pure liquid concentration.

Cold finger experimental set up and analysis

Figure 2 shows the cold finger apparatus that was set up to evaluate the rate of wax deposition of crude oil. This cold finger equipment is suitable to correlate wax deposition data to the temperature differences between the bulk oil and wall of the equipment [15].

Figure 2: Cold Finger apparatus set up

Method of analysis

First, the cold finger was placed within the center of a stainless steel jar filled with 130 mL of crude oil. The crude oil samples need to be chilled for 1 hour above wax appearance temperature (WAT) for thermal treatment in an oven to solubilize any precipitated wax. The stirrer also attached at the middle of the cold finger to make the field flow influences both the shear stress field and the rate of heat transfer at the cold finger surface.

The cold finger and jar then placed inside a heating water bath to maintain a specific temperature over a long period of time. The heating water bath was initially fixed with a predefined temperature of 50℃. The cold finger in the heating water bath was connected to chiller while circulation system was set up and while the crude oil was heated up. The cold fluid valve was opened to condition the cold finger after it has reached the thermal equilibrium of the bath and jar. Crude oil with diethanolamine (DEA) and maleic anhydride copolymer (MAC) were tested in the cold finger experiment. The stirring rate was maintained to 400ppm throughout experiments. The experiment was carried out for 2, 13, and 24 hours to presume the effect of inhibitors on the wax deposition rate. Lastly, the deposited was then scrapped from the cold finger, weighed and saved for further analysis [16].

III. RESULTS AND DISCUSSION

Characteristic of crude oil sample

For this study, the details of crude oil sample characteristics used in this study such as asphaltenes, resin, wax, solid part, water content, saturated hydrocarbon, polar and aromatic hydrocarbon are shown in Table 2 below.

Table 1: Chemical properties of crude oils sample

Chemical analysis	(%w/w)
Asphaltenes	0.37
Resin	32.01
Solid part	0.26
Water content	2.91
Saturated hydrocarbon	45.63
Polar	8.42
Aromatic hydrocarbon	45.95
Wax	15.37

Figure 3, 4, 5, 6, 7 and 8 represents the result of cold finger testing for Malaysian crude oil with two different chemical inhibitors. The chemical inhibitors performance that mixed with the crude oil in the jar was stirred constantly at 400rpm. The test was conducted at 3 variations temperature 5℃, 10℃, and 15℃. The duration for all experiment was set to 2 hours, 13 hours and 24 hours with concentration of inhibitors are 500ppm, 2750ppm and 5000ppm respectively.

Figure 3: Effect of DEA and MAC inhibitors on wax deposition for temperature 5℃

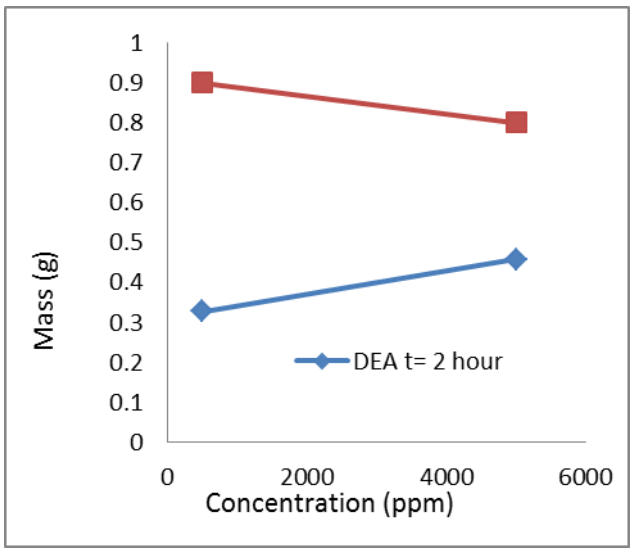
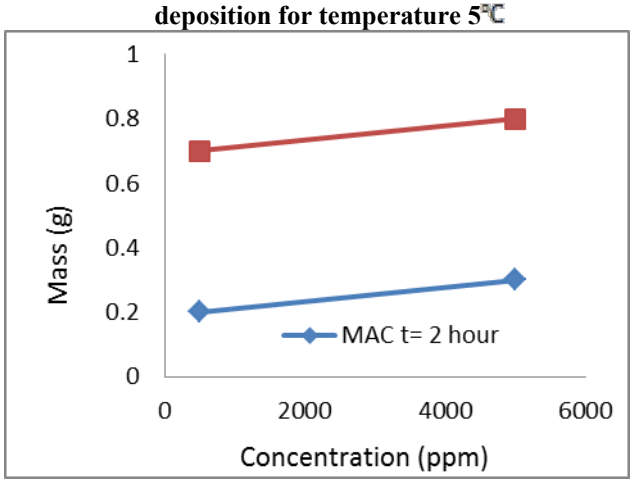


Figure 4: Effect of DEA and MAC inhibitors on wax deposition for temperature 5℃



From the study, it was found that wax deposit was found to decrease significantly when the concentration of inhibitors increase from 500ppm to 5000ppm. This is because when the concentration of the inhibitors is higher or increase, the viscosity of the crude oil also decrease thus reduce the wax deposition rate [17]. Minimum wax was observed at 5000ppm for all chemical inhibitors. It also observed that maleic anhydride copolymer (MAC) decreases the viscosity of the

Figure 5: Effect of DEA and MAC inhibitors on wax deposition for temperature 10℃

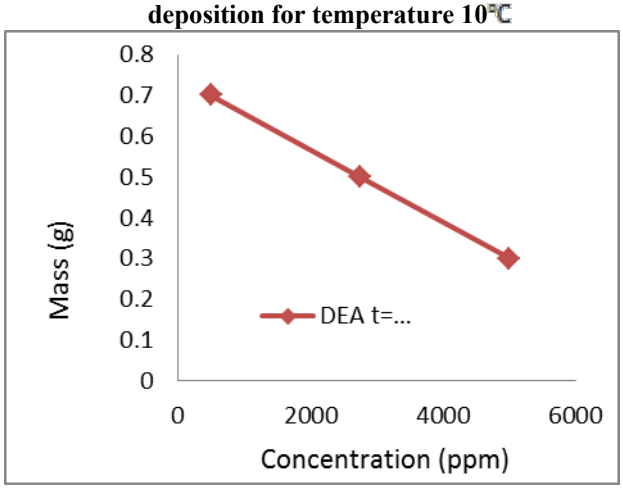
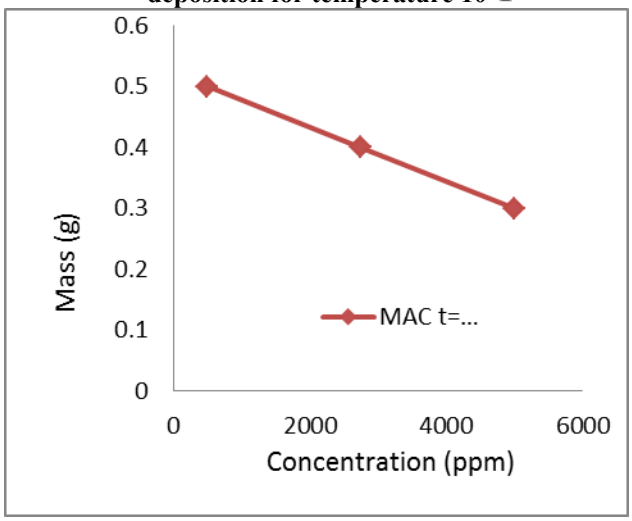


Figure 6: Effect of DEA and MAC inhibitors on wax deposition for temperature 10℃



crude oil higher than diethanolamine (DEA) so the lowest minimum wax observed at MAC(5000ppm) with duration 2 hours.

The cold finger temperature was set below its wax appearance temperature and it is believe that the crude oil at the cold finger area will show non-Newtonian behavior. From the stirring rate, the heat transfer produced by the stirring of the impeller to the cold finger increased. When this is happened, the internal energy changed to Newtonian region from non-Newtonian region. Other than that, when the temperature around the cold finger is changed the rheology of the wax deposit also changed.

Figure 7: Effect of DEA and MAC inhibitors on wax deposition for temperature 15℃

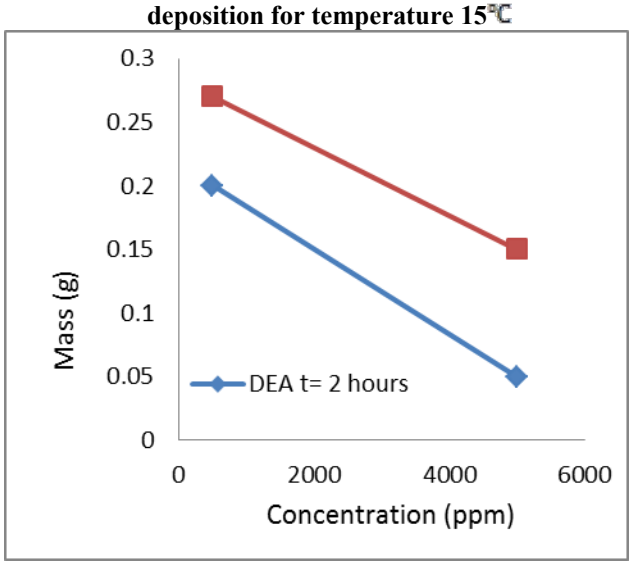
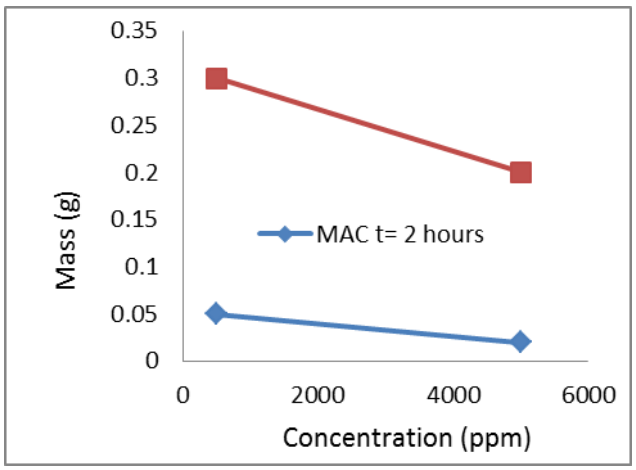


Figure 8: Effect of DEA and MAC inhibitors on wax deposition for temperature 15℃



The capability of the wax to stick to each other would be lower due to van der Waals interaction. Therefore, the solubility of chemical inhibitor in crude oil plays an important role in viscosity reduction. The experiment shows that the MAC inhibitor shows the best performance to reduce and inhibit wax formation. The order of inhibitor is:

MAC > DEA

For the result of DEA and MAC wax deposit, it can be suggested that DEA cannot give strong van de Waals interaction because DEA inhibitor possess a hydroxyl group (OH) that could not incorporate into the wax molecules. This study confirmed that different types on inhibitors can affect and decrease the viscosity of the crude oil. The higher the concentration inhibitors suggest lower probability of wax deposition rate and solid crystallization process because the viscosity of the crude oil decrease and reduce flow problems. Therefore, different rates of crystal growth are affected by different types of chemical inhibitors [18]. In order to expand this study about mass diffusion in cold-finger equipment during wax deposition analysis, it is recommended to use more types of inhibitors such as cocamide diethanolamine (C-DEA), polyethylene-co-vinyl acetate (EVA), and poly maleic anhydride-alt-1-octadecene (MEA) to choose the best and the most suitable type of inhibitor to be used in the industry.

According to previous study by Oriental Journal of Chemistry, when the cold finger was set below wax appearance temperature, it believed that the crude oil at the cold finger area will show non-Newtonian behavior. Then, they also stated that by introducing stirring rate, the heat transfer produced by the stirring of the impeller to the cold finger increased. This activity changed the internal energy of both system involved, which is from non-Newtonian to Newtonian region. Furthermore, changing the temperature around the cold finger also changed the rheology of the wax deposit. However, when the samples were stirred rapidly at higher shear rate, the amount of deposit increased slightly. This happens due to the shear thickening fluid behavior resultant from a very viscous liquid. The non-Newtonian behavior increased the tendency of the wax to precipitate out from the crude oil to from waxes through crystallization process. Once the crystal have formed, the tendency of the crystal to aggregate is higher.

IV. Conclusion

Maleic anhydride copolymer (MAC) inhibitor shows the best performance to reduce wax deposition. This study found that as the concentration of inhibitors increase, the amount of the wax deposition was observed to be decreased. It is also show that due to low van de Waals interaction from DEA inhibitors that possess a hydroxyl group makes MAC inhibitors shows better result in this experiment.

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